Sorbent Research for the Capture of Carbon Dioxide

19 December 2016
Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference therein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

Cover Illustration: Photo of the bench-scale packed bed reactor that was charged with an amine-enriched sorbent.


An electronic version of this report can be found at:
http://www.netl.doe.gov/research/on-site-research/publications/featured-technical-reports
Sorbent Research for the Capture of Carbon Dioxide

Henry W. Pennline

U.S. Department of Energy, National Energy Technology Laboratory, AECOM, 626 Cochran Mill Road, Pittsburgh, PA 15236

NETL-TRS-19-2016

19 December 2016

NETL Contacts:
David P. Hopkinson, Technical Portfolio Lead
Cynthia Powell, Executive Director, Research & Innovation Center
# Table of Contents

**EXECUTIVE SUMMARY** ......................................................................................................................... 1

1. **INTRODUCTION** ............................................................................................................................. 17

2. **ZEOLITES** ............................................................................................................................................ 23
   2.1 **INTRODUCTION** .......................................................................................................................... 23
   2.2 **LABORATORY-SCALE EXPLORATORY TESTING** ......................................................................... 24
   2.3 **MODELING EFFORT WITH ZEOLITE 13X** .................................................................................. 39
   2.4 **BENCH-SCALE TESTING** ............................................................................................................. 42
   2.5 **MODULAR CARBON DIOXIDE CAPTURE FACILITY (MCCF)** ..................................................... 53
   2.6 **PDU-SCALE TESTING** ................................................................................................................ 57
   2.7 **CURRENT PRE-COMBUSTION AND POST-COMBUSTION ZEOLITIC SCHEMES** ..................... 90

3. **ALKALI/ALKALINE EARTH SORBENTS** ............................................................................................ 94
   3.1 **INTRODUCTION** .......................................................................................................................... 94
   3.2 **POTASSIUM-BASED SORBENTS** ................................................................................................. 100
   3.3 **CALCIUM-BASED SORBENTS** .................................................................................................... 109
   3.4 **LITHIUM-BASED SORBENTS** ..................................................................................................... 118
   3.5 **SODIUM-CONTAINING SORBENTS** ............................................................................................. 135
   3.6 **MAGNESIUM-CONTAINING SORBENTS** ....................................................................................... 145

4. **AMINE-ENRICHED SORBENTS FOR POST-COMBUSTION APPLICATION** ..................................... 157
   4.1 **INTRODUCTION** .......................................................................................................................... 157
   4.2 **EARLY STUDIES WITH AMINE-ENRICHED SORBENTS** ............................................................ 161
   4.3 **TARGET ESTABLISHMENT FOR POST-COMBUSTION USAGE OF AMINE-ENRICHED SORBENTS WITH REACTOR DESIGN CONSIDERATIONS** .............................. 182
   4.4 **BASIC IMMOBILIZED AMINE SORBENTS (BIAS)** ..................................................................... 208
   4.5 **CLAY-BASED SORBENTS** ........................................................................................................... 263
   4.6 **ADA RESULTS WITH NETL-DEVELOPED AMINE-ENRICHED SORBENTS** .............................. 275
   4.7 **COMPLEMENTARY RESEARCH** .................................................................................................. 286

5. **POROUS COORDINATION POLYMERS (MOFS)** ................................................................................. 288

6. **ACTIVATED CARBON** ..................................................................................................................... 296

7. **REFERENCES** ..................................................................................................................................... 299
This page intentionally left blank.
List of Figures

Figure 1: Block diagram illustrating a PC system with post-combustion CO₂ capture.......................... 18
Figure 2: Block diagram illustrating an IGCC system with pre-combustion CO₂ capture.................. 20
Figure 3: Adsorption isotherms of CO₂, N₂, and H₂ on molecular sieve 13X at 25°C..................... 28
Figure 4: Adsorption isotherms of CO₂ and N₂ on zeolite 13X...................................................... 29
Figure 5: Desorption of CO₂ during the introduction of N₂ at 25°C with zeolite 13X after CO₂ adsorption................................................................................................................................. 30
Figure 6: Temperature-programmed desorption (TPD) studies with zeolite 13X after CO₂ adsorption................................................................................................................................. 30
Figure 7: Adsorption of CO₂ on zeolite 13X at 120°C, 1 atm (15 vol % CO₂, 82 vol % N₂, and 3 vol % O₂, and H₂O, 5 cm³/min). ........................................................................................................ 31
Figure 8: Thermogravimetric analysis (TGA) of zeolites as a function of temperature.................. 33
Figure 9: Adsorption and desorption isotherms of zeolite 1............................................................ 34
Figure 10: Amount of CO₂ desorbed at 25°C during the introduction of nitrogen with zeolite 1 after CO₂ adsorption. .................................................................................................................. 35
Figure 11: Amount of CO₂ desorbed during temperature-programmed desorption with zeolite 1. ............................................................................................................................... 35
Figure 12: FTIR analysis of 1 vol % CO₂-N₂ adsorption at ambient temperature onto the 120°C pretreated 13X zeolite. ......................................................................................................... 37
Figure 13: FTIR analysis of 1 vol % CO₂-N₂ adsorption at ambient temperature onto the 350°C pretreated 13X zeolite. ......................................................................................................... 37
Figure 14: Four-step operation of PSA and FVPSA processes.......................................................... 40
Figure 15: Schematic of bench-scale packed bed reactor system..................................................... 43
Figure 16: Typical results for packed bed experiment.............................................................. 45
Figure 17: MCCF in flue gas mode of operation................................................................................. 55
Figure 18: MCCF in fuel gas mode of operation................................................................................. 56
Figure 19: MCCF process flow diagram.......................................................................................... 70
Figure 20: Photographs of MCCF equipment..................................................................................... 71
Figure 21: Instrumentation ports on sidewall of adsorber bed........................................................ 72
Figure 22: Adsorption, desorption, and regeneration results during a typical test (MCCF-03-1).75
Figure 23: MCCF-03-1 adsorption data............................................................................................ 76
Figure 24: MCCF-03-1 desorption data............................................................................................. 77
Figure 25: MCCF-03-1 regeneration data.......................................................................................... 78
Figure 26: Effect of moisture in flue gas on adsorption and regeneration for MCCF-02. .............. 80
Figure 27: Four-cycle adsorption test for MCCF-03......................................................................... 81
Figure 28: Four-cycle desorption/regeneration test for MCCF-03.................................................. 82
Figure 29: Effect of flue gas flowrate on adsorption for MCCF-04.................................................. 83
Figure 30: Desorption/regeneration cycles for MCCF-04................................................................. 84
Figure 31: Effect of SO₂ spiking on three-cycle adsorption test for MCCF-05............................... 85
Figure 32: Effect of SO₂ and NO₃ spiking on three-cycle adsorption test for MCCF-06.............. 86
Figure 33: Three-cycle desorption/regeneration test for MCCF-06................................................. 87
Figure 34: CO₂ capture process with zeolite sorbent for IGCC systems........................................ 91
Figure 35: Modeling scheme for screening solid CO₂ sorbents..................................................... 99
Figure 36: Schematic of thermogravimetric analyzer....................................................................... 101
Figure 37: Schematic of bench-scale packed-bed reactor............................................................... 103
List of Figures (cont.)

Figure 38: Typical TGA experiment (Batch #1 sorbent at 80°C absorption) ........................................... 106
Figure 39: Effect of inlet CO₂ level on CO₂ breakthrough ............................................................................. 108
Figure 40: Typical TGA experiment (calcium oxide reagent at 850°C absorption) .................................... 112
Figure 41: Cycling test with calcium carbonate reagent at 750°C absorption .............................................. 113
Figure 42: TGA results with calcium/silica sorbent ....................................................................................... 114
Figure 43: TGA experimental result for Batch #1 alumina-based sorbent at various absorption temperatures .......................................................................................................................... 115
Figure 44: TGA test with type A Ca/Zirconia sorbent at 500°C absorption .................................................... 116
Figure 45: Multiple cycle TGA test with lithium zirconate reagent at 500°C absorption ......................... 120
Figure 46: Comparison of TGA results for lithium zirconate with and without an additive at 500°C absorption .............................................................................................................................. 121
Figure 47: Impact of additives on TGA results ............................................................................................... 124
Figure 48: CO₂ Sorption profiles of ternary lithium zirconate sorbent. Effect of temperature on CO₂ absorption rate and CO₂ capacity .............................................................................................................. 125
Figure 49: TGA experiment with Toshiba lithium silicate sorbent at various absorption temperatures .................................................................................................................................................. 128
Figure 50: TGA experiment with Toshiba lithium silicate sorbent at 700°C absorption .............................. 130
Figure 51: Sorption of CO₂ from a simulated IGCC gas stream (12% CO₂, 35.9% CO, 27.1% H₂, and 25% He, saturated with H₂O, at 5 cm³/min) on a NaOH/CaO sorbent at 315°C, 1 atm, and cycle 1. .............................................................................................................................. 138
Figure 52: Multicycle sorption test of CO₂ from a simulated IGCC gas stream (12% CO₂, 35.9% CO, 27.1% H₂, and 25% He, saturated with H₂O, at 5 cm³/min) on a NaOH/CaO sorbent at 315°C and 1 atm ........................................... 139
Figure 53: Sorption isotherms of CO₂ at 315°C with NaOH/CaO (1:4). ....................................................... 141
Figure 54: Effect of Na₂CO₃/CaO system composition on the thermal decomposition of Na₂CO₃. .............................................................................................................................................................................. 144
Figure 55: Thermodynamic equilibrium analysis as a function of temperature for a system of 1 mol of CO₂, 1 mol of Mg(OH)₂, 1 mol of H₂O, and 0.1 mol of N₂ at a pressure of 30 atm.147
Figure 56: Thermodynamic equilibrium analysis as a function of temperature for a system of 1 mol of MgCO₃, 1 mol of H₂O, and 0.1 mol of N₂ at a pressure of 20 atm.148
Figure 57: Thermodynamic equilibrium analysis as a function of temperature for a system of 1 mol of MgO, 1 mol of H₂O, and 0.1 mol of N₂ at a pressure of 20 atm.149
Figure 58: Bench-scale flow reactor CO₂ capture data over Mg(OH)₂ sorbent at 200°C, 280 psig, GHSV = 500 h⁻¹ with CO₂/H₂O/N₂ = 28%/15%/57%M .............................................................. 153
Figure 59: Desorption of CO₂ during regeneration of the sorbent at 280 psig and 400°C while flowing GHSV = 500 h⁻¹ of N₂...................................................................................................................... 153
Figure 60: Proposed CO₂ capture process ................................................................................................... 154
Figure 61: Proposed reaction sequence for the capture of CO₂ by liquid amine-based systems.161
Figure 62: Proposed reactions for preparation of an amine-enriched carbon-based sorbent ................. 163
Figure 63: Schematic of experimental unit .................................................................................................. 164
Figure 64: Transmission infrared spectra of SBA-15, fresh APTS-SBA-15, and regenerated APTS-SBA-15 ......... 168
Figure 65: CO₂ MS intensity profiles during CO₂ adsorption ....................................................................... 169
Figure 66: CO₂ MS profile during desorption of CO₂ by a TPD technique .................................................. 172
List of Figures (cont.)

Figure 67: Adsorption breakthrough curves for sorbent 139a at various temperatures............ 176
Figure 68: Adsorption isotherms for DEAB sorbent ......................................................... 178
Figure 69: Sorption of CO₂ on DEAB as a function of time................................................. 179
Figure 70: Cumulative sorption of CO₂ on DEAB ............................................................. 180
Figure 71: Absorption of CO₂ on DEAB sorbent after successive regenerations.................. 181
Figure 72: Effect of regeneration temperature on CO₂ absorption for DEAB sorbent .......... 181
Figure 73: Comparison of regenerative heats between amine-enriched sorbent and MEA .... 184
Figure 74: Fixed bed absorption system. ............................................................................. 186
Figure 75: Radial flow reactor concept................................................................................. 188
Figure 76: Novel fixed bed sensitivity cases ........................................................................ 190
Figure 77: Conceptual sorbent process in a transport-type system......................................... 193
Figure 78: Moving bed conceptual schematic. ..................................................................... 196
Figure 79: Fluid bed conceptual schematic. .......................................................................... 197
Figure 80: Each heat exchanger within the bed. .................................................................... 199
Figure 81: Each bed of the structural sorbent system........................................................... 200
Figure 82: Fixed bed concept............................................................................................... 201
Figure 83: Graph of regenerative heat duty versus sorbent working capacity....................... 202
Figure 84: Sensitivity study for moving-bed concept............................................................ 204
Figure 85: Plot of heat duty (regeneration energy) versus sorbent loading using Equation 1... 206
Figure 86: Schematic of isotherms for sorbent. ................................................................. 207
Figure 87: This illustrates three potential pathways to making solid amine sorbents.............. 209
Figure 88: a) Class 1 adsorbent: PEI impregnated in porous silica (PQ-9023). b) Class 2 adsorbent: 3-aminopropylsilyl-functionalized silica (PQ-9023). c) Class 3 adsorbent: in situ aziridine polymerization on a porous silica surface (MCF)................................................. 210
Figure 89: TEPAN, Michael adduct produced by reaction of TEPA with acrylonitrile............. 211
Figure 90: Photograph of the TGA system. ........................................................................... 212
Figure 91: Schematic of laboratory-scale packed bed reactor. .............................................. 213
Figure 92: Schematic of bench-scale packed bed reactor system......................................... 214
Figure 93: Single-component CO₂ adsorption isotherm for a highly-loaded HAS adsorbent at 35 and 75°C............................................................................................... 217
Figure 94: Amounts of CO₂ adsorbed by HAS and PEHAS adsorbents with different amine loadings at 13.5 min.................................................................................. 219
Figure 95: Chemical structure of a highly branched polyethylenimine compound having two carbons per nitrogen with a ratio of 1:2:1 between primary, secondary, and tertiary amine groups............................................................................................................. 220
Figure 96: TGA profiles for PEI supported Cariact® G10 sample in pure CO₂, N₂, and air, where temperature ranged between 40°C to 200°C and heating rate was 0.25°C/min. .......... 221
Figure 97: Graphic illustration of breakthrough curve of the adsorption and regeneration of CO₂ with PEI/silica sorbent. ..................................................................................... 223
Figure 98: Absorption and regeneration TGA curves for CARiACT sorbent.......................... 224
Figure 99: Typical heat capacity results from NETL laboratory ........................................... 226
Figure 100: Schematic of proposed process with BIAS sorbents............................................ 229
List of Figures (cont.)

Figure 101: Sorbent performance of mixed-amine (APTES+PEI) sorbents in TGA under pure CO₂ at 60°C, 1.01 bar. .................................................................................................................. 233
Figure 102: Multiple adsorption–desorption testing of the (PEI-25-APTES-25)-silica in a simulated humidified flue gas stream containing 12% CO₂, 4% O₂, balance N₂, with 9 vol % water vapor............................................................................................................. 234
Figure 103: Material balances for 196c for water and carbon dioxide comparing absorption and regeneration recoveries. ............................................................................................................. 237
Figure 104: Equilibrium absorption loading curves for CO₂ and H₂O with sorbent 196c at 60°C. ................................................................................................................................. 239
Figure 105: Sorbent 196c regeneration curves with desorption at 60°C followed by a temperature ramp. .................................................................................................................. 240
Figure 106: Moisture loading curves for PEI with different substrates at temperatures of 45 and 60°C................................................................................................................................. 240
Figure 107: Absorption/regeneration with 196c at near total steam conditions at 105°C. ....... 242
Figure 108: Conceptual BIAS Process for PEI/silica sorbent with continuous sorbent flow between absorber and regenerator (steam sweep). ........................................................................... 244
Figure 109: Impact of steam regeneration on the performance of PEI/silica (PEI-Si) and PEI/silica with silane (PEI-Sil-Si). ............................................................................................................. 247
Figure 110: DRIFTS absorbance spectra during SO₂ adsorption on APTS-SBA-15 in the presence of H₂O. ......................................................................................................................... 251
Figure 111: Summary data of CO₂ and SO₂ uptake profiles of silica supported PEI sorbent, using simulated flue gas of 10 vol% CO₂, 3.5% O₂, balance N₂ containing 1,000 ppmv SO₂. .... 256
Figure 112: Scanning electron microscopy micrographs of PEI/silica sorbent particles (A) before SO₂ exposure, (B) after 1,000 ppmv SO₂ exposure. ................................................................. 256
Figure 113: Pictures of sorbent. .................................................................................................................. 257
Figure 114: Summary of SO₂ and NO₂ contamination with PEI/silica and PEI/PMMA sorbents. Graph reflects cyclic impact of SO₂ on PEI/PMMA sorbent. ............................................................. 258
Figure 115: Effect of SO₂ exposure on NETL sorbent containing PEI on silica or polymer supports........................................................................................................................................ 259
Figure 116: Effect of SO₂ exposure on NETL sorbent containing PEI on silica or polymer supports. ................................................................................................................................. 259
Figure 117: Comparison of experimental fractional uptake (marker) to Weibull reaction model (lines) at different temperature for 20% CO₂ concentration............................................. 261
Figure 118: Effect of temperature on reaction rate using 100% CO₂ .................................................... 262
Figure 119: Bench-scale tests with NETL liquid-impregnated solid sorbent (Sud-Chemie prepared extrudates) at high pressure (20 atm; 30°C; space velocity 1,000 h⁻¹; feed composition of 16% CO₂, 84% N₂). .......................................................................................... 265
Figure 120: Extrudates prepared by Sud-Chemie. .................................................................................. 266
Figure 121: Spray dried formulations prepared by Sud-Chemie – average particle size is 80 microns........................................................................................................................................... 266
Figure 122: CO₂ capacity data for sorption on a spray dried clay-based sorbent. 15% CO₂, 3% O₂, 3% H₂O and 79% N₂ at 40°C, 15 cc/min in atmospheric reactor. ........................................ 268
Figure 123: CO₂ capacity data for spray dried sorbent from Sud Chemie at 100°C with 90% CO₂ and remainder N₂. ......................................................................................................... 268
List of Figures (cont.)

Figure 124: Laboratory-scale flow reactor multicycle test data with sorbent (particle diameter less than 200 micron) at 1 atm; 60°C; space velocity ~500 h⁻¹; feed composition of 16% CO₂, 3% O₂, 82% N₂, saturated with water. ................................................................. 269
Figure 125: Desorption of CO₂ and H₂O at 60°C with nitrogen after sorption at 60°C with 15% CO₂, 3% O₂, 82% N₂, and saturated with water. ................................................................. 270
Figure 126: Laboratory-scale flow reactor 20-cycle test data with sorbent at 1 atm in the presence of 20 ppmv SO₂ at 40°C; space velocity ~500 h⁻¹; feed composition of 15% CO₂, 3% O₂, 20 ppm SO₂ in N₂................................................................. 271
Figure 127: Curve fitting to experimental data to obtain Kₑq and maximum loading. .............. 273
Figure 128: Effect of reaction temperature on amine/bentonite particle and CO₂ reaction...... 274
Figure 129: Comparison between kinetic model predictions and experimental data at several temperatures in isothermal condition. ................................................................. 275
Figure 130: Schematic of sorbent screening unit................................................................. 277
Figure 131: CO₂ working capacity during laboratory tests. ................................................. 278
Figure 132: Comparison of theoretical regeneration energies based on laboratory fixed bed tests with humid simulated flue gas. ................................................................. 279
Figure 133: Working capacity during field testing. ................................................................. 280
Figure 134: Schematic of 1kW pilot CO₂ system................................................................. 281
Figure 135: Pan dryer at Pressure Chemical Company.......................................................... 282
Figure 136: CO₂ concentrations and removal during continuous 1kW testing of sorbent R..... 284
Figure 137: Maximum CO₂ removal for sorbent R at Martin Lake and sorbent AX at Sherco. 285
Figure 138: A generalized synthetic scheme showing how a PCP can be formulated using metal clusters and inorganic/organic linkers. ................................................................. 288
Figure 139: Isotherms at 293ºK for 3 linkers used with the Ni[Ni(CN)₄]₅................................ 289
Figure 140: A) Surface and B) cross-sectional images of a NETL synthesized Cu-based metal organic framework material successfully grown on a metal oxide support.............. 290
Figure 141: Adsorption (solid symbols)/desorption (open symbols) isotherms for CO₂ on Ni-DBM-BPY at 0°C (diamonds) and 25°C (circles). ................................................................. 292
Figure 142: The change in mole percent of CO₂ (delta-CO₂) in the headspace after equilibrium exposure of gas mixtures (as indicated) to Ni-DBM-BPY at 308°C (303 K) and Ps. ...... 294
Figure 143: Adsorption isotherms of CO₂, N₂, and H₂ on activated carbon at 25°C. .......... 297
Figure 144: Adsorption isotherms of CO₂ on three sorbents at 25°C.................................. 298
Figure 145: Microreactor data on CO₂ separation with activated carbon – 14.8 vol% CO₂/85.2% N₂ mixture. ................................................................. 298
This page intentionally left blank.
List of Tables

Table 1: Technical advantages and challenges for post-combustion sorbent technologies. ......... 19
Table 2: Technical advantages and challenges for pre-combustion sorbent technologies .......... 20
Table 3: Physical and chemical properties of five synthetic zeolites ........................................ 25
Table 4: Physical properties of three natural zeolites ................................................................. 25
Table 5: Bulk and surface elemental ratios of three natural zeolites. ....................................... 26
Table 6: Zeolite breakthrough times for Cycle 1 and heat of CO₂ adsorption values at 120°C .. 32
Table 7: Multi-cycle test of baseline condition (dry). Inlet gas composition (vol %): 16%CO₂/3.5%O₂/balance N₂ ................................................. 49
Table 8: Multi-cycle test results for the effect of 2%H₂O. Inlet gas composition (dry vol %): 16%CO₂/3.5%O₂/balance N₂ ........................................................................... 50
Table 9: Multi-cycle test results for the effect of 4%H₂O. Inlet gas composition (dry vol %): 16%CO₂/3.5%O₂/balance N₂ ........................................................................... 51
Table 10: Parametric effect of adsorption temperature and CO₂ mole fraction. Baseline inlet gas composition (vol %): 16%CO₂/3.5%O₂/balance N₂ ................................................. 52
Table 11: Effect of high CO₂ mole fraction (as a sweep gas) on regeneration temperature. Inlet gas composition (vol %): 85%CO₂/15%N₂ .................................................. 53
Table 12: Summary of zeolite tests in MCCF .................................................................................. 73
Table 13: Adsorber temperature data ............................................................................................. 79
Table 14: Surface area and chemical composition of zeolite samples .......................................... 88
Table 15: Cumulative material balance for MCCF-06, adjusted for residual sulfur on zeolite ... 89
Table 16: Sorption capacities over Zeolite 13X sorbent during bench-scale flow reactor testing with CO₂ and 7% H₂O and balance N₂ at a GHSV of 500 h⁻¹ .............................................................................. 91
Table 17: Calculated thermodynamic properties of reactions ....................................................... 97
Table 18: Temperature ranges of reactions for absorption and regeneration ............................... 97
Table 19: Composition and eutectic temperatures of binary and ternary eutectic mixtures studied in the TGA .............................................................................................................. 123
Table 20: Parasitic power loss and performance summary ........................................................... 133
Table 21: Summary of economic results ......................................................................................... 134
Table 22: Laboratory-Scale Flow Reactor Data Summary for the Mg(OH)₂ Sorbent ............... 150
Table 23: Sorption capacities over Mg(OH)₂ during bench-scale flow reactor testing with feed composition of 28% CO₂, 10% H₂O, GHSV = 250 h⁻¹. Regeneration was at 20 psig. .... 151
Table 24: Sorption capacities over Mg(OH)₂ during bench-scale flow reactor testing with feed composition of 28% CO₂, 10% H₂O, GHSV = 250 h⁻¹. Regeneration was at 280 psig. .... 152
Table 25: XPS analysis of amine-enriched fly ash carbon sorbents ............................................ 165
Table 26: TPD CO₂ desorption results of substrates and sorbents .............................................. 166
Table 27: XPS and BET results ...................................................................................................... 169
Table 28: TPD CO₂ desorption and XPS data of the amine-enriched sorbents ............................. 170
Table 29: CO₂ capture capacity of amine-enriched sorbents ...................................................... 172
Table 30: TPD/MS CO₂ adsorption and XPS data for the amine-enriched sorbents ..................... 174
Table 31: Comparison of CO₂ carrying capacity of solid sorbent and MEA solvent .................. 183
Table 32: Comparison of solid sorbent and wet scrubbing plant performance and economics 189
Table 33: CO₂ capture properties for TEPA-based sorbents at 25°C .......................................... 214
Table 34: Performance of DBU-based sorbent at 25°C in a 10 vol% CO₂/2% H₂O/88% helium atmosphere ......................................................................................................................... 216
List of Tables (cont.)

Table 35: Performance of DBU-3 at 25–65°C in a 10 vol% CO₂/2% H₂O/88% He atmosphere ........................................................................................................................................... 216
Table 36: Capture loading capacities at 40°C for PEI sorbents. aTGA measured at 100% CO₂.
bLab reactor at 10% CO₂ in helium. ........................................................................................................................................... 223
Table 37: Sensitivity analysis for immobilized amine sorbent .................................................................................................................. 230
Table 38: Initial cyclic testing of aminosilane/PEI sorbents ........................................................................................................................................... 231
Table 39: Test conditions and results for selected TEPAN/BED sorbent experiments where inlet gas composition in vol% is 9.0% CO₂, 3.5% O₂, ppmv NO, ppmv SO₂, and N₂ balance. 253
Table 40: NETL sorbents tested at ADA ........................................................................................................................................... 277
Table 41: Key flue gas characteristics for field tests ........................................................................................................................................... 280
Table 42: PEI sorbent key ......................................................................................................................................................... 283
## Acronyms, Abbreviations, and Symbols

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADA</td>
<td>ADA Environmental Solutions</td>
</tr>
<tr>
<td>APTS</td>
<td>Aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance Fourier transform infrared spectrometer</td>
</tr>
<tr>
<td>BIAS</td>
<td>Basic immobilized amine sorbent</td>
</tr>
<tr>
<td>CCSI</td>
<td>Carbon Capture Simulation Initiative</td>
</tr>
<tr>
<td>CD</td>
<td>Complete discretization</td>
</tr>
<tr>
<td>CDF</td>
<td>Cumulative distribution function</td>
</tr>
<tr>
<td>CEM</td>
<td>Continuous emission monitors</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>COE</td>
<td>Cost of electricity</td>
</tr>
<tr>
<td>CPAHCL</td>
<td>Chloropropylamine-hydrochloride</td>
</tr>
<tr>
<td>CRADA</td>
<td>Cooperative Research and Development Agreement</td>
</tr>
<tr>
<td>CSSs</td>
<td>Cyclic steady states</td>
</tr>
<tr>
<td>DBN</td>
<td>Diazobicyclonorene</td>
</tr>
<tr>
<td>DBU</td>
<td>Diazobicycloundecene</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>DEAB</td>
<td>Diethanolamine bentonite</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeters</td>
</tr>
<tr>
<td>EDXS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FGD</td>
<td>Flue gas desulfurization</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FVPSA</td>
<td>Fractionated vacuum pressure swing adsorption</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HAS</td>
<td>Hyperbranched aminosilicas</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
</tr>
<tr>
<td>HK</td>
<td>Horvath-Kawazoe</td>
</tr>
</tbody>
</table>
### Acronyms, Abbreviations, Symbols (cont.)

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAS</td>
<td>Immobilized amine sorbent</td>
</tr>
<tr>
<td>ID</td>
<td>Induced draft</td>
</tr>
<tr>
<td>IGCC</td>
<td>Integrated gasification combined cycle</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared spectrometer</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer-by-layer</td>
</tr>
<tr>
<td>LCTS</td>
<td>Life Cycle Test System</td>
</tr>
<tr>
<td>MATRIC</td>
<td>Mid-Atlantic Technology, Research and Innovation Center</td>
</tr>
<tr>
<td>MCCF</td>
<td>Modular Carbon Dioxide Capture Facility</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methyldiethanolamine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>MOFs</td>
<td>Metal organic frameworks</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometer</td>
</tr>
<tr>
<td>MTHP</td>
<td>Methyltetrahydropyrimidine</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>NGCC</td>
<td>Natural gas combined cycle</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>PC</td>
<td>Pulverized-coal</td>
</tr>
<tr>
<td>PCPs</td>
<td>Porous coordination polymers</td>
</tr>
<tr>
<td>PDU</td>
<td>Process developmental unit</td>
</tr>
<tr>
<td>PEHAS</td>
<td>Pore-expanded hyperbranched aminosilica</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylenimine</td>
</tr>
<tr>
<td>PHI</td>
<td>Physical Electronics</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure swing adsorption</td>
</tr>
<tr>
<td>R-IAS</td>
<td>Reformulated immobilized amine sorbent</td>
</tr>
<tr>
<td>RUA</td>
<td>Regional University Alliance</td>
</tr>
<tr>
<td>SANS</td>
<td>Small angle neutron scattering</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SD</td>
<td>Single discretization</td>
</tr>
</tbody>
</table>
### Acronyms, Abbreviations, Symbols (cont.)

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEPA</td>
<td>Tetraethylenepentamine</td>
</tr>
<tr>
<td>TEPAN</td>
<td>Tetraethyleneamineacyrilonitrile</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetric</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analyzer</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TSA</td>
<td>Temperature swing adsorption</td>
</tr>
<tr>
<td>TVA</td>
<td>Tennessee Valley Authority</td>
</tr>
<tr>
<td>WGS</td>
<td>Water-gas shift</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZIFs</td>
<td>Zeolitic imidazolate frameworks</td>
</tr>
</tbody>
</table>
Acknowledgments

This work was completed over the span of 13 years as part of National Energy Technology Laboratory (NETL) research for the U.S. Department of Energy’s (DOE) Fossil Energy Program.

The author wishes to thank the many contributors to this document. First and foremost, James Hoffman, McMahan Gray, and Ranjani Siriwardane deserve recognition for their outstanding contributions to the sorbent area of research. This triumvirate pioneered the carbon dioxide sorbent research effort at NETL and have made great strides towards the advancement of the technology. Many other NETL employees have contributed during this era and many thanks are given to them: George Richards, Daniel Fauth, Jared Ciferno, James Fisher, Yuhua Duan, Larry Shadle, Thomas Tarka, Sheila Hedges, David Hopkinson, Kevin Resnik, Paul Zandhuis, Christopher Matranga, David Miller, Yee Soong, Sonia Hammache, Evan Granite, Esmail Monazam, Robert Stevens, James Poston, Bryan Morreale, Jeff Culp, and Edward Fisher. The author expresses regrets to any whose contributions have been overlooked.
EXECUTIVE SUMMARY

The removal of carbon dioxide (CO₂) from a gas stream is an important and necessary step in the overall carbon sequestration process. From the initial direction of the Carbon Sequestration Program that is implemented by the U.S. Department of Energy’s National Energy Technology Laboratory (NETL), the point sources of interest were those involved in the production of energy. Capture techniques could be retrofitted onto existing conventional air-based fossil-fuel-fired power plants or integrated into new power generation facilities. Although the capture and separation of CO₂ from other gas constituents can be approached in different fashion, the ultimate goal of a strategy for carbon capture and separation should facilitate the removal of CO₂ from other stream components, thus allowing the CO₂ to be concentrated into a process stream that is more amenable for further carbon sequestration treatment, including compression, transportation, and storage. The selection of a technology for a given capture application depends on many factors, including partial pressure of the CO₂ in the gas stream; temperature; total system pressure; the process gas composition; extent of CO₂ recovery; sensitivity to impurities, such as acid gases and particles; purity of the recovered CO₂ product; capital and operating costs of the process; and environmental impacts.

Fossil-fuel fired power plants for electric generation in the United States represent significant stationary sources of emitted CO₂ and are the targets for regulatory control. The application of a CO₂ capture technology into a power plant cycle is greatly dictated by the operating conditions required for the CO₂ capture step and can broadly be defined as post-combustion and pre-combustion. Post-combustion CO₂ capture systems are primarily applicable to conventional pulverized-coal fired power plants. Post-combustion CO₂ capture refers to removal of CO₂ from combustion flue gas prior to discharge to the atmosphere. In this approach, the combustion product CO₂ is separated from nitrogen, which is the primary constituent of the flue gas. Separating CO₂ from this flue gas is challenging for several reasons: a high volume of gas must be treated because the CO₂ is dilute (13 to 15 volume percent in coal-fired systems, three to four volume percent in gas-fired turbines); the flue gas is at low pressure (15 to 25 pounds per square inch absolute (psia)); trace impurities (particulate matter, sulfur oxides, nitrogen oxides, etc.) can degrade the CO₂ capture materials; and compressing captured CO₂ from near atmospheric pressure to pipeline pressure (about 2,200 psia) requires a large auxiliary power load.

Alternatively, pre-combustion systems are designed to separate CO₂ from hydrogen (H₂) and other constituents in the synthesis gas (also known as syngas or fuel gas) stream produced by the gasifier in integrated gasification combined cycle (IGCC) power plants or other industrial facilities. In a gasifier, fuel is converted into gaseous components by applying heat under pressure in the presence of steam and sub-stoichiometric oxygen (O₂). By carefully controlling the amount of O₂, only a portion of the fuel burns to provide the heat necessary to decompose the remaining fuel and produce syngas, a mixture of H₂ and carbon monoxide (CO), along with minor amounts of other gaseous constituents. To facilitate pre-combustion capture, the syngas is further processed in a water-gas shift (WGS) reactor, which converts CO and steam into CO₂ while producing additional desired H₂, thus increasing the H₂ and CO₂ concentrations. A CO₂ capture technology can then be used to separate the CO₂ from the H₂. Because CO₂ is present at much higher concentrations in syngas (after WGS) than in flue gas, and because the syngas is at higher total pressure, CO₂ capture should be easier and less expensive for pre-combustion capture than for post-combustion capture. In addition, the volume of syngas that requires processing is much lower than the volume of flue gas from a comparable pulverized coal
combustion power plant, which results in smaller capture equipment sizes and potential lower capital costs. After CO₂ removal, the H₂ is used as a fuel in a combustion turbine combined cycle to generate electricity. Note also that the trend in IGCC gas cleanup has been to remove the minor gas contaminants (for example, hydrogen sulfide) at elevated temperature (~300–700°F) since this provides a plant thermal efficiency improvement as compared to lower temperature removal for these contaminants.

One CO₂ capture technology, dry scrubbing, uses a solid material (sorbent) that is involved in gas/solid interactions and may also be regenerable. Simplistically, depending on the nature of the gas/solid interactions, the CO₂ may be physically adsorbed (physisorption) or chemically absorbed/adsorbed (chemisorption). In the case of chemical absorption, CO₂ undergoes a chemical reaction with an active compound present on the solid to form a new product, such as a carbonate or bicarbonate. Hence, chemical absorption involves heterogeneous gas/solid chemical reactions. However, in the case of physical adsorption, the CO₂ is sorbed onto the surface of the solid and does not undergo chemical reaction on the surface to form a new species. Adsorption capacities and kinetics are influenced by pore size, pore volume, surface area, and the affinity of the solid for weakly bonding the CO₂. In any event, the scrubbing step is normally followed by regeneration of the CO₂-rich sorbent, thus releasing the CO₂ from the solid medium. Such a regenerable technique reuses the sorbent over multiple cycles. A temperature-swing and/or pressure-swing regeneration can occur, but the particular path will be dependent on various factors. An ideal sorbent would exhibit all desirable properties, but realistically, it is not expected that any one sorbent will exhibit all of the best properties. Tradeoffs will occur and economic analyses will be vital in the determination of which sorbent and which combination of properties will result in the lowest costs for a particular plant. While the ultimate goal is to capture CO₂ with minimal impact on cost of energy service, the total capture cost for each sorbent and associated process can come from a number of different factors and be heavily influenced by the various properties of the sorbents.

At the commencement of the Carbon Sequestration Program, the in-house research effort at NETL became pro-active in the sorbent development area. Much expertise was tapped in the effort since NETL in-house had a plethora of past experience with sorbents in the gas cleanup area for both flue gas and fuel gas streams. However, typically the contaminant cleanup in gas streams required significantly less sorbent as compared to carbon dioxide capture. A good example is in the mercury mitigation area where the amount of mercury that would need to be removed in a flue or fuel gas application is orders of magnitude smaller than carbon dioxide in the same flue or fuel gas application. As the fledgling research effort in the Carbon Sequestration Program matured, the knowledge base for the capture technologies increased and correspondingly, the researchers became more aware of new research problems and challenges that required resolution. Some of the results in the early studies impacted the direction of future work with sorbents and thus elucidated the needs of sorbents.

The earlier studies at NETL aimed to provide experimental data bases employing dry, regenerable solids for CO₂ removal in a temperature swing adsorption mode or pressure swing adsorption mode. Baseline performances of CO₂ removal processes were established with the use of zeolites, alkali/alkaline earth materials, and activated carbon. These early studies established the foundation from which more recent sorbent investigations have been initiated and from which comparisons have been made. Initial research with these sorbents occasionally did not significantly differentiate between post-combustion and pre-combustion applications. However,
as research results materialized and system analyses improved, a distinction as to where the sorbents could be used became more apparent.

This report details the initial NETL in-house research efforts in the CO₂ capture area with sorbents over nearly thirteen years and the lessons learned during this timeframe. In general, sorbents can be categorized with respect to the following families: zeolites, carbons, hydrotalcites, alkali/alkaline earth materials, amine functionalized sorbents, and metal organic frameworks. Except for the hydrotalcites, the NETL in-house research effort has encompassed all of these different families of sorbent materials at one time or another.

**Zeolites**

Carbon dioxide can be physically adsorbed onto high surface area solids without undergoing chemical reaction. High surface area materials can be created through surface activation (for example, by steam or oxygen treatment) of the material, resulting in very fine surface porosity. Naturally occurring zeolites are an example of a material having high surface area and are capable of gas adsorption. For solid adsorption, adsorption capacities and kinetics are influenced by such parameters as pore size, pore volume, surface area, and the affinity of the solid for weakly bonding the CO₂.

Once the gas is adsorbed onto the solid, several modes of operation are used to release, or regenerate the adsorbed gas from the solid. Pressure and/or temperature are manipulated during regeneration so that the adsorption step can be subsequentially repeated. Pressure swing adsorption (PSA) entails adsorbing the gas at higher pressure, isolating the solid, and then desorbing the sorbed gas by lowering the system pressure. Vacuum pressure swing adsorption utilizes a vacuum pressure during the regeneration step. In temperature swing adsorption (TSA), gases are adsorbed at lower temperature, the solid isolated, and then temperature is raised during the regeneration step to release the trapped gas. Cycle time for regeneration is typically much shorter for PSA than for TSA.

Molecular sieves and activated carbons have been popular sorbents for the separation process. The use of PSA to capture CO₂ from different types of coal-using power plants, including pulverized coal combustion, pressurized fluidized-bed combustion, and integrated gasification combined cycle, was earlier investigated by Japanese researchers. Molecular sieve zeolites and a molecular sieve carbon were tested in the study, and the best performing zeolite was selected as the adsorbent to separate CO₂ from simulated coal gas at 150°C. The coal gas composition simulated that of a fuel gas downstream of a shift converter and dehumidifier. The molecular sieve zeolite showed a high effective capacity for CO₂ capture in a pressurized condition at 150°C. Also during this time, another set of Japanese researchers studied CO₂ removal from a coal/oil-fired power plant (TEPCO’s Yokosuka Thermal Power Station) using a combination of both pressure and temperature swing adsorption. The adsorbent material was described as a pelletized Ca-X type zeolite, belonging to the faujasite type (X type) family of zeolites, but the identity of the material was somewhat ambiguous in the study. A two-stage adsorption tower system was employed. The adsorption temperature was 30–50°C and the adsorption pressure was 1.1–1.2 atm. Desorption was conducted at lower pressure (0.1–0.3 atm). The plant was able to maintain 90% overall CO₂ removal with 99% purity in the recovered CO₂. It must be noted that the flue gas was first dehumidified using beds of alumina prior to CO₂ removal, since moisture will impact the adsorptivity of the zeolite sorbent. The moisture was removed to -50°C dew point in the flue gas to prevent deterioration of the zeolite.
Thus, a logical starting point for some of the sorbent work at NETL was with zeolites. (Section 2) As mentioned, earlier studies had used zeolites, especially the synthetic 13X. Since it is a nominal physisorbent, its use in a PSA application was of interest, especially in a pre-combustion situation (i.e., IGCC) where the high pressure of the system exists. The use of the zeolite in a PSA application at post-combustion conditions is not as clear due to the relative low pressure of that system. However, with respect to the gas compositions, the potential use of zeolites at both pre-and post-combustion conditions were determined during the course of the testing.

- The venture into the zeolitic research initially concentrated on the study of synthetic and naturally-occurring zeolites within a variety of research instruments, including laboratory-scale reactors and analytical equipment. Investigations at temperatures and pressures related to pre-combustion and post-combustion led to the selection of synthetic zeolite 13X as a prime candidate for further study. Isotherms at 25°C and 120°C for 13X indicate a significant increase in CO₂ capture with pressure as contrasted to much lower uptake with nitrogen and hydrogen. The CO₂ capture is greater at the lower temperature. Work with the natural zeolites did not extend beyond initial studies since the capture capacities were much lower than with the synthetic zeolites. By performing a combined pressure/temperature swing, the spent CO₂ enriched 13X sorbent was able to be fully regenerated under a nitrogen flow up to 120°C. In situ analytical studies would confirm that the most abundant surface species observed throughout the CO₂ adsorption study appeared to be physically adsorbed CO₂.

- Based on initial laboratory information with 13X, a modeling effort was initiated where a pressure-swing adsorption process, which uses zeolite 13X as an adsorbent to recover carbon dioxide from a mixture of gases (nitrogen and carbon dioxide), was investigated through dynamic simulation and optimization. The modeling adopted new isotherm data for 13X ranging from 30°C to near 120°C and optimized three types of adsorption processes: a normal-temperature PSA, a high-temperature PSA, and a modified fractionated vacuum pressure swing adsorption (FVPSA) process to improve the CO₂ purity as well as the N₂ purity. The PSA operation adopted a Skarstrom cycle and the modified FVPSA operation consisted of four steps: pressurization, adsorption, cocurrent blowdown, and countercurrent regeneration. It was summarized that the high-temperature FVPSA is much better than PSA in obtaining high purity of CO₂ (~90%) while maintaining high values of other performance measures. Although this initial modeling effort gave some hope for pressure swing application with zeolites, the presence of moisture and other trace components within the processed gas would need to be further considered to project a realistic post- or pre-combustion application.

- While the exploratory research with synthetic zeolites was occurring on the laboratory-scale units, an internal NETL decision was made to proceed with the design and construction of a modular carbon dioxide capture facility, known as the MCCF. The first carbon capture technology candidate to be investigated was the sorbent technology based on zeolite 13X. However, before the testing on the larger scale (0.07-MWe) of the MCCF was to commence, a bench-scale data base was to be assembled that would complement the earlier laboratory studies but also elucidate any potential engineering issues that could impact the scale-up design of the MCCF. Simulated flue gas mixtures flowed over molecular sieve 13X in the bench-scale packed bed reactor, and the amount of adsorbed carbon dioxide was quantified. Molecular sieve 13X demonstrated the affinity to adsorb
Sorbent Research for the Capture of Carbon Dioxide

CO₂ from simulated flue gas mixtures. Removal is most favored at lower temperature and higher partial pressure of CO₂. The sorbent capacity ranged near 3.5 mol CO₂/kg sorbent at baseline conditions, somewhat higher but comparable to the capacity of the laboratory-scale work. Two important observations were identified. First, an exotherm that occurred in this larger bench-scale packed bed reactor during adsorption indicated that heat management will be a critical issue in eventual reactor design. Second, moisture was found to have a very negative impact on sorbent performance and subsequently its adsorption caused the required swing in temperature to be raised to maintain suitable regeneration with respect to CO₂. It must be remembered that zeolites like 13X have been used as desiccants in industrial processes. Competitive adsorption between CO₂ and H₂O is speculated, as determined in the laboratory testing. Regeneration at 120°C is sufficient for dry adsorption conditions, but a much higher regeneration temperature (350°C) is required when moisture levels approached 2–4% in the adsorption gas. Actual flue gas from a coal-burning utility can have 6–7 vol% water, and this moisture concentration is even greater if the flue gas needs to be cleaned beforehand in a flue gas desulfurization unit. These results coupled with some of the earlier laboratory-scale results established guidelines for the 13X sorbent that would be used in scale-up for the modular carbon dioxide capture facility.

- To accelerate the development of low cost capture and separation technologies, NETL was to implement the design and construction of a modular, flexible CO₂ capture test facility, labeled the Modular Carbon Dioxide Capture Facility (MCCF), as mentioned above. The facility would be able to test new capture technologies on coal combustion flue gas and, additionally, on process gas from advanced fossil fuel conversion systems, such as coal gasification. Ultimately, a database for a particular capture technology would provide experimental information from which further engineering scale up decisions could be formulated. The concept of the MCCF was unique at the time and could have been used to further advance new technologies in the carbon dioxide capture/separation area. However, after its initial campaign with zeolite 13X, the work with the MCCF was abandoned due to two main reasons: (1) the CO₂ capture technologies developed up to calendar year 2004 were not technologically advanced to make a significant investment in and (2) there was considerable uncertainty in the budgeting process for a long-term investment. It is interesting to note that the concept of the MCCF as a “user facility” has been adopted by NETL and the Carbon Sequestration Program in the form of the National Carbon Capture Center in Wilsonville, AL.

- Due to a research milestone to produce an operable testing system, because of the maturity—at the time—of the zeolite 13X system, and based partially on the commercial use and availability of 13X, the MCCF was used initially to study this physical adsorbent to remove CO₂ from flue gas. The objective was to establish baseline performance of the MCCF using a commercially available material in a post-combustion mode. A stationary packed bed reactor was chosen. An actual flue gas was produced and used. Results from this first campaign, which magnified the earlier bench-scale results, indicated favorable CO₂ removal and the adsorption reaction was highly exothermic. Moisture was found to negatively impact the performance of the zeolite; the material is used commercially as a desiccant. A concern with this sorbent in future reactor design would be associated with the exothermic heat release due to both CO₂ and H₂O adsorption. Heat management
would be critical and would be a concern with all CO\textsubscript{2} capture sorbents. Other flue gas contaminants, including SO\textsubscript{2} and NO\textsubscript{x}, were adsorbed onto the zeolite, with both species being almost irreversibly adsorbed. The adsorption reaction was most favored at temperatures near 38°C. Thermal regeneration under a nitrogen sweep can be conducted at 120°C for dry flue gas, but a much higher temperature (350°C) is required after moisture laden flue gas is processed.

**Alkali/Alkaline Earth Sorbents**

As previously mentioned, dry scrubbing uses a solid instead of a liquid scrubbing medium. The system involves regenerable gas/solid interactions. Depending on the nature of the gas/solid interactions, the CO\textsubscript{2} may be physically adsorbed or chemically absorbed. In the case of chemical absorption, CO\textsubscript{2} undergoes a chemical reaction with an active compound present on the solid to form a new product, such as a carbonate or bicarbonate. Hence, chemical absorption involves heterogeneous gas/solid chemical reactions. The reaction of CO\textsubscript{2} with alkali/alkaline earth materials falls in this category (Section 3).

For chemical absorption of CO\textsubscript{2} onto a solid, a heterogeneous reaction occurs on the surface of the solid to form a new chemical species. Because CO\textsubscript{2} is an acid gas, reaction often involves neutralization of the CO\textsubscript{2} with a base compound on or within the solid. Such acid/base neutralization reactions are commonly employed in commercial wet scrubbing of CO\textsubscript{2} using basic solvents, including alkanolamines, NH\textsubscript{3}, hot K\textsubscript{2}CO\textsubscript{3}, and so on. Hence, analogous reactions can be extended to a gas/solid system in place of the liquid scrubbing medium.

Compounds of alkali and alkaline earth metals can be employed in chemical reactions with CO\textsubscript{2}. As an example, an alkali metal carbonate can react with CO\textsubscript{2} and H\textsubscript{2}O to form an alkali metal bicarbonate:

\[
X_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{XHCO}_3
\]

\((X = \text{Li, Na, K, etc.})\)

Another class of reactions involves alkaline earth metals, whereby an alkaline earth metal oxide can react with CO\textsubscript{2} to form an alkaline earth metal carbonate:

\[
\text{XO} + \text{CO}_2 \rightleftharpoons \text{XCO}_3
\]

\((X = \text{Mg, Ca, etc.})\)

A different type of reaction involves substitution of metals to form a metal carbonate, for example, in the case of Li and Zr:

\[
\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \rightleftharpoons \text{Li}_2\text{CO}_3 + \text{ZrO}_2
\]
During the inception of this research, a thermodynamic analysis was used to identify ranges of temperature for absorption and regeneration for a particular reaction. Carbonate/bicarbonate reactions using alkali metals were projected to occur at temperatures less than 100–200°C and can be applicable to flue gas temperatures. The alkaline earth metal reactions, depending on the specific metal, can occur over a wide and elevated range of temperature (approximately 500–900°C). The high-temperature materials may have application suitable for CO₂ capture in process streams at elevated temperature, such as in IGCC or other advanced power systems. Regarding temperatures for suitable operation, it is difficult to generalize any one group of reactions, but rather, a specific reaction should be considered in its entirety. This rudimentary thermodynamic analysis was used as a gauge to further test various alkali/alkaline earth materials as capture sorbents in the early stages of development at NETL.

A more sophisticated technique for predicting the identity of applicable CO₂ sorbents has been more recently developed. The methodology or computational hierarchy for screening a large number of candidates for suitability as CO₂ sorbents for either pre-combustion or post-combustion capture applications was established. In this study, analysis is applied based on calculation of the thermodynamic data using first-principles density functional theory (DFT) and lattice phonon dynamics to screen a large number of alkaline earth metal oxides, hydroxides, and their corresponding composites, and to explore their CO₂ capture properties systematically. Predictions are compared with the available thermodynamic data to assess the accuracy of the approach and to outline a general screening scheme that can be used to predict the CO₂ capture properties of the new types of materials for which thermodynamic data might not be available.

Most of the research with these compounds occurred during the early years of the Carbon Sequestration Program and revolved around the preliminary thermodynamic and preliminary exploratory tests with the materials. Testing with potassium-, calcium-, and lithium-based sorbents occurred chronologically followed by more recent experimentation with sodium- and magnesium-based sorbents. For the alkali/alkaline earth materials, their use in a pre-combustion application is probably more feasible. Although predictions have directed the use of the materials in a post-combustion application, post-combustion systems analysis studies reveal that the regenerative heat duties for some of the materials are quite large, in part due to the large heat of the carbonation reaction. This significantly impacts the overall regeneration heat duty of the sorbent and makes the process energetically inferior when compared to the post-combustion benchmark technology of monoethanolamine (MEA) scrubbing.

- Some of the initial investigations at NETL began with potassium-based sorbents. From the initial thermodynamic study, potassium carbonate was chosen as a valid candidate. Due to its temperature constraints, it was envisioned that the sorbent would be used in a lower temperature post-combustion application, with the absorption temperature less than 145°C. The approach undertaken in the potassium carbonate study was to investigate various concentrations of potassium carbonate deposited on an alumina substrate using a thermogravimetric analyzer (TGA) and a bench-scale packed bed reactor with 10 vol% CO₂ in a simulated flue gas at an absorption temperature of 60°C. TGA results indicate CO₂ capture is favored at low absorption temperature (50–60°C), with sorbent utilization strongly decreasing with higher absorption temperature (80–100°C). The results with the two reactor systems impacted the research direction with potassium. One issue with the sorbent was the overall utilization of the potassium on the substrate indicating that the absorptive capacity was low and thus the working capacity of the sorbent would be low.
As seen in regenerative energy calculations for post-combustion sorbents, the low working capacity would significantly impact the heat duty for the sorbent. (Monoethanolamine scrubbing has a higher capacity than this potassium sorbent.) Another significant issue was with the kinetics of the sorbent. TGA information revealed that the reaction with this sorbent was relatively slow. A kinetic model indicated that the rate was very slow compared to other gas-solid reactions. Although the thermodynamics estimated that the carbonation of potassium carbonate was feasible, operational problems would occur because of the poor kinetics. Due to the above issues, the work with potassium was abandoned.

- Thermodynamic analysis of carbonation of calcium oxide indicates that the reaction has potential application for systems at relatively high temperature. Based on the calculated equilibrium constants, the CO$_2$ absorption reaction appears more favorable between 750–860°C, while thermal regeneration is attainable at temperatures higher than 860°C (near 1000°C). Due to the high temperature of operation for this sorbent and envisioned operational difficulties, a post-combustion application was not feasible. For this type of sorbent, a pre-combustion application was assumed more appropriate. The research with the calcium sorbent was divided into testing with calcium oxide and calcium carbonate powders and then testing with supported calcium on silica, on alumina, or on a zirconia support. With the pure reagent tests, the initial rate of reaction is very fast, achieving perhaps 15–20% sorbent conversion; the reaction then slows significantly and enters a regime characterized by very long residence time required to achieve minimal increase in sorbent conversion. This regime is partially attributed to increased gas diffusional resistance through a product layer of calcium carbonate. Similar to the reagent tests, the absorption reaction with the calcium/alumina-supported sorbent is initially very quick and then enters a slower kinetic regime. Utilizing this information, a rudimentary systems analysis was performed for a pre-combustion application. The high absorption temperature of the calcium oxide/carbonate systems limits its application to the gasifier exit for the IGCC application. This application would not capture the CO$_2$ associated with the CO in the syngas. If all CO$_2$ is removed from the raw gas exiting the gasifier, 80 percent of the carbon (as CO and CH$_4$) remains in the syngas. Also, regeneration temperatures (near 2000°F) for calcium carbonate are above any temperature in these systems. Additional fuel is required to heat the sorbent for regeneration, making a sole temperature-swing regeneration impractical. If possible, a pressure swing regeneration would be more appropriate to avoid the use of additional fuel for regeneration. However, due to the findings of the systems analysis and the overwhelming inherent problems with the calcium sorbent system, (particularly the fact that the sorbent’s high absorption temperature in an IGCC plant scheme equates to only about 20% capture of the theoretical carbon content), work in this area was suspended.

- Research with lithium-based sorbents at NETL commenced because of the advanced research level of the sorbent attributed, most notably, to the Japanese. Initially, lithium zirconate was studied at a temperature near 500°C, while the regeneration was examined at higher temperature (600–700°C). Unlike calcium-based sorbents, the absorption reaction continues steadily with conversion and does not appear to enter a regime of significantly lower kinetics at high conversion. Additionally, additives were used to dope the material to form eutectic compounds whereby the production of a liquid interface
within the solid matrix would hopefully lessen the diffusional resistance of CO₂ and enhance the reaction kinetics. Although the eutectic work showed an improvement in the Li₂ZrO₃ sorbent, work was concluded with this sorbent since eutectic mixtures could not lower the temperature of absorption and regeneration significantly, making them impractical for power generation facilities. Additionally, preliminary work with lithium silicate yielded significant improvements in reactivity and conversion as compared to lithium zirconate sorbent. One of the first internal NETL systems analysis was conducted using the in-house experimental information with a focus on the capture system used in an IGCC application and a conventional pulverized coal power plant. The basic conclusion from these results was that the Li₄SiO₄ regenerable sorbent, developed to capture CO₂ from either an IGCC or a pulverized coal-fired power plant, is not competitive with Selexol and amine (MEA) wet scrubbing technologies, respectively. The analysis showed that the relatively high heat of reaction, combined with high absorption and regeneration temperatures associated with CO₂ capture using Li₄SiO₄, resulted in an increase in parasitic load and the cost of electricity compared to the existing CO₂ removal technologies for post- or pre-combustion applications. Based on the analysis, it was concluded that this particular sorbent was not a potential candidate for commercial use and further studies with it were not justifiable.

- With respect to sodium-containing sorbents, other researchers had earlier approached low temperature usage in a post-combustion application. However, the issue with the product sodium carbonate is the high heat of reaction required to regenerate the sorbent (1320-Btu/lb CO₂), and it is extremely doubtful that heat integration in a post-combustion application would be significant enough to decrease the overall regenerative heat duty so that it would be 30–50% better than that of the MEA process. Therefore, with respect to sodium-containing compounds, their use in post-combustion applications is extremely doubtful and a better use of these sorbents would be in pre-combustion schemes. Several sodium-based sorbents showed very high CO₂ capture capacities (4 to 6 moles/kg) at 315°C with simulated fuel gas and at regeneration conducted at 700°C. Further investigative studies with sodium-containing sorbents used a novel sorbent that contained a mixture of sodium hydroxide and calcium oxide (1:2 weight ratio) where it was revealed NaOH was the main contributor to the capture reaction. The sorbent demonstrated a very high capture capacity in the presence of steam and a rehydroxylation process after the regeneration is critical to the performance of the sorbent during subsequent cycles. Additional regeneration studies indicated that the presence of calcium aided in the regeneration of the sodium carbonate product by lowering its decomposition temperature. Work with the sodium systems was discontinued. Although the sodium/calcium mixture had lowered the regeneration temperature for sodium carbonate, the applicability of the sorbent system incorporated into a pre-combustion scheme is still in question, since the sensible heat that is required to heat the sorbent between the absorption and regeneration temperatures can still be appreciable.

- More recent work at NETL with alkali/alkaline earth-based sorbents encompasses the use of magnesium hydroxide. The use of magnesium-based sorbent in a post-combustion application is not realistic due to its optimum temperature range of absorption (200–315°C). As envisioned in a temperature swing scheme, the regeneration is near 375–400°C, and thus the absorption and regeneration conditions make this sorbent more
applicable in a pre-combustion situation. This sorbent is more operable than the previous sorbents discussed in relation to an IGCC design since the sensible heat in the regenerative heat duty will be much less because of the lower difference in temperature between the absorption and regeneration steps. Additionally, in a temperature swing scheme, the pressure of the carbon dioxide will remain at that of the CO$_2$ removal process and this is a significant advantage, since the energy for the concentrated CO$_2$ to be compressed to the transport pipeline will be much less as compared to a capture pressure-swing scheme. Thermodynamic analysis and laboratory- and bench-scale testing indicate (1) the formation of magnesium carbonate is favored at elevated pressures and that it can be decomposed at relatively lower temperatures as compared to the other alkali/alkaline earth sorbents investigated at NETL; (2) the presence of magnesium hydroxide or magnesium oxide with steam is necessary for CO$_2$ capture; and (3) rehydroxylation of magnesium oxide after regeneration is necessary to obtain the magnesium hydroxide sorbent. Results from a preliminary systems analysis indicated that the IGCC plant thermal efficiency for the magnesium-based sorbent compared favorably with the Selexol process. Of the alkali/alkaline earth-based sorbents tested to date, the magnesium-based sorbent is the most applicable to a pre-combustion power generation scenario.

**Amine-Enriched Sorbents**

Amine-enriched sorbents were originally prescribed for post-combustion application to replace monoethanolamine (MEA) scrubbing. (Section 4) Aqueous solutions of amine compounds are used in industrial wet scrubbing for CO$_2$ removal, and the use of amine compounds as a dry, regenerable sorbent was initially pursued at NETL. Although amine-based, wet scrubbing systems have been proposed as capture techniques for CO$_2$ removal from flue gas streams, they are energy intensive due, in part, to the excessive amount of water needed in these systems. Initial research was conducted with amine compounds deposited onto a fly ash enriched in carbon. After adsorption studies were conducted under ambient pressure and at temperatures between 30 and 120°C, it was concluded that the amine-enriched samples chemically absorb CO$_2$ and H$_2$O upon contact with a gaseous stream, thereby forming amine complexes. However, it was possible that a combination of both adsorption and absorption processes was occurring. From some of these initial experimental studies and DOE programmatic goals, it was concluded that use of this type of sorbent would be most applicable in post-combustion capture schemes.

The key objective was to develop sorbent-based post-combustion CO$_2$ capture systems for both existing plants and advanced power generating facilities that lower the energy penalty and costs associated with capturing CO$_2$ from large point sources. During most of this sorbent research effort, the overall programmatic goal for the carbon sequestration scenario (of which carbon capture is the key step) was to develop fossil fuel conversion systems that achieve 90% CO$_2$ capture with 99% storage permanence at less than a 35% increase in the cost of energy services for post- and oxy-combustion capture at new and existing pulverized coal-fired power plants. Sorbent-based capture techniques with amine-enriched sorbents have the potential to meet this programmatic goal.

During the earlier stages of conducting research on CO$_2$ capture with amine-enriched solid sorbents, a preliminary systems analysis study was initiated to determine the merit of using this type of solid sorbent. The main advantage of using solid versus liquid scrubbing (i.e., aqueous monoethanolamine or MEA) was borne out in the lower anticipated heat duty of regeneration. Several factors contribute to this, including lower heat capacity of the solid; higher amine
loading on the solid as well as higher CO₂ loading on the solid; considerably negligible water in the solid versus the liquid MEA solvent (and therefore less evaporative loss); and less swing in temperature to regenerate the solid. A comparison between amine-enriched sorbents and MEA scrubbing illustrated the potential energy benefits of the sorbent system, including an overall heat duty of 783 Btu/lb CO₂ versus 1934 Btu/lb CO₂ for MEA, due primarily to lower sensible heat and evaporative considerations. (It should be noted that advances in MEA scrubbing technologies have also lowered the MEA heat duty to lower than 1,500 Btu/lb CO₂.) Additionally, a sensitivity study related to cost of electricity and gauging the ranges of various parameters, such as sorbent cost, heat duty, sorbent replacement rate, and working capacity, was conducted for a stationary bed design in a coal-fired combustion system. Results revealed that the amine-enriched sorbent system could reach the goal of the program at that time. Although this study was rudimentary with respect to the sorbent, since the basis was on some of the initial amine-enriched sorbents developed to that date, the results are meaningful and would have implications and confirmations in studies that would follow.

As a result of a more detailed systems analysis (MATRIC study), the amine-enriched sorbent work evolved as a collaboration between the areas of sorbent development and reactor design. A concerted effort began in fiscal year 2007 with a continuation of two routes of sorbent investigation: immobilized amines on supports and encapsulated amine clay-based sorbents. The first type of sorbent used various amine-based compounds that were deposited onto a substrate. The second type of sorbent involves the encapsulation of an amine and/or polar liquid material within a clay substrate, for example bentonite. The clay matrix is inexpensive, readily available, and has a low heat capacity.

In order for potential sorbent/reactor technology candidates to be experimentally evaluated at larger scale, it is prudent to perform engineering and economic analyses (i.e., system studies) upfront. The level of effort required depends on the maturity of the process to date. Amine-enriched solid sorbents were developed at laboratory/bench-scale by the NETL in-house researchers for their potential application in CO₂ removal processes. In support of these activities, reactor designs utilizing solid sorbents for flue gas applications continued to be developed, such as the collaboration that had occurred with MATRIC. Possible reactor configurations included non-stationary sorbent reactors, such as fluidized bed or moving bed, isothermal fixed bed, and fixed bed reactor with inter-staged cooling. System analyses of conceptual systems have traditionally been conducted by groups other than the in-house research effort at NETL and required coordination among the various investigations.

Once an understanding of the sorbent process is obtained, further reactor design and process development activities can occur. Down-selecting to a particular reactor design can happen once all the basic information is obtained in the sorbent studies. For example, if moisture adsorption, separate from moisture that reacts with CO₂ and amine, plays a major role with a particular sorbent, then this could direct designers to reactors where sorbent is transported between the adsorption and regeneration steps. Once a determination of a transport type system is made, then engineering research can proceed to determine information that is pertinent to the sorbent system within a specific transport design, for example, magnitude of internal heat transfer surfaces, heat transfer coefficients, etc.

More recently, greater research efforts entail reactor development where the overall goal is to characterize the performance of sorbents used during post-combustion CO₂ capture in various promising reactors suitable for processing flue gas under near atmospheric conditions. The data
generated are being used to validate simulated computer models and where necessary, generate constitutive laws consistent with theory and experimental results. Bench-scale facilities have been fabricated (C2U facility) and initially operated adiabatically with sorbents in a dry simulated flue gas. Test data results are cataloged for model validation. Operations with an immobilized amine sorbent have included batch isolated absorption and regeneration, as well as fully integrated performance between the absorption and regeneration steps. Measurement, analytical, and diagnostic tools have been applied to evaluate process performance parameters that are critical for designing and scaling these process reactors. A fully integrated warm unit, the C2U facility, capable of conducting CO$_2$ capture and solid sorbent regeneration continuously, was designed, constructed, and operated. Literature and performance parameters for MEA, supported sorbents, and selected novel concepts will be used to compare various process concepts against the benchmark and further identify process targets needed to optimize economic performance. More importantly, the information obtained will be used to validate computational fluid dynamic simulations assembled within the Carbon Capture Simulation Initiative (CCSI).

- For the immobilized amine sorbent, initial studies revolved around the development and understanding of key variables. The type of amine—primary, secondary, or tertiary amine—is important with respect to the removal of CO$_2$ from the flue gas. How the amine is attached to the substrate is also critical, as well as the availability of the amine to the carbon dioxide molecule. This has a direct relation to the type of substrate involved and its surface area and ability to bond (attach) the amine. Additionally, sorbent fabrication technique can have an impact on the sorbent performance. In all, these key parameters were initially investigated with the immobilized amine sorbents and the results directed the later work with this type of sorbent. For these immobilized amines on supports, various amine-based compounds were used and were deposited onto a substrate. Candidate compounds included tetraethylene pentamine, aminopropyltriethoxysilane, polyethyleneimine, and others, and the supports included carbon, polymethylmethacrylate, polystyrene, and silicas. After screening studies, one of the choice materials was polyethyleneimine (PEI) on mesoporous silica. PEI can be linear or branched and can contain primary, secondary, and tertiary amines. Typical loadings of PEI on silica ranged from 40–50% by weight. Due to the sorbent’s reactivity with CO$_2$ even at elevated temperatures, adequate regeneration under an atmosphere of CO$_2$ is unlikely, leading to the use of steam as a sweep during the regeneration step. The working capacity of the sorbent at typical flue gas conditions is 3–4 mole CO$_2$/kg sorbent. More recent work involves stabilization of the sorbent by using silane compounds to perform a cross-linking function.

- The second type of amine-enriched sorbent involves the encapsulation of an amine and/or polar liquid material within a clay substrate, for example bentonite. The clay matrix is inexpensive and readily available and has a low heat capacity. The amine and/or ether that are encapsulated within the clay substrate consist of about 50 weight percent of the sorbent. The sorbent acts by capturing compounds contained in gaseous mixtures via chemisorption and/or physisorption between the layers of the substrate lattice where the polar amine/ether is located. The patented scheme for sorbent fabrication contains various amines and ethers in a bentonite matrix. The sorbent can be regenerated in the presence of CO$_2$ in the temperature range of 80–100°C, and the sorbent working capacity is near
1.7 mol CO$_2$/kg sorbent. Results have been confirmed on the small units and testing within a bench-scale fluid bed reactor system.

- As the sorbents proceeded through additional development and continued to show promise, NETL sought industrial participation to help advance the technology out of the laboratory and towards commercialization, especially with an eye towards reactor process engineering and design. Mid-Atlantic Technology, Research and Innovation Center (MATRIC) was commissioned by the in-house research effort at NETL to perform a systems study for conceptualized reactor configurations for a sorbent-based CO$_2$ capture process. Spreadsheet calculations for energy and mass balances were performed. The primary metric of performance was to compare the regeneration heat duty for the sorbent/reactor configuration versus a conventional wet scrubbing process using MEA. In order to meet DOE program goals, the study recommended certain targets and that the sorbent process should have a regeneration heat duty that is at least 30–50 percent less than the MEA heat duty, corresponding to the sorbent process having a heat duty generally between 500 and 1,000 Btu/lb CO$_2$. Specific success criteria or performance targets for the sorbent were established based on assumed sorbent properties, leading to the identification of critical process parameters and information that were required for further development evaluation, including: isotherms (Δ (delta) loadings or working capacity of the sorbent) covering rich loading (absorption) and lean loading (regeneration); heat of reaction (ΔH$_r$) for CO$_2$ absorption; heat capacity (C$_p$) for sorbent; role of H$_2$O in the process; role of trace components (SO$_2$ and NO$_x$); and reaction kinetics.

- For the amine-enriched sorbents, a temperature swing is the choice method of regeneration. With respect to the encapsulated amine clay-based sorbent, regeneration can occur at elevated temperature under a sweep of CO$_2$. Although this is the preferred method of regeneration, the sorbent working capacity is on the low side. In contrast to this sorbent, the immobilized amine sorbent cannot be adequately regenerated under an atmosphere of CO$_2$ without having a significant impact on the delta loading measured for CO$_2$. A recycle stream of the CO$_2$ regenerator off-gas (after moisture is removed) has always been considered an option for a sweep gas to be used during regeneration (MATRIC assumed this type of regeneration). However, the higher partial pressure of CO$_2$ in the regenerator impacts the level of sorbent regeneration achieved, and therefore the CO$_2$ delta loading or working capacity. Results with this sorbent type point to the need to use an inert sweep gas during regeneration. The obvious choice is steam, since it can be separated (condensed) from the CO$_2$ in the off-gas. However, a whole host of questions arose since little work with sorbents exposed to direct steam regeneration had been conducted. Therefore, with this type of sorbent, studies were conducted using direct steam regeneration and the implications for this type of temperature swing were determined.

- Heat management is important. Earlier experimental studies with zeolites and alkali/alkaline earth materials and subsequent systems analysis revealed that the large amount of heat that had to be removed during sorption had major implications for the design of the reactor systems, and in fact this was a primary problem to be dealt with in the process design effort. Heat would need to be extracted from the sorbent during the absorption step and a massive amount of heat would need to be added during the
regeneration step. From past experimental work with the amine-enriched sorbents and other post-combustion sorbents at NETL, the adiabatic temperature rise in a fixed, packed bed could be substantial, and heat would need to be removed so that the absorption temperature could remain near the optimum temperature rather than increase to near the regeneration temperature (less CO₂ removal capacity) or even near the decomposition temperature of the sorbent.

- Various types of experimental facilities have been used at both the Pittsburgh and Morgantown research campuses: thermogravimetric analyzers, laboratory- and bench-scale packed bed reactors, and calorimeters. The packed bed reactor units typically used mass spectrometers to determine inlet and exit gas compositions to and from the reactor, and the capability of the instrument was extended to facilitate measurement of H₂O in the process gas. The goal allowed breakthrough curves for both CO₂ and H₂O to be simultaneously measured. There was always a desire to obtain consistent results between the types of units and the campuses. Additionally, as a form of an outside cross-check, external collaborators related to the work, such as ADA-ES and Tennessee Valley Authority, have validated NETL in-house results. Good material balances with the laboratory- and bench-scale units were always strived for.

- For both types of amine-enriched sorbents, kinetic studies have been conducted. The kinetic studies were performed on representative sorbents from each of the two families to obtain a model that would represent each. Although further variations in the sorbents could impact each sorbent, it was felt that the kinetic expression would not significantly deviate from a representative sample. Experimental results were obtained from thermogravimetric analyzers and a volumetric isotherm system. Results from the kinetic study will be fed into a computational modeling effort. If information from a systems analysis promotes a particular technology, then a computational model would be the next step in the evolution of the technology. For example, if in the sorbent work, a cross-flow moving bed is the projected best design, then a mathematical model that incorporates kinetic information, hydrodynamics, etc. can be commissioned. This model could then be used in scale-up determinations and in more realistic cost/system studies.

- Depending on the type of coal burned in a power plant, large concentrations of sulfur dioxide and nitric oxides may exist in the flue gas. Accelerated exposure testing of the sorbent with high concentrations of SO₂ (1,000-ppm) and NOx (750-ppm) poisoned immobilized amine sorbents revealing that for every mole of SO₂ or NO₂ that is absorbed by the sorbent, the capacity of the sorbent for CO₂ absorption decreases by a mole. It can be inferred that these type of sorbents behave similar to MEA with respect to SO₂/NOx and that scrubbing in the form of flue gas desulfurization/selective catalytic reduction would be needed upstream of CO₂ sorbent reactors. Auxiliary scrubbing (a polishing step) may also be needed to deep clean the flue gas with respect to these minor, but important, constituents. These results were confirmed by two outside collaborators.

- In these sorbent systems, water may play an important role. In the post-combustion absorption step and depending on the temperature, the sorbent will most likely see a water content in the flue gas of around 15 vol%. Since these sorbents are prone to sulfur dioxide poisoning, the sulfur dioxide will need to be reduced to levels that would be similar to those of MEA scrubbing. Flue gas desulfurization scrubbing before the CO₂
capture sorbent reactor in a process would thus cause the high moisture content. If the sorbent is hydrophilic as seen in the one immobilized amine study, water not related to the carbonation reaction would adsorb on sorbent. If this is desorbed at higher temperature during regeneration, then a negative impact with respect to the regenerative heat duty will occur. Additionally, for the immobilized amine sorbent, steam regeneration is needed and the possibly of steam causing some instability of the CO$_2$ capture capacity function of the sorbent is being addressed. With this sorbent in continuous flow operation between absorber and regenerator, an offset of water adsorption between the two reactors is possible to some extent to minimize the heat duty effect from water adsorption. In any case, the impact of water adsorption must always be addressed in amine-enriched sorbents.

**Other Sorbents**

Research has been conducted with CO$_2$ capture sorbents belonging to two other sorbent families: metal organic frameworks (MOFs) and activated carbon. MOFs are crystalline compounds consisting of metal ions or clusters coordinated to organic and inorganic linker molecules to form one-, two-, or three-dimensional structures that are porous. (Section 5) The pores in these materials are stable and can be used for the capture or storage of gases, such as CO$_2$. An attractive feature of these materials is that by appropriate choice of metal ion clusters and organic/inorganic linker molecules, the pore structure of the material can be engineered into a particular size or shape depending on what performs best for the end use application. Furthermore, the organic linker molecules that comprise the pores can be functionalized to increase their affinity for CO$_2$ or any other gas that needs to be stored or separated. Combining the ability to engineer pore size/shape with the additional ability to control the presence of functional groups creates a working platform where a balance can be struck between physisorption-type interactions controlled by the pore size/shape and chemisorption interactions that are dictated by functional groups on the linker molecules.

- Part of the current research effort at NETL is focused on further changing the organic linkers to contain functional groups such as OH, C=O, C-O-C, and R-NH$_2$ in an effort to increase the affinity of the sorbent to capture CO$_2$. The objective is to find a trade-off between engineering the pore size/shape by adjusting the size of the linkers in combination with modulating the chemical affinity of the linker towards CO$_2$ by adding functional groups. This combined approach allows better control for adsorption/desorption kinetics and energetics for capturing CO$_2$ from, for example, low pressure flue gas. In this fashion, some of the technical barriers associated with the regeneration of CO$_2$ sorbents can be overcome by adding extra layers of control over the kinetics and energetics associated with the adsorption/desorption process.

- MOFs lend a great deal of structural versatility to gas separation applications, especially those for pre-combustion applications. A combination of organic and inorganic building blocks, these multi-dimensional hosts can be tailored for selective adsorption of one guest over another via methods, such as pore size exclusion, mesh-size adjustable sieving, and guest-dependent structural dynamics. The numerous reports on structurally dynamic MOFs illustrate the potential of these materials for adsorption applications, yet there are only a few reports demonstrating actual gas separations using these sorbents. A structural breathing phenomenon in the MIL-53 family of MOFs was found to have a significant role in the ability of this sorbent to separate CO$_2$ and CH$_4$. Despite the detailed studies of
MIL-53, there are few experimental or theoretical methodologies to predict gas selectivities in other structurally dynamic systems or to indicate how generally applicable the MIL-53 separation mechanism may be. Additional studies with actual gas mixtures have been conducted at NETL that advance the theoretical and empirical understanding of structurally dynamic MOFs.

Activated carbon is a good physical adsorbent for removal of certain species from a gas mixture. (Section 6) With respect to carbon sequestration, activated carbon has been proposed as a sorbent for the removal of CO$_2$ from flue or fuel gas. One of the main advantages is that it is less costly than other proposed sorbents, such as synthetic zeolites. In general, zeolites have higher adsorption capacities for CO$_2$ as well as higher equilibrium selectivities for CO$_2$ over N$_2$ than activated carbon. On the other hand, the heat of adsorption of CO$_2$ on activated carbon is lower than on zeolite, so that the use of activated carbon in a PSA process may result in less severe heat effect on the PSA performance.

- From initial studies at NETL, the average calculated value of heat of adsorption for CO$_2$ over various surface coverages was 20 kJ/mol for activated carbon, and this was lower than that of the zeolites to which it was compared. The selectivity with respect to CO$_2$ versus N$_2$ and H$_2$ was skewed more favorably to the zeolites as compared to the activated carbon at pressures below 150 psi. If the sorbent was to be used in a PSA or TSA application in flue gas or fuel gas, there are other components present that could impact the reactivity/selectivity of the sorbent. Moisture is one that will impact both sorbents and can be in appreciable amounts in both applications. Activated carbon can remove SO$_2$ and NO$_x$ from flue gas, and other components in the gas stream are known to adsorb on the carbon and thus make separation more difficult for pure CO$_2$. Because of the issues with resulting purity of the CO$_2$ product gas stream, further CO$_2$ capture investigations with activated carbon have not proceeded at NETL.
1. INTRODUCTION

The removal of carbon dioxide (CO\textsubscript{2}) from a gas stream is an important step in the overall carbon sequestration process. From the initial direction of the Carbon Sequestration Program, the point sources of interest were those involved in the production of energy. Capture techniques could be retrofitted on existing conventional air-based fossil-fuel-fired power plants or integrated into new power generation facilities. The capture technologies included solvent wet scrubbing with chemical or physical absorbents, solid dry scrubbing with physical adsorbents or chemical absorbents, cryogenic methods, and gas membrane separation. The capture and separation of CO\textsubscript{2} from other gas constituents can be approached in different fashion. However, the ultimate goal of a strategy for carbon capture and separation should facilitate the removal of CO\textsubscript{2} from other stream components, thus allowing the CO\textsubscript{2} to be concentrated into a process stream that is more amenable for further carbon sequestration treatment, including compression, transportation, and storage. The selection of a technology for a given capture application depends on many factors, including partial pressure of the CO\textsubscript{2} in the gas stream; extent of CO\textsubscript{2} recovery; sensitivity to impurities, such as acid gases and particles; purity of the recovered CO\textsubscript{2} product; capital and operating costs of the process; and environmental impacts (White et al., 2003).

Dry scrubbing uses a solid material (sorbent) that is involved in gas/solid interactions and may also be regenerable. Simplistically, depending on the nature of the gas/solid interactions, the CO\textsubscript{2} may be physically adsorbed (physisorption) or chemically absorbed/adsorbed (chemisorption). In the case of chemical absorption, CO\textsubscript{2} undergoes a chemical reaction with an active compound present on the solid to form a new product, such as a carbonate or bicarbonate. Hence, chemical absorption involves heterogeneous gas/solid chemical reactions. However, in the case of physical adsorption, the CO\textsubscript{2} is sorbed onto the surface of the solid and does not undergo chemical reaction on the surface to form a new species. Adsorption capacities and kinetics are influenced by pore size, pore volume, surface area, and the affinity of the solid for weakly bonding the CO\textsubscript{2} (White et al., 2003). In any event, the scrubbing step is normally followed by regeneration of the CO\textsubscript{2}-rich sorbent, thus releasing the CO\textsubscript{2} from the solid medium. Such a regenerable technique reuses the sorbent over multiple cycles. A temperature-swing and/or pressure-swing regeneration can occur, but the particular path will be dependent on various factors.

Fossil-fuel fired power plants for electric generation in the United States represent significant stationary sources of emitted CO\textsubscript{2} and are the targets for future regulatory control. The application of a CO\textsubscript{2} capture technology into a power plant cycle is greatly dictated by the operating conditions required for the CO\textsubscript{2} capture step. Temperature, as well as pressure, of the capture process strongly governs the integration of the capture step into the power cycle. Additional considerations include process gas composition (i.e., flue gas or fuel gas resulting from the type of power generation) as well as secondary stream effects (acid gases, particulate, etc.), which may have an adverse effect on the CO\textsubscript{2} capture process. The applications can broadly be defined as post-combustion and pre-combustion.

Post-combustion CO\textsubscript{2} capture systems are primarily applicable to conventional pulverized-coal (PC) fired power plants. Post-combustion CO\textsubscript{2} capture refers to removal of CO\textsubscript{2} from combustion flue gas prior to discharge to the atmosphere. In this approach, CO\textsubscript{2} is separated from nitrogen (N\textsubscript{2}), which is the primary constituent of the flue gas. A simplified process schematic of post-combustion CO\textsubscript{2} capture is shown in Figure 1. In a typical coal-fired power plant, fuel is burned with air in a boiler to produce steam that drives a turbine/generator to produce electricity. Flue gas from the boiler consists mostly of N\textsubscript{2} and CO\textsubscript{2}. The CO\textsubscript{2} capture
process would be located downstream of the conventional pollutant controls. Chemical solvent-based technologies currently used in industrial applications are being considered for this purpose. The chemical solvent process requires the extraction of a relatively large volume of low-pressure steam from the power plant’s steam cycle, which decreases the gross electrical generation of the plant. The steam is required for release of the captured CO$_2$ and regeneration of the solvent. Separating CO$_2$ from this flue gas is challenging for several reasons: a high volume of gas must be treated because the CO$_2$ is dilute (13 to 15 volume percent in coal-fired systems, three to four volume percent in gas-fired turbines); the flue gas is at low pressure (15 to 25 pounds per square inch absolute (psia)); trace impurities (particulate matter, sulfur oxides, nitrogen oxides, etc.) can degrade the CO$_2$ capture materials; and compressing captured CO$_2$ from near atmospheric pressure to pipeline pressure (about 2,200 psia) requires a large auxiliary power load. Post-combustion CO$_2$ capture offers the greatest near-term potential for reducing power sector CO$_2$ emissions because it can be retrofitted into existing coal-based power plants and can also be tuned for various levels of CO$_2$ capture, which may accelerate market acceptance. Although post-combustion capture technologies would typically be applied to conventional coal-fired power plants, they can also be applied to the combustion flue gas from integrated gasification combined cycle (IGCC) power plants, natural gas combined cycle (NGCC) power plants, and industrial facilities that combust fossil fuels. The use of sorbents is one of the advanced post-combustion CO$_2$ capture technologies being investigated by DOE/NETL (Vora et al., 2012). Table 1 presents a general summary of some of the technical advantages and challenges related to post-combustion sorbent-based technologies (Ciferno et al., 2010; Vora et al., 2013).

Figure 1: Block diagram illustrating a PC system with post-combustion CO$_2$ capture.
Table 1: Technical advantages and challenges for post-combustion sorbent technologies.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO₂ partial pressure</td>
<td>Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases)</td>
</tr>
<tr>
<td>Higher capacities on a per mass or volume basis than similar wet-scrubbing chemicals</td>
<td>Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic</td>
</tr>
<tr>
<td>Lower heating requirements than wet-scrubbing in many cases (CO₂ and heat capacity dependent)</td>
<td>Pressure drop can be large in flue gas applications</td>
</tr>
<tr>
<td></td>
<td>Sorbent attrition</td>
</tr>
</tbody>
</table>

Pre-combustion systems are designed to separate CO₂ from hydrogen (H₂) and other constituents in the synthesis gas (also known as syngas or fuel gas) stream produced by the gasifier in IGCC power plants or other industrial facilities. In a gasifier, fuel is converted into gaseous components by applying heat under pressure in the presence of steam and sub-stoichiometric oxygen (O₂). A simplified process schematic for pre-combustion CO₂ capture is shown in Figure 2. By carefully controlling the amount of O₂, only a portion of the fuel burns to provide the heat necessary to decompose the remaining fuel and produce syngas, a mixture of H₂ and carbon monoxide (CO), along with minor amounts of other gaseous constituents. To enable pre-combustion capture, the syngas is further processed in a water-gas shift (WGS) reactor, which converts CO and steam into CO₂ while producing additional H₂, thus increasing the CO₂ and H₂ concentrations. A CO₂ capture technology can then be used to separate the CO₂ from the H₂. Because CO₂ is present at much higher concentrations in syngas (after WGS) than in flue gas, and because the syngas is at higher pressure, CO₂ capture should be easier and less expensive for pre-combustion capture than for post-combustion capture. In addition, the volume of syngas that requires processing is much lower than the volume of flue gas from a comparable pulverized coal combustion power plant, which results in smaller capture equipment sizes and lower capital costs. After CO₂ removal, the H₂ is used as a fuel in a combustion turbine combined cycle to generate electricity. Note also that the trend in gasification gas cleanup has been to remove the contaminants at elevated temperature (~300–700°F) since this provides a plant thermal efficiency improvement as compared to lower temperature removal. The use of sorbents is one of the advanced pre-combustion CO₂ capture technologies being investigated by DOE/NETL (Vora et al., 2012). Table 2 presents a general summary of some of the technical advantages and challenges related to pre-combustion sorbent-based technologies (Ciferno et al., 2010; Vora et al., 2013).
Figure 2: Block diagram illustrating an IGCC system with pre-combustion CO₂ capture.

Table 2: Technical advantages and challenges for pre-combustion sorbent technologies

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ recovery is primarily based on pressure swing (versus heat energy)</td>
<td>CO₂ pressure is lost during flash recovery</td>
</tr>
<tr>
<td>Common for H₂S to also have high solubility in the same sorbent, meaning CO₂ and H₂S capture can be combined</td>
<td>Depending on solid sorbent composition and reaction mechanism with CO₂, some sorbents require cooling of the syngas for CO₂ capture. The syngas is then re-heated and humidified prior to firing in the combustion turbine</td>
</tr>
<tr>
<td>System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems</td>
<td>System H₂ may be lost with the CO₂</td>
</tr>
</tbody>
</table>

Since the beginning of the CO₂ capture research area, there have been numerous reviews covering the different CO₂ capture technologies, and more specifically, CO₂ capture sorbents (White et al., 2003; Feng, 2009; Choi et al., 2009; Liu et al., 2009; Hedin et al., 2010; Olajire, 2010; Samanta et al., 2012; Yu et al., 2012). Certainly the application of the sorbent is important (post-combustion or pre-combustion) along with the mechanism of CO₂ removal (physisorption versus chemisorption). However, in all the studies, a generalization can be made with respect to the sorbents that are being researched. The sorbents can be categorized with respect to the following families: zeolites, carbons, hydrotalcites, alkali/alkaline earth materials, amine functionalized sorbents, and metal organic frameworks (MOFs). Except for the hydrotalcites, the
NETL in-house research effort has investigated all of these different families of sorbent materials at one time or another.

In general, there are various characteristics and properties that impact a CO$_2$ capture sorbent and its ability to be successful in its use in a relevant application within a particular reactor design. A list of these as compiled from various sources is itemized (Vora et al., 2013; Yu et al., 2012; Samanta et al., 2012; Choi et al., 2009; White et al., 2003).

- Adsorption capacity for CO$_2$ (equilibrium capacity)
- Working capacity or difference between rich and lean CO$_2$ loadings
- Selectivity for CO$_2$
- Mechanical/thermal/chemical stability under cycling between adsorption and regeneration
- Adsorption/desorption kinetics
- Surface area, porosity, and particle size
- Thermodynamic properties, such as heat capacity and heat of adsorption that impact energy consumption
- Impact of other components within the flue or fuel gas, such as moisture, sulfur dioxide, nitric oxides, hydrogen sulfide, ammonia, mercury, etc.
- Cycle time
- Sorbent fabrication and raw materials cost

An ideal sorbent would exhibit all desirable properties, but realistically, it is not expected that any one sorbent will exhibit all of the best properties. Tradeoffs will occur and economic analyses will be vital in the determination of which sorbent and which combination of properties will result in the lowest costs for a particular plant. While the ultimate goal is to capture CO$_2$ with minimal impact on cost of energy service, the total capture cost for each sorbent and associated process can come from a number of different factors and be heavily influenced by the various properties of the sorbents.

At the commencement of the Carbon Sequestration Program, the in-house research effort at NETL became pro-active in the sorbent development area. Much expertise was tapped in the effort since NETL in-house had a plethora of past experience with sorbents in the gas cleanup area for both flue gas and fuel gas streams. However, typically the contaminant cleanup in gas streams required little sorbent as compared to carbon dioxide capture. A good example is in the mercury mitigation area where the amount of mercury that would need to be removed in a flue or fuel gas application is orders of magnitude smaller than carbon dioxide in the same flue or fuel gas application. As the fledgling research effort in the Carbon Sequestration Program matured, the knowledge base for the capture technologies increased and correspondingly, the researchers became more aware of the new research problems and challenges that required resolution. Some of the results in the early studies impacted the direction of future work with sorbents and thus elucidated the needs of sorbents, as seen in the above characteristic/property list for sorbents.

The earlier studies at NETL aimed to provide experimental data bases employing dry, regenerable solids for CO$_2$ removal in a temperature swing adsorption mode or pressure swing...
adsorption mode. Baseline performances of CO₂ removal processes were established with the use of zeolites, activated carbon, and alkali/alkaline earth materials. These early studies established the foundation from which more recent sorbent investigations have been initiated and from which comparisons have been made. Initial research with these sorbents occasionally did not significantly differentiate between post-combustion and pre-combustion applications. However, as research results materialized and system analyses improved, a distinction as to where the sorbents could be used became more apparent.

These sorbent-based in-house research efforts in the carbon dioxide capture area began during the infancy of the overall Carbon Sequestration Program. Various sorbent systems had been investigated, but further studies of some were discontinued because of inherent deficiencies. An effort was devoted to zeolites, specifically 13X and others, but because of their strong attraction to moisture, a component in most gas streams of interest that contain CO₂, the work was all but abandoned. Most recently, a new concept realizing the importance of moisture has been proposed. Alkali/alkaline earth compounds were also investigated, but poor energetics, such as high heats of reaction and large temperature differences between absorption and regeneration conditions eliminated most of them from further investigation. Activated carbons, although relatively inexpensive, are typically not selective to only CO₂, since other components in the gas to be decarbonated will also readily adsorb. More recent work with MOFs and ZIFs (zeolitic imidazolate frameworks) has been reported. For post-combustion applications, these sorbents have very low CO₂ capacities at ambient pressures and can be sensitive to moisture. Pre-combustion application is more relevant. Development work at NETL had concentrated on amine-enriched sorbents for post-combustion application. Preliminary systems analysis indicated that these type of sorbents could meet the overall programmatic goal, at that time, for the carbon sequestration scenario (of which carbon capture is the key step): to develop fossil fuel conversion systems that achieve 90% CO₂ capture with 99% storage permanence at less than a 35% increase in the cost of energy services for post-combustion capture at new and existing pulverized coal-fired power plants.

The following sections of this report detail the in-house research efforts in the CO₂ capture area with sorbents over nearly thirteen years. The sections are divided by the family of sorbent, i.e., zeolites, alkali/alkaline earth materials, amine-enriched sorbents, MOFs, and activated carbon. Much of the technical information can be found in journals or conference proceedings, but additional information was located in internal topical reports and internal communications. As will be seen, the in-house effort at NETL has significantly contributed in this research area.
2. ZEOLITES

2.1 INTRODUCTION

As mentioned previously, CO$_2$ capture with dry scrubbing employs a solid material, known as a sorbent. The process involves gas/solid interactions and should be regenerable as well. Depending on the nature of the gas/solid interactions, the CO$_2$ may be physically adsorbed or chemically absorbed. Solid adsorption methods employ a physical attraction between the gas and “active sites” on the solid, whereas solid absorption methods employ a chemical reaction to capture the target gas. Carbon dioxide can be physically adsorbed onto high surface area solids without undergoing chemical reaction. High surface area materials can be created through surface activation (for example by steam, or oxygen treatment) of the material, resulting in very fine surface porosity. Naturally occurring zeolites are an example of a material having high surface area and are capable of gas adsorption. For solid adsorption, adsorption capacities and kinetics are influenced by such parameters as pore size, pore volume, surface area, and the affinity of the solid for weakly bonding the CO$_2$ (White et al., 2003).

Once the gas is adsorbed onto the solid, several modes of operation are used to release, or regenerate the adsorbed gas from the solid. Pressure and/or temperature are manipulated during regeneration so that the adsorption step can be repeated. Pressure swing adsorption (PSA) entails adsorbing the gas at higher pressure, isolating the solid, and then desorbing the sorbed gas by lowering the system pressure. Vacuum pressure swing adsorption utilizes a vacuum pressure during the regeneration step. In temperature swing adsorption (TSA), gases are adsorbed at lower temperature, the solid isolated, and then temperature is raised during the regeneration step to release the trapped gas. Cycle time for regeneration is typically much shorter for PSA than for TSA (Riemer et al., 1994).

PSA processes are based on preferential adsorption of the desired gas (CO$_2$) on porous materials at a high pressure. When the pressure is decreased, the gas is desorbed from the porous sorbent and the sorbent can be reused for subsequent adsorption. Molecular sieves and activated carbons have been popular sorbents for the separation process. It is also reported that the PSA process can concentrate CO$_2$ to high purity from flue gas, but at a low recovery rate. The main reason for low recovery was insufficient regeneration. Low adsorption pressures and low concentration of CO$_2$ in the feed gas have also contributed to the lower adsorption and lower recovery. It was also reported that higher energy penalties are associated with the utilization of molecular sieves than with the wet scrubbing amine process (Fulkerson et al., 1990). However, newer PSA process concepts have been reported in the literature to improve the performance of the process. While it is important to consider the improved process design of the PSA systems to enhance the recovery rate, it is equally important to utilize sorbents with high CO$_2$ adsorption capacity, high selectivity for CO$_2$, high diffusivity, high rates of adsorption, and high regenerability.

The use of PSA to capture CO$_2$ from different types of coal derived power plants, including pulverized coal combustion, pressurized fluidized-bed combustion, and integrated gasification combined cycle, was investigated by Japanese researchers (Ito et al., 1999). Five kinds of molecular sieve zeolites and a molecular sieve carbon were tested in the study, and the best performing zeolite was selected for the adsorbent of PSA to separate CO$_2$ from simulated coal gas at 150°C. The coal gas composition simulated that of a fuel gas downstream of a shift converter and dehumidifier. The molecular sieve zeolite showed a high effective capacity for CO$_2$ capture in a pressurized condition at 150°C, and other coal gas constituent effects were
small regarding CO$_2$ adsorption. At higher temperature, the adsorbent acted as a catalyst for the shift reaction and carbon deposition occurred on the adsorbent.

Japanese researchers studied CO$_2$ removal from a coal/oil-fired power plant (TEPCO’s Yokosuka Thermal Power Station) using a combination of both pressure and temperature swing adsorption (Ishibashi et al., 1999). The adsorbent material was described as a pelletized Ca-X type zeolite, belonging to the faujasite type (X type) family of zeolites, but the identity of the material was somewhat ambiguous in the study. Since calcium is the predominant cation, the material was likely not 13X (Na zeolite); zeolite type 5A is rich in calcium and remains one possibility. A two-stage adsorption tower system was employed. The adsorption temperature was 30–50°C and the adsorption pressure was 1.1–1.2 atm (absolute). Desorption was conducted at lower pressure (0.1–0.3 atm). The plant was able to maintain 90% overall CO$_2$ removal with 99% purity in the recovered CO$_2$. It is worth noting that the flue gas was first dehumidified using beds of alumina prior to CO$_2$ removal, since moisture will impact the adsorptivity of the zeolite sorbent. The moisture was removed to -50°C dew point in the flue gas to prevent deterioration of the zeolite.

Recovery rates can also be enhanced if PSA systems are utilized in high pressure gas streams, since some PSA sorbents have shown superior adsorption capacity at higher pressures. Sorbent tests conducted at NETL (Siriwardane et al., 2001a, 2001c, 2003) have shown that the amount of CO$_2$ adsorbed on some synthetic and natural zeolites can be increased substantially by increasing the pressure from 1 atm to 20 atm. Calculations also indicated that the sorbents achieve their maximum adsorption capacity at 20 atm. The adsorption capacities observed with these sorbents are considerably better than the values reported for commercial processes, such as the wet scrubbing amine process (Siriwardane, 2001b). It could be possible to make the PSA/TSA technique superior to the existing CO$_2$ capture techniques by utilizing proper system designs and zeolite-based sorbents that have both high selectivity, high regenerability, and high adsorption capacity for CO$_2$.

Thus, a logical starting point for some of the sorbent work at NETL was with zeolites. As mentioned, earlier studies had used zeolites, especially the synthetic 13X (Ito et al., 1999; Ishibashi et al., 1999; Chue et al., 1995). Since it is a nominal physisorbent, its use in a PSA application was of interest, especially in a pre-combustion situation (i.e. IGCC) where the high pressure of the system exists. The use of the zeolite in a PSA application at post-combustion conditions is not as clear due to the relative low pressure of that system. However, with respect to the gas compositions, the potential use of the zeolites at both pre-and post-combustion conditions were determined during the course of the testing.

### 2.2 LABORATORY-SCALE EXPLORATORY TESTING

Zeolites have been investigated at NETL to potentially be used in a PSA and/or TSA application. Zeolites that were investigated were either synthetic or naturally-occurring. Siriwardane (2001a, 2003, 2005) was the initial investigator with a parallel detailed bench-scale study by Hoffman (2004). In one of the earliest studies, zeolites 13X (Z10-02) and 4A (Z4-01) were obtained from Zeochem, Inc.; zeolites WE-G 592 and APG-II were obtained from UOP; and zeolite 5A was obtained from Aldrich Chemical Co. The three natural zeolites, natural herschelite-sodium chabazite (sodium alumino silicate), clinoptilolite (sodium alumino silicate), and another form of clinoptilolite (potassium calcium alumino silicate), were obtained from GSA Resources Inc.,
American Absorbents Natural Products Inc., and St. Cloud Mining Co., respectively. The analysis of the zeolites can be seen in the following three tables (Siriwardane et al., 2003, 2005).

**Table 3: Physical and chemical properties of five synthetic zeolites**

<table>
<thead>
<tr>
<th>Property</th>
<th>13X</th>
<th>5A</th>
<th>4A</th>
<th>WE-G 592</th>
<th>APG-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>710</td>
<td>ND*</td>
<td>ND*</td>
<td>625</td>
<td>710</td>
</tr>
<tr>
<td>Pore diameter (Å)</td>
<td>10</td>
<td>5</td>
<td>4</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Composition (wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>11.7</td>
<td>3.8</td>
<td>10.8</td>
<td>13.7</td>
<td>8.8</td>
</tr>
<tr>
<td>Aluminum</td>
<td>14.2</td>
<td>14.8</td>
<td>13.6</td>
<td>15.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Silicon</td>
<td>18.2</td>
<td>16.7</td>
<td>16.1</td>
<td>16.5</td>
<td>14.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.5</td>
<td>7.8</td>
<td>0.8</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.2</td>
<td>0.8</td>
<td>0.9</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.2</td>
<td>1.0</td>
<td>1.2</td>
<td>ND</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* Not determined

**Table 4: Physical properties of three natural zeolites**

<table>
<thead>
<tr>
<th>Property</th>
<th>Zeolite 1</th>
<th>Zeolite 2</th>
<th>Zeolite 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Natural herschelite – sodium chabozite (sodium alumino silicate)</td>
<td>Clintopile (sodium alumino silicate – Type 4A zeolite)</td>
<td>Clintopile (potassium calcium sodium alumino silicate)</td>
</tr>
<tr>
<td>HK pore diameter (Å)</td>
<td>4.3</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>DFT total pore volume (cm³/g)</td>
<td>0.29</td>
<td>0.029</td>
<td>0.024</td>
</tr>
<tr>
<td>DFT surface area (m²/g)</td>
<td>671</td>
<td>11.2</td>
<td>11.3</td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>485</td>
<td>18.4</td>
<td>13.3</td>
</tr>
<tr>
<td>Langmuir surface area (m²/g)</td>
<td>540</td>
<td>23.2</td>
<td>15.9</td>
</tr>
</tbody>
</table>
Table 5: Bulk and surface elemental ratios of three natural zeolites.

<table>
<thead>
<tr>
<th>Elemental Ratios</th>
<th>Zeolite 1</th>
<th></th>
<th>Zeolite 2</th>
<th></th>
<th>Zeolite 3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Natural herschelite – sodium chabozite (sodium alumino silicate)</td>
<td></td>
<td>Clintopile (sodium alumino silicate – Type 4A zeolite)</td>
<td></td>
<td>Clintopile (potassium calcium sodium alumino silicate)</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
<td>Surface</td>
<td>Bulk</td>
<td>Surface</td>
<td>Bulk</td>
<td>Surface</td>
</tr>
<tr>
<td>Al/Si</td>
<td>0.32</td>
<td>0.35</td>
<td>0.19</td>
<td>0.20</td>
<td>0.23</td>
<td>0.38</td>
</tr>
<tr>
<td>Na/Si</td>
<td>0.24</td>
<td>0.24</td>
<td>0.10</td>
<td>0.12</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>K/Si</td>
<td>0.02</td>
<td>0.02</td>
<td>0.06</td>
<td>0.02</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca/Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.09</td>
</tr>
</tbody>
</table>

At the Morgantown site, various reactor systems and analytical tools were used in the investigation (Siriwardane et al., 2005). A volumetric adsorption apparatus was used to obtain adsorption isotherms up to 120°C in pure CO₂ (99.5%, Jackson Welding Supply Co.), N₂ (99.5%, Jackson Welding Supply Co.), and oxygen (99.6%, Jackson Welding Supply Co.) and hydrogen (99.95%, Butler Gas Products) on the sorbents, up to an equilibrium pressure of about 300 psi (2 MPa). Approximately 10 ml of the sorbent material was placed in the sample chamber, and then the chamber was evacuated to 5 x 10⁻⁵ Torr. The amount of CO₂ adsorbed was calculated using the pressure measurements before and after exposure of the sample chamber to CO₂. Baseline data with CO₂ were obtained using 10 ml of glass beads (2 mm in diameter).

Surface areas and information about micropores were determined using a Micromeritics model ASAP 2010 micropore-volume analyzer. The samples were evacuated initially at 90°C for 1 h and then at 350°C for 24 h. N₂ adsorption was measured at the liquid N₂ temperature (-196°C). Micropore analyses of the data were conducted using the Horvath-Kawazoe (HK) method; cylindrical pores were assumed in the calculations (Siriwardane et al., 2003). Density functional theory (DFT) was used to calculate the total pore volume and surface area.

Competitive gas adsorption studies and temperature programmed desorption (TPD) studies were conducted in a laboratory-scale fixed-bed reactor (Micromeritics model Autochem 2910 atmospheric flow reactor) at 14.7 psi (0.101 MPa), using gas mixtures with the following typical compositions: (a) 15 vol% CO₂, 82 vol% N₂, and 3 vol% O₂ (certified gas mixture by Butler Gas Products Co.), in the presence of water vapor at ambient temperature, to represent a coal-combustion flue gas stream; and (b) 12 vol% CO₂, 35.9 vol% CO, 27.1 vol% H₂, and 25 vol% helium (a certified gas mixture, supplied by the Messer Gas Technology and Service Group) saturated with water to represent a coal-gasification fuel gas stream. The premixed gas mixtures were passed through a water bubbler to introduce moisture into the gas stream before introduction of the gas mixture to the reactor. The outlet gas stream from the reactor was analyzed using a mass spectrometer (Pfeiffer Vacuum Thermostat). The samples (with a volume of 1.7 x 10⁻³ L) were pretreated at 120°C for 1 h in the flow reactor, under helium, prior to exposure to the gas mixtures. A switching valve was used to direct the gas stream to the mass spectrometer through either the sample or sample bypass loop. During the pretreatment of the zeolites with helium, the gas mix that contained CO₂ was introduced to the mass spectrometer.
through the sample bypass loop. It was possible to establish the initial composition of the gas mixture during this time. After the helium pretreatment, the gas mix was directed to the zeolite sample, using the switching valve. There was an abrupt decrease in the CO₂ concentration when the gas mix was directed to the sample, from either 12 or 15 vol % to <1 vol %. The starting point of all the plots of CO₂ concentration versus time was selected at the time when the CO₂ concentration reached 0.5%. In the TPD studies, CO₂ adsorption was conducted at ambient temperature and then N₂ was introduced at ambient temperature and at a flow rate of 10 cm³/min, until the CO₂ level was <1%. The temperature then was increased at a rate of 8.5°C/min while the CO₂ concentration was measured with the mass spectrometer (Siriwardane et al., 2005).

The high-pressure flow-reactor tests were conducted with a flow reactor from Parr Reactor Co. The pressure during the tests was 280 psi (1.9 MPa), and the temperature was 120°C. The gas compositions were similar to those used during low-pressure studies; however, water vapor was not present.

Measurements of the heat of adsorption were conducted with a calorimeter (Setaram model DSC 111). The calorimeter operated in the vertical mode, utilizing flow reactor tubes. The zeolites were heated at 120°C in helium for 2 h, and baseline heat-versus-time data were recorded during this time. CO₂ then was introduced at a flow rate of 15 cm³/min and exothermic heat-versus-time data were recorded. Integration of the heat curve to obtain the heat of adsorption was performed using software provided by Setaram, Inc. The TGA analysis was conducted utilizing a TA Instruments 951 analyzer. Zeolite samples were heated to 150°C under N₂ immediately prior to the adsorption of CO₂. Gas mixtures that contained 2, 7, and 15 vol % CO₂, 82–95 vol % N₂, and 3 vol % O₂ were introduced at 120°C, and the weight gain was recorded as a function of time.

The foray into this zeolitic research (Siriwardane et al., 2001a; 2005) concentrated on 13X along with four other synthetic zeolites. Volumetric adsorption isotherms of CO₂, N₂, and H₂ on molecular sieve 13X at 25°C are shown in Figure 3. The shape of the isotherms appears to be similar to type 1 (Langmuir). The CO₂ adsorption increased rapidly when the pressure was increased up to 50 psi. The increase in CO₂ adsorption after 50 psi appears to be gradual. The adsorption isotherms for repeated cycles were very similar. This indicated that the adsorption is fully reversible and complete regeneration can be obtained by evacuation of the material after adsorption. At all pressures, adsorption isotherms of both nitrogen and hydrogen were lower than those of CO₂. Both nitrogen and hydrogen isotherms were also completely reversible. Preferential adsorption of CO₂ on molecular sieve 13X indicates that this material can be used for separation of CO₂ from some gas mixtures. The final adsorption isotherm (cycle 9 was obtained after the completion of adsorption experiments with nitrogen and hydrogen) was conducted with CO₂ and it was very similar to the previous adsorption isotherms with CO₂. This indicated that the sorbent was not affected by the adsorption of nitrogen and hydrogen.
Figure 3: Adsorption isotherms of CO$_2$, N$_2$, and H$_2$ on molecular sieve 13X at 25°C.

Adsorption isotherms of CO$_2$ were similar between 13X and 4A, but the capacity of 4A was always less than 13X, which could be related to the pore size of the material (10 angstrom for 13X and 4 angstrom for 4A (Siriwardane, 2001b). Both molecular sieves 13X and 4A exhibited high uptake of moles of CO$_2$ per kg of the sorbent at pressures less than 30 psi; a leveling of uptake occurred after 30 psi.

Isosteric heats of adsorption as a function of surface coverage were calculated using adsorption isotherms at different temperatures (30, 40, 50°C). The Clausius-Clapeyron equation was utilized in these calculations. Isosteric heats of adsorption of molecular sieve 13X decreased from 50 to 10 kJ/mol with increasing coverage from 1 to 5 mol/kg. The wide range of activation energies observed for the molecular sieve 13X indicated that there is a wide range of sites with varying adsorption energies present in molecular sieve 13X.

Later studies with 13X and other synthetic zeolites (Siriwardane et al., 2005) were conducted at higher temperatures that would be representative of pre-combustion conditions. Adsorption isotherms for 13X at ambient and elevated temperature (120°C) are shown in Figure 4. The isotherms for CO$_2$ adsorption were higher than those for N$_2$, which indicated that there was preferential adsorption of CO$_2$ on the zeolite. For zeolite 13X, the amount of CO$_2$ adsorbed increased rapidly with increasing pressure up to 25 psi, and adsorption was very slow up to 300 psi. CO$_2$ adsorption was significantly higher at 30°C than at 120°C, especially in the lower-pressure region. At high pressures, it was possible to adsorb substantial amounts of CO$_2$, even at 120°C.
These studies conducted in the laboratory indicated that the synthetic zeolites can preferentially adsorb CO₂ from gas mixtures representing both coal combustion (flue gas) and gasification streams (fuel gas) at ambient temperature. Zeolite desorption must be understood if zeolites are to be used in PSA/TSA processes. Thus, a temperature programmed desorption (TPD) study was conducted with zeolite 13X after CO₂ adsorption at ambient temperature (Siriwardane et al., 2005). N₂ was introduced, thus reducing the partial pressure of CO₂ above the sorbent, and the CO₂ concentration was measured as a function of time, as shown in Figure 5. Most of the CO₂ was desorbed at ambient temperature, because the CO₂ was physically adsorbed. When the CO₂ level was <1%, the temperature was increased to 200°C. Figure 6 shows the CO₂ concentration measured during the temperature ramp. The temperature at the maximum CO₂ concentration was about 120°C, as shown in Figure 6, and this indicated that strongly bound CO₂ can be removed at 120°C. The amount of weakly adsorbed CO₂ calculated from Figure 5 is about 1.4 mol/kg and the amount of strongly bound CO₂ calculated from Figure 6 is about 0.85 mol/kg. This indicates that most of the CO₂ (62%) was weakly adsorbed on zeolite 13X. Because the CO₂ can be completely desorbed at 120°C, it was interesting to investigate the CO₂ adsorption/desorption behavior of the zeolites at 120°C. If sufficient CO₂ adsorption can be conducted at 120°C, where it also desorbs rapidly, then the adsorption/desorption process can potentially be conducted, in a pre-combustion application, using a simple pressure swing process and not a combination PSA/TSA process.
Figure 5: Desorption of CO₂ during the introduction of N₂ at 25°C with zeolite 13X after CO₂ adsorption.

Figure 6: Temperature-programmed desorption (TPD) studies with zeolite 13X after CO₂ adsorption.
CO₂ adsorption tests were conducted on the zeolites in the Micromeritics laboratory-scale fixed-bed reactor with gas mixtures that contained CO₂ to evaluate competitive gas adsorption behavior at 120°C. Figure 7 shows results of the competitive gas adsorption tests on zeolite 13X, utilizing a gas mixture that contained 15 vol % CO₂, 3 vol % O₂, and 82 vol % N₂ and that was saturated with water vapor at 120°C, in an atmospheric reactor at a flow rate of near 5 cm³/min. After the gas mixture was introduced, the CO₂ concentration decreased to the ppm level, whereas the N₂ level increased to 100%, until breakthrough occurred. This indicated that there was an excellent separation of CO₂ from the gas mixture. Repeated measurements showed a similar separation. Following CO₂ adsorption, the sorbent was regenerated at 120°C with N₂. CO₂ adsorption capacity decreased during the first and second cycle; however, the capacity stabilized after the second cycle, as shown in Figure 7.

![Figure 7: Adsorption of CO₂ on zeolite 13X at 120°C, 1 atm (15 vol % CO₂, 82 vol % N₂, and 3 vol % O₂, and H₂O, 5 cm³/min).](image)

The breakthrough times (the time required to reach 1% CO₂) of the first cycle, which represent the capacity of the sorbent to adsorb CO₂, are listed in Table 6 for the various synthetic zeolites. Zeolites 13X and WE-G 592 had long breakthrough times, whereas zeolites 5A and 4A had shorter breakthrough times. The longer breakthrough times for zeolites 13X and WE-G 592 indicate that these two zeolites have higher CO₂ adsorption capacities per unit volume, because approximately similar volumes of each sorbent were used in the reactor studies. The number of moles of CO₂ adsorbed per unit weight was calculated using CO₂ concentration-versus-time data up to CO₂ saturation. As shown in Table 6, zeolites 13X and WE-G 592 also have the largest CO₂ adsorption capacity per unit weight of sorbent. The amount of CO₂ adsorbed during the atmospheric flow reactor tests on zeolite 13X at 120°C was about 0.70 mol/kg. The amount of strongly bound CO₂ desorbed on zeolite 13X during the TPD tests after CO₂ adsorption at ambient temperature was near 0.85 mol/kg. The amount of CO₂ adsorbed at 120°C was slightly
lower than the amount of strongly bound CO\textsubscript{2} obtained during the TPD tests. Zeolite 4A showed slow adsorption of CO\textsubscript{2} from the breakthrough point up to the saturation point and, therefore, indicated the adsorption of a high number of moles of CO\textsubscript{2}, even though this zeolite had a short breakthrough time (Siriwardane et al., 2005).

**Table 6: Zeolite breakthrough times for Cycle 1 and heat of CO\textsubscript{2} adsorption values at 120°C**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Breakthrough time for 1% CO\textsubscript{2} (min)</th>
<th>CO\textsubscript{2} adsorption capacity (mol/kg)</th>
<th>Heat of Adsorption (kJ/kg)</th>
<th>Heat of Adsorption (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13X</td>
<td>20</td>
<td>0.70</td>
<td>-44</td>
<td>-63</td>
</tr>
<tr>
<td>5A</td>
<td>13</td>
<td>0.38</td>
<td>-24</td>
<td>-63</td>
</tr>
<tr>
<td>4A</td>
<td>9</td>
<td>0.50</td>
<td>-28</td>
<td>-56</td>
</tr>
<tr>
<td>WE-G 592</td>
<td>24</td>
<td>0.60</td>
<td>-33</td>
<td>-55</td>
</tr>
<tr>
<td>APG-II</td>
<td>15</td>
<td>0.38</td>
<td>-25</td>
<td>-66</td>
</tr>
</tbody>
</table>

Zeolites like 13X have been used as desiccants in industrial processes (Plastic Services and Equipment, 2003). With respect to CO\textsubscript{2} capture, they can be very susceptible to changes in activity due to the presence of water vapor. The capacity of the sorbents decreased – especially zeolites 13X and WE-G 592 – during the first and the second cycles. Water vapor was used during the flow reactor studies. The adsorption of water vapor during the first cycle and incomplete desorption of water vapor during regeneration with dry N\textsubscript{2} at 120°C may have caused the decrease in capacity. To investigate dehydration behavior, TGA tests were conducted on the zeolites. The samples were heated at a rate of 2.3°C/min, and the weight loss was monitored. TGA results are shown in Figure 8. All the zeolites showed a rapid weight loss up to ~350°C. The weight loss indicated that dehydration of the zeolites seemed to be complete at 350°C. TPD experiments were also conducted to study the desorption of water and CO\textsubscript{2}. In TPD experiments when the temperature was ramped up to 400°C at a rate of 8.5°C/min, a maximum in CO\textsubscript{2} concentration was observed at ~120°C but CO\textsubscript{2} desorption continued up to ~250°C, whereas the desorption of water was initiated at ~350°C. When the temperature was ramped up to 120°C and maintained there for 60 min, the amount of CO\textsubscript{2} desorbed was similar to that observed during the TPD with a 400°C ramp. This indicated that all the CO\textsubscript{2} can be desorbed at 120°C, whereas water can be desorbed only at ~350°C. Water vapor was present during the first cycle, but CO\textsubscript{2} adsorption was not affected by the presence of the water vapor. However, water vapor that was retained on the surface of a zeolite after the first cycle affected the performance in the second cycle. Additionally, microreactor tests were conducted on zeolite WE-G 592 after regeneration at 350°C and the breakthrough curves overlapped during the four-cycle test, indicating that there was no loss in capacity after regeneration at 350°C (Siriwardane et al., 2005).
A study was also conducted with natural zeolites (Siriwardane et al., 2003). Adsorption isotherms of CO₂, N₂, and O₂ with zeolite 1 (properties of the selected natural zeolites are listed in Tables 4 and 5) and the adsorption isotherm of CO₂ for glass beads are shown in Figure 9. The isotherm for CO₂ is higher than that for the other gases, which indicates that there is preferential adsorption of CO₂ on zeolite 1. The amount of CO₂ adsorbed increased rapidly with increasing pressure up to 12 psi, and then there was a gradual linear increase in adsorption up to 300 psi. The saturation of CO₂ adsorption was not observed in this pressure range. The adsorption isotherm of the first cycle appeared to be higher than that of the second cycle indicating that some changes in the material may have taken place during the first adsorption cycle. The desorption isotherms of CO₂ were slightly higher than that of the adsorption isotherms indicating that the adsorption is fairly reversible. The amount of CO₂ adsorbed is about 2.5 to 3 mol/kg of the sorbent at 250 to 300 psi. This value is smaller than that was obtained with synthetic zeolite 13X and 4A (Siriwardane et al., 2001a, 2001b, 2005). Work with the natural zeolites did not progress beyond this study.
Figure 9: Adsorption and desorption isotherms of zeolite 1.

Similar trends can be found with the natural zeolites and synthetic zeolites. To initially identify the different types of CO₂ species adsorbed on the zeolites, temperature-programmed desorption (TPD) studies were conducted in the fixed bed reactor with the natural zeolites after the CO₂ adsorption from the gas mixture. After the CO₂ adsorption, nitrogen was introduced to the zeolite at 25°C (10 cm³/min) and CO₂ concentration of the outlet gas was measured with the mass spectrometer. When the CO₂ concentration was below 1%, the temperature was gradually increased to 200°C at a rate of 8.5°C/min and the concentration of the CO₂ was measured. The amount of CO₂ desorbed (as a function of time) during the nitrogen purge at 25°C, and during TPD with zeolite 1, is shown in Figures 10 and 11 (see Tables 4 and 5 for properties of natural zeolites 1–3.) As shown in Figure 10, the desorption curve at 25°C was fairly broad, which indicated that there is continuous distribution of weakly adsorbed CO₂ with different sorption strengths. It is also possible that desorption of CO₂ is transport limited at this temperature and this may also have contributed to the broadening of the desorption curve. The ratio of the amount of CO₂ desorbed at 25°C, under nitrogen, to that desorbed during the TPD (up to 200°C) is 1.57. This indicates that the majority of the CO₂ was physically (weakly) adsorbed, and desorbed, during the introduction of nitrogen at room temperature. There was also a substantial amount of strongly bound CO₂, and the maximum temperature of desorption of the CO₂ was 115°C, as shown in Figure 11. Similar results were observed with zeolite 2. The ratio of the amount of CO₂ desorbed during the nitrogen flush to that during the TPD for zeolite 2 is 2.14, indicating that zeolite 2 had more physically adsorbed CO₂ than zeolite 1. Elemental compositions at the surface (measured with XPS) and of the bulk (as reported by the suppliers) are listed in Table 5. The major cation in both zeolite 1 and 2 is sodium, but the sodium content was higher in zeolite 1. The major cations in zeolite 3 are potassium and calcium, while the sodium content of zeolite 3 is very low. Zeolite 1 contains more sodium than zeolite 2, as shown in Table 5. The presence of
more sodium in zeolite 1 may have contributed to the more strongly bound CO$_2$. Analytical evidence indicates that the more strongly bound carbon could be attributed to either bicarbonate or bidentate carbonate type species (Siriwardane et al., 2003).

Figure 10: Amount of CO$_2$ desorbed at 25°C during the introduction of nitrogen with zeolite 1 after CO$_2$ adsorption.

Figure 11: Amount of CO$_2$ desorbed during temperature-programmed desorption with zeolite 1.
Similarly, correlations were made between the capacity reactivity of the synthetic zeolites and their compositions (Siriwardane et al., 2005). Surface areas and measured pore volumes of the zeolites are listed in Table 3. Elemental compositions of the zeolites, measured using the inductively coupled plasma technique, are also listed in Table 3. The major cation in the zeolite 5A was calcium; in all the other zeolites, the major cation was sodium. Both Na/Al and Na/Si ratios were highest with zeolites 13X and WE-G 592. Of the synthetic zeolites evaluated at elevated temperatures (Siriwardane et al., 2005), zeolites 13X and WE-G 592 showed the highest CO$_2$ adsorption capacity and the highest heats of adsorption at 120°C. The interaction of CO$_2$ at 120°C was stronger than a physical interaction. Thus, the most likely CO$_2$ interaction sites on the surface of the zeolites at 120°C were those in the vicinity of Na$^+$ ions present on the surface. Zeolites 13X and WE-G 592 had the highest Na/Si ratios: 0.72 and 0.83, respectively. This along with having the larger pore diameters may have contributed to the higher CO$_2$ adsorption capacity at 120°C.

A further study was conducted with synthetic zeolites to investigate the CO$_2$ capture mechanism through use of in situ Fourier transform infrared (FTIR) analysis in an effort to elucidate the relationship between the chemistry of CO$_2$ capture and sorbent performance (Stevens et al., 2008). The adsorption of CO$_2$ onto five zeolite materials (13X, WEG, AGP, 4A, and 5A whose physical and chemical properties can be seen in Table 3) was studied by in situ infrared spectroscopy at 1 atm as a function of the pretreatment temperature (120 and 350°C) and adsorption temperature (30 and 120°C). In this work, the as-received zeolite samples were ground into a powder to maximize spectral quality via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis. For each test, a zeolite sample of approximately 20 mg was charged to a DRIFTS reactor cell (Thermo Electron product 0031-902). The DRIFTS cell is a cold-walled reactor that features temperature control and ZnSe windows for IR transmission within the 650–4000 cm$^{-1}$ range. Infrared spectra were collected with a Thermo-Nicolet Nexus 670 FTIR instrument, which housed the DRIFTS reactor cell. Spectra were collected at a resolution of 4 cm$^{-1}$ with 50 co-added scans using a liquid N$_2$-cooled MCT/A detector.

Two variables were investigated: (i) pretreatment temperature and (ii) adsorption temperature. Prior to each experiment, the zeolite samples were pretreated in situ by heating to the pretreatment temperature (120 or 350°C) and held at 1 atm in flowing N$_2$ for 1 h. The pretreated sample was then cooled to the adsorption temperature (30 or 120°C). The pretreated zeolite sample at the desired adsorption temperature served as the IR background for each experiment. Adsorption of CO$_2$ onto the zeolite samples was started via terminating N$_2$ flow followed by initiating the 1 vol % CO$_2$-N$_2$ flow. Sample IR spectra were collected during selected intervals during adsorption to observe changes in the sample surface (i.e., formation and/or destruction of adsorbed species). The adsorption phase of the test was conducted for approximately 30 min. After the adsorption phase of testing, the CO$_2$-N$_2$ flow was returned to pure N$_2$ (40 sccm) to evaluate desorption of CO$_2$ from the zeolite via FTIR analysis. Two experiments were also conducted with zeolite 13X using moist CO$_2$-N$_2$. Moisture was introduced to the test cell through use of a H$_2$O saturator (bubbler).
Figure 12: FTIR analysis of 1 vol % CO₂-N₂ adsorption at ambient temperature onto the 120°C pretreated 13X zeolite. The purge phase was also conducted at ambient temperature under pure N₂ flow. Adsorption times indicated are relative to the onset of CO₂ exposure; purge times indicated are relative to the onset of the N₂ purge.

Figure 13: FTIR analysis of 1 vol % CO₂-N₂ adsorption at ambient temperature onto the 350°C pretreated 13X zeolite. The purge phase was also conducted at ambient temperature under pure N₂ flow. Adsorption times indicated are relative to the onset of CO₂ exposure; purge times indicated are relative to the onset of the N₂ purge phase.
Typical FTIR results for zeolite 13X can be seen in Figures 12 and 13. Figure 12 depicts FTIR spectra of the 120°C pretreated 13X sample after exposure to CO₂ at 30°C. The spectra indicate that there is formation of bridged bidentate carbonate bands at 1,688 and 1,361 cm⁻¹, a band at 1,623 cm⁻¹, a physisorbed CO₂ band at 2,353 cm⁻¹, as well as a negative (loss) peak at 3,693 cm⁻¹. Increased exposure time led to growth of all bands described as well as further loss at 3,693 cm⁻¹. Desorption in a pure N₂ flow at ambient temperature led to the disappearance of the bridged bidentate carbonate bands and a decrease in the intensity of physisorbed CO₂, which still remained even after 3 h. No recovery of the band at 3,693 cm⁻¹ that was removed during CO₂ exposure was observed. The removal of a band at 3,693 cm⁻¹ suggests that CO₂ may be interacting with surface OH, which is likely to be present on the surface of 13X after activation at 120°C. Interaction of the CO₂ with OH may lead to the formation of bicarbonate or formate. Bands at 3,605, 1,640, 1,480, and 1,235 cm⁻¹ were assigned to bicarbonate. Other than the band at 1,623 cm⁻¹, no other bands corresponding to bicarbonate were observed. Formate would be expected to yield bands at 1,597 and 1,377 cm⁻¹, but these bands were not observed. The band at 1,623 cm⁻¹ may be assigned to a shifted monodentate carbonate.

In Figure 13, the lack of a negative change in the OH region of the IR spectrum during adsorption of CO₂ over the 350°C pretreated zeolite suggests that the activation temperature likely drove off surface hydroxyl groups from the sample in the form of water, thereby yielding less OH present for the interaction with CO₂. It is likely that the removal of surface OH during the higher activation temperature also led to an increased number of available adsorption sites for CO₂, as evidenced by the observation of bridged bidentate carbonate over the 350°C activated sample, whereas it was not observed over the 120°C activated sample.

Certain conclusions can be drawn from the FTIR results above combined with 120°C CO₂ adsorption and purge results with the pretreated 13X. Adsorbed H₂O on the surface of the zeolite may block the adsorption sites of the zeolite, inhibiting the formation of carbonates yet still allowing for formation of physisorbed CO₂ (path 1). Removal of adsorbed H₂O through heating may allow for the direct interaction between the incident CO₂ molecule and surface hydroxyl groups, resulting in displacement and/or removal of the OH groups to form adsorbed water and carbonates (path 2); bridged bidentate carbonate is the most common adsorbate observed during testing. Further heating of the zeolite sample may lead to the removal of the OH groups in the form of H₂O prior to exposure to CO₂, resulting in the formation of carbonates without the removal of OH during CO₂ exposure (path 3); bidentate carbonate formation may be facilitated through this pathway. The 350°C pretreatment appeared to lead to a combination of both paths 2 and 3 in addition to physisorbed species, whereas pretreatment at 120°C appeared to lead to a combination of paths 1 and 2 (Stevens et al., 2008).

Also in this study, zeolite 13X was observed by FTIR for competitive CO₂/H₂O adsorption testing: sequential flows of H₂O followed by H₂O/CO₂ followed by CO₂ at 120°C onto a 350°C pretreated 13X. Conclusions drawn reveal that after H₂O exposure, exposure to CO₂ led to no adsorbed species, suggesting that H₂O can block the adsorption sites of the zeolite sorbent. The competitive adsorption between CO₂ and H₂O shows that, not only can H₂O block the adsorption sites, but it can also displace adsorbed CO₂ species from the surface even while in a CO₂-rich environment. Relative concentrations of CO₂ and H₂O appear to affect the adsorption of individual species because both appear to be competing for the same adsorption sites on the zeolites. FTIR results with the other zeolites were reported with some mechanistic differences between the types (A or X) of zeolites. Overall, the most abundant surface species observed

Sorbent Research for the Capture of Carbon Dioxide
throughout the CO₂ adsorption study appeared to be physisorbed CO₂, which is believed to be largely responsible for the CO₂ capture capacity of the zeolite sorbent.

2.3 MODELING EFFORT WITH ZEOLITE 13X

From the initial research with 13X, a modeling effort was initiated. Here, a pressure-swing adsorption process, which uses zeolite 13X as an adsorbent to recover carbon dioxide from a mixture of gases (nitrogen and carbon dioxide), was investigated through dynamic simulation and optimization (Ko et al., 2003). Many studies have dealt with the simulation and optimization of adsorption processes. These systems require the solution of partial differential algebraic equations to model adsorption in each bed, enforcement of periodic boundary conditions to describe cyclic steady states (CSSs), and the determination of optimal design and operating variables. However, little has been published on the optimization of PSA processes using zeolite 13X for CO₂ sequestration. This modeling effort concentrated on the dynamic simulation and optimization of a bench-scale PSA system with zeolite 13X as the adsorbent, to remove CO₂ from gas mixtures consisting of N₂ and CO₂. The feed composition is 15% CO₂ and 85% N₂. The mathematical model including the adsorption rate, mass balance, and heat balance influenced by adsorption heat had been formulated for a four-step operating PSA cycle (pressurization, adsorption, depressurization, and regeneration) in a single bed, as shown on the left in Figure 14. The selected adsorbent, zeolite 13X, is very good at separating CO₂ from the mixture gas consisting of N₂ and CO₂. Pure gas adsorption isotherm parameters were calculated from experimental data (Siriwardane et al., 2001a) and the Langmuir equation for a mixture gas isotherms was used to describe the competitive adsorption behavior in this work. The study (Ko et al., 2003) considered the optimization of PSA at cyclic steady state by using a single discretization (SD) approach that discretizes just the spatial domain; hybrid features in the gProms allow switching of the boundary conditions associated with modeling of different operating steps in the cycle. As demonstrated, the adopted methodology is more reliable than the complete discretization (CD) method for the optimization of cyclic adsorption processes in the gProms modeling system.
The PSA cycle with beds packed with zeolite 13X as an adsorbent is operated in four steps: pressurization, adsorption, depressurization, and desorption as can be seen in Figure 14. During the pressurization step, high-pressure feed gas consisting of 85% N\textsubscript{2} and 15% CO\textsubscript{2} at ambient temperature is supplied to the bottom of the bed. During the adsorption step, CO\textsubscript{2} is adsorbed on a fixed adsorbent (zeolite 13X); N\textsubscript{2} is obtained as a product at the top of the bed; and the high-pressure feed gas enters the bed continuously as in the pressurization step. During the depressurization step, CO\textsubscript{2} starts being recovered. The desorption step also obtains CO\textsubscript{2} at the bottom of the bed, and N\textsubscript{2} at ambient pressure is employed as a purge gas. The target process in this initial modeling effort was limited to a bench-scale design.

The summary of the initial modeling and optimization strategy, the process model, the constraints for the optimization problem, and the discretization method can be found in the literature along with the numerical results for the optimization problem (Ko et al., 2003). From extensive sensitivity studies about the optimum solutions, the required power is affected only by the feed pressure and adsorption gas velocity and not by the bed length, purge pressure, and operating step times – the power requirement increases as the adsorption gas velocity and feed pressure increase. The purity of CO\textsubscript{2} is improved when the purge operating times (the depressurization and regeneration times) increase. The purity of CO\textsubscript{2} decreases as the purge pressure and linear gas velocity of the regeneration step increase. The recovery of CO\textsubscript{2} increases, as the purge pressure, regeneration gas velocity, and purge step times increase, and it decreases accordingly as the feed pressure, adsorption gas velocity, and feeding operation times (the pressurization and adsorption times) increase. Though the purity of N\textsubscript{2} is hardly affected by the decision variables and is over 99%, it is slightly enhanced when the bed length, feed pressure, and pressurization time increase. The purity of N\textsubscript{2} deteriorates when the adsorption gas velocity increases. The recovery of N\textsubscript{2} decreases as the bed length, feed pressure, adsorption gas velocity, and pressurization time increase and the adsorption time decreases. Optimization tolerance and
reasonable initial conditions were deemed important in this exercise. It was concluded that the PSA process using zeolite 13X could give a high purity of the components with low energy cost. Later, a refinement of the initial modeling effort was conducted with the goal to improve the purity and recovery of carbon dioxide (Ko et al., 2005). The modeling adopted new isotherm data for 13X ranging from 30°C to near 120°C and optimized three types of adsorption processes: a normal-temperature PSA, a high-temperature PSA, and a modified fractionated vacuum pressure swing adsorption (FVPSA) process to improve the CO₂ purity as well as the N₂ purity. The PSA operation adopts a Skarstrom cycle, and the modified FVPSA operation consists of four steps: pressurization, adsorption, cocurrent blowdown, and countercurrent regeneration (see the right side of Figure 14.)

An updated, new optimization procedure was used that led to several observations. First, the optimal feed pressure of high-temperature PSA is lower than that of normal-temperature PSA. The optimal feed pressure of high-temperature FVPSA is much lower than those of PSA cases. In high-temperature FVPSA, higher feed pressure is required to achieve higher CO₂ purity. Second, the optimal purge and blowdown pressures are almost at the lower bounds of the optimization constraints, meaning that the regeneration of CO₂ can be improved by reducing the pressure at the regeneration (purge) step. The cocurrent blowdown step of FVPSA to evacuate the N₂ within the bed also requires a low pressure (lower bound). Third, in PSA, the optimized depressurization and regeneration times are the upper bounds of optimization constraints to obtain the required CO₂ purity. In FVPSA, the optimal regeneration time also hits the upper bound to get the high CO₂ purity.

It was summarized that the high-temperature FVPSA is much better than PSA in obtaining high purity of CO₂ (~90%) while maintaining high values of other performance measures (recoveries of both components and N₂ purity) (Ko et al., 2005). In other words, the FVPSA shows good performance to get high purities and recoveries of both components from the 85% N₂ and 15% CO₂ feed. The characteristic of zeolite 13X and the operating conditions are important here. Also, the average power (watts) for FVPSA operation is considerably larger than that for PSA operation because of a high velocity (and valve coefficient) in the feed pressurization and countercurrent blowdown steps. Subsequently, the specific power (the average power per mole of CO₂ recovered) values of FVPSA are larger than those of the PSA cases.

There have been previous optimization studies for PSA removal using zeolites, including 13X. In these studies, different reactor schemes had been identified and some were based on the Skarstrom cycle. Kikkinides et al. (1993) uses a 4-step PSA but with an activated carbon. Park et al. (2002) investigate the first stage of a complicated coupled two-stage PSA process. Gomes et al. (2002) based a two bed, 4-step PSA model on the use of 13X. Chue et al. (1995) model a three bed seven step cycle with 13X.

Although some hope is given to PSA in post-combustion applications with the modeling effort, it is shown in the actual Yokosuka pilot plant testing with a zeolite (Ishibashi et al., 1999) that PSA would probably be too costly and energy intensive with flue gas. From these studies, a pre-combustion capture condition appears to be more acceptable with respect to costs as compared to the post-combustion condition. The cost of compression of the inlet gas is a factor. Additionally, if the product CO₂ is under vacuum pressure, then there is a cost associated in compressing the gas from vacuum to the eventual sequestration pressure around 2,200 psia. One additional concern with most of the zeolite modeling is that, generally, the interaction of the zeolite with the
major/minor components present in either flue gas or fuel gas are not considered. Certain components can poison the zeolite, for example sulfur dioxide or nitric oxides (Hoffman, 2005). As determined in the research of Hoffman et al. (2004), Siriwardane et al. (2005), and Stevens et al. (2008), the presence of water will have a deleterious effect on the reactivity of the sorbent and the eventual regeneration of said zeolitic sorbent. These impacts will need to be considered in further modeling efforts with zeolites.

2.4 BENCH-SCALE TESTING

While the exploratory research with the synthetic zeolites was occurring on the laboratory-scale units, an internal NETL decision was made to proceed with the design and construction of a modular carbon dioxide capture facility, known as the MCCF. One of the first carbon capture technology candidates to be investigated was a sorbent technology based on zeolite 13X. However, before the testing on the larger scale (0.07-MWe) of the MCCF was to commence, a bench-scale data base was to be assembled that would complement the earlier laboratory studies but also elucidate any potential engineering issues that could impact the scale-up design of the MCCF. Simulated flue gas mixtures flowed over the molecular sieve in the bench-scale packed bed reactor, and the amount of adsorbed carbon dioxide was quantified (Hoffman et al., 2004). The sorbent was regenerated by using a temperature swing. The impacts of temperature, carbon dioxide concentration, moisture content, and minor gaseous components on the adsorption and the ensuing regeneration were described, and recommendations for operation of this type of capture system were discussed.

The sorbent used in the study was a pelletized molecular sieve, a light tan color of spherical shape, and the same material utilized in the earlier laboratory studies (Siriwardane et al., 2001a). Information reported in that study reveals that the material is termed Zeochem-Z10-02/molecular sieve 13X (8 x 12 mesh) obtained from Sud Chemie Inc. It is comprised mainly of sodium aluminosilicate and has an average pore diameter of 10 angstroms. The nitrogen BET surface area was reported as 506 m²/g. The skeletal and bulk densities as determined by mercury porosimetry were 1.87 and 1.06 g/cm³, respectively.

Bench-scale experiments were conducted in a packed-bed reactor system, shown in Figure 15. The reactor is comprised of a quartz tube measuring 40 mm internal diameter by 450 mm length. Sorbent sample was placed on a fritted filter in the center of the quartz tube, and then positioned at the center of a 400 mm long clam-shell furnace. The furnace has a heating zone of 300 mm length and is controlled by a linear programmable controller. Bed temperature was measured and controlled using a dual type K thermocouple located in the sample bed. A sample charge of 60 grams of sorbent resulted in a bed height of about 3 inches, and the thermocouple was positioned midway along the bed height. Secondary temperature controls for heater tapes along the gas inlet path served to control the temperatures of several gas mixing chambers and a water humidification chamber. A superficial gas contact time of 3.7 seconds was provided based on total gas flow rate (1.5 standard liter/min) and sample bulk density. A gas composition was established by blending from gas cylinders using thermal mass flow controllers; water was metered using a variable flow dispensing pump. The packed-bed system is configured with gas analyzers for continuous monitoring of flue gas components (SO₂, NO₂, O₂, CO₂, hydrocarbons, etc.), but for this particular study, only several gas analyzers were required to monitor gas composition. The process gas is passed through a Perma Pure drying tube to remove moisture prior to the stream entering the gas analysis train. The reactor system operated slightly above
atmospheric pressure (5–7 psig); positive system pressure is necessary to maintain sufficient gas flow to the gas analyzer train. Data were acquired using an automated data logger instrument manufactured by Linseis (model LSB 36 III). Instrument outputs from thermocouple readouts, mass flow controllers, and continuous emission monitors (CEM) for gas analysis are acquired and recorded to computer disk at 1-minute sampling interval. The data file was converted into a format compatible for importing into spreadsheet software (EXCEL).

The experimental procedure and test conditions employed for the packed-bed tests were chosen such that the CO$_2$ breakthrough and saturation curves during adsorption, and CO$_2$ release curves for subsequent regeneration, could be monitored and quantified. Once the sample was charged to the system, it was dried at elevated temperature (maximum of 350°C) under nitrogen for several hours to achieve a state of maximum regeneration. The reactor temperature was then lowered to the adsorption temperature of interest. The reactor was isolated (i.e., bypass of gas flow) while the inlet gas composition was established to simulate a typical flue gas composition. This flow was then introduced to the reactor. For the baseline condition during CO$_2$ adsorption, the gas inlet flow rate was 1.5 liter/min; the gas composition was typically 16% CO$_2$, 3.5% O$_2$, and balance N$_2$; and the reactor temperature was 40°C. For some experiments, the gas mixture was also humidified by the addition of water in the feed system. Regeneration was conducted in pure N$_2$ at the same initial adsorption temperature, followed by heating the sorbent to an elevated temperature to thermally regenerate the material.

**Figure 15: Schematic of bench-scale packed bed reactor system.**
At time “zero”, the reactor was switched in-line and the sample was exposed to the CO\textsubscript{2} gas mixture during the “adsorption” step. Some of the gas components were physically adsorbed onto the solid and a temperature rise was noted due to exothermic heat of reaction. Once the bed becomes saturated, that is, the CO\textsubscript{2} breakthrough was complete and the exit gas reached the inlet CO\textsubscript{2} level, the adsorption step was halted. Desorption or regeneration is conducted in two stages. The inlet gas is switched to pure nitrogen and allowed to sweep out the reactor at the same temperature of adsorption. This first “desorption” stage is characterized by evolution of CO\textsubscript{2} appearing in the exit stream and a usual drop in temperature, due to endothermic heat of reaction. Eventually the CO\textsubscript{2} approached zero concentration in the tail gas. The second “desorption” stage is known as “thermal regeneration” initiated by raising the bed temperature while maintaining the reactor under nitrogen flow. Additional gases may be desorbed from the solid due to elevated temperature. Once desorption is completed, the sorbent is cooled to the desired adsorption conditions to begin another cycle.

Results from a typical packed-bed experiment are shown in Figure 16, with CO\textsubscript{2} exit concentration and bed temperature plotted versus time. This particular set of parameters represented the “baseline” condition for the study (gas inlet flow rate was 1.5 liter/min; the gas composition was 16% CO\textsubscript{2}, 3.5% O\textsubscript{2}, balance N\textsubscript{2}; and reactor temperature was 40°C – roughly the temperature found at the exit of a flue gas desulfurization unit). At time zero minutes, which began by switching gas flow through the reactor, all of the CO\textsubscript{2} is adsorbed onto the sorbent. At approximately 12 minutes, the CO\textsubscript{2} starts to appear in the exit stream. The “breakthrough time” was defined as the elapsed time period until a measurable level of CO\textsubscript{2} (0.1–0.2 vol %) was detected in the off-gas stream. The initial stage of adsorption is characterized by significant temperature rise (over 50°C) due to the exothermic adsorption reaction. Calculations of the adiabatic temperature rise verify that an exotherm will occur in the bed, will affect heat management, and could have an impact on bed design. As the CO\textsubscript{2} begins to break through the bed and the concentration slowly rises, the adsorption is continued until the exit CO\textsubscript{2} approaches the inlet concentration (16%). This period can typically last for 90 or more minutes, during which the bed temperature cools down close to the initial adsorption temperature (40°C).

Upon bed saturation, the input gases (except N\textsubscript{2}) are terminated and the desorption phase proceeds (beginning at the 105 minute mark in Figure 16). The CO\textsubscript{2} is desorbed from the sorbent, and a sharp temperature drop is observed, presumably due to the reverse desorption reaction that is endothermic. The endotherm drop is typically about 20°C. A much longer period of time (3–4 hours) is required for the CO\textsubscript{2} to approach negligible concentration in the exit stream. The bed temperature proceeds through a minimum value and slowly rises back to the initial temperature (40°C).

The material is then thermally regenerated by raising the bed temperature, in this case, up to 120°C (beginning at the 360 minute mark in Figure 16). Once the upper temperature target is arrived, little time is required to achieve the remainder of CO\textsubscript{2} evolved from the sorbent; an additional quantity of CO\textsubscript{2} is liberated from the sorbent. When a material balance for CO\textsubscript{2} is performed (using area integration in Figure 16), the thermally regenerated amount is a small fraction (typically 10–15%) of the combined sum of the initial desorption and thermal regeneration phases. This result is similar to Stevens et al. (2008) who found that most of the CO\textsubscript{2} is physisorbed – weakly bound to the zeolite.
The baseline condition was repeated over multiple cycles, under both dry and humidified conditions, to gauge the repeatability of the results. A six-cycle test for the dry baseline condition is summarized in Table 7. The material was initially activated at 300°C for 3 hr prior to the first cycle; moisture or ambient CO₂ would be driven from the sorbent. Periodic reactivation of the sorbent at high temperature is recommended based on prior operating experience (Siriwardane et al., 2001a). The six cycles in Table 7 are very similar and indicate negligible degradation in performance. The condition of regeneration (3 hr at 120°C) appears sufficient to maintain sorbent performance, under dry adsorption conditions. The breakthrough time (12 min) and exotherm were reliably consistent. The amount of CO₂ adsorbed/ liberated is calculated for the adsorption/regeneration steps. The sorbent capacity ranged near 3.5 mol CO₂/kg sorbent. This value is slightly higher as compared to the adsorption study by Siriwardane et al. (2001a) where a sorbent capacity around 2–2.5 mol CO₂/kg sorbent at atmospheric pressure and 25°C was obtained. A later study with 13X (Siriwardane et al., 2005) indicates a capacity at ambient temperature and CO₂ partial pressure representing that found in flue gas at greater than 2.5 mol CO₂/kg sorbent. A material balance for CO₂ is calculated by comparing the total desorbed amount to the total adsorbed amount. Differences are reported as a percent error of the total adsorbed quantity of CO₂. The CO₂ material balances are good and generally agree within 10 percent. In general, a major indicator of system degradation is the shorter breakthrough time and smaller temperature rise (exotherm).
Effect of Moisture on Adsorption

The bench-scale study appeared to confirm the need for high temperature reactivation after moist gas adsorption conditions. A nine-cycle test of the baseline condition, with 2% moisture in the inlet gas mixture, is given in Table 8. The material was again initially activated at 300°C for 3 hr prior to the first cycle. Subsequent cycles were regenerated at 120°C for 3 hr. The first cycle appears similar in performance to the dry results, with respect to breakthrough time, exotherm, and sorbent capacity. However, after the first cycle, there is a noted degradation in activity for cycles 2–5, and then the performance remains near constant for the remainder of the cycles. The sorbent is reduced to approximately one-half of its initial activity, resulting in a sorbent capacity of approximately 1.3 mol CO₂/kg sorbent. Thus the effect of 2% water has a negative impact on CO₂ adsorption for the stated regeneration conditions (3 hr at 120°C). The CO₂ material balances are generally in good agreement.

The impact of higher moisture (4%) on sorbent performance was examined and results are listed in Table 9. It was during these series of tests that minimum conditions of regeneration (temperature and time) were explored. The material was initially activated at a higher temperature (350°C for 3 hr) to further assure complete drying and regeneration. Cycle 1 yielded results similar to the dry baseline condition (12 min breakthrough time and 3.1 mol CO₂/kg sorbent capacity.). However, the CO₂ adsorption of cycle 2 was greatly degraded after cycle 1 regeneration of 3 hr at 120°C. Cycle 3 showed slightly worse performance than cycle 2 for the same repeat regeneration conditions. Cycle 3 had a breakthrough time of 3 min versus the initial baseline time of 12 min.

Prior to cycle 4, the sorbent was regenerated for 1 hr at 120°C, followed by 300°C for 3 hr. Cycle 4 was an improvement over cycle 3, with the breakthrough time increasing from 3 to 8 min. The higher temperature of regeneration obviously improved the sorbent performance, but the material was not reactivated to its initial state. Thus the material was regenerated at even higher temperature (350°C for 3 hr) prior to cycle 5. Cycle 5 was slightly improved over cycle 4 (10 min versus 8 min breakthrough time), but was still slightly less than the baseline performance of 12 min. To further improve reactivation, the material was regenerated overnight at the same temperature (350°C), but for a longer duration (11 hr) prior to cycle 6. The sorbent was successfully returned to its baseline performance for cycle 6, with breakthrough time, exotherm, sorbent capacity, etc. in good agreement with the first cycle. Cycle 7 was repeated in the same manner as cycle 2, and the same precipitous drop-off in CO₂ capacity was noted.

The above moisture tests reaffirm the necessity to regenerate at higher temperature, especially for the 4% moisture level. For a dry gas mixture, regeneration at 120°C for 3 hr is sufficient to maintain sorbent performance. Even at 2% moisture, the sorbent is degraded to about one half of its initial state after 5 cycles, and appears constant thereafter. But for 4% moisture, regeneration at 120°C for 3 hr is insufficient, and a much higher regeneration temperature (350°C) is required. This negative effect of moisture is consistent with the TEPCO power plant demonstration study (Ishibashi et al., 1998) in which the flue gas was first dehumidified using beds of alumina prior to CO₂ removal to prevent deterioration of the zeolite. In the previous section pertaining to the laboratory results, Siriwardane et al. (2005) found similar results for 13X. According to product specifications by one supplier of molecular sieve 13X (Plastic Services & Equipment, 2003), the equilibrium water capacity of molecular sieve 13X is 29 wt%. This is equivalent to a loading of 16.1 mol H₂O/kg sorbent. In the study described here, the average dry adsorption gas capacity
was measured near 3.5 mol CO$_2$/kg sorbent. Thus the sorbent has higher capacity for H$_2$O compared to CO$_2$ (by a factor of 4.6 on a molar basis).

**Effects of temperature and CO$_2$ concentration on adsorption**

Table 10 is a summary of conditions in which either temperature or CO$_2$ concentration were varied from the dry baseline condition. Since the tests were without moisture, regeneration at 120°C for 3 hr was conducted for all cycles. The first three tests illustrate the effect of changing the initial reactor temperature among nominally 40, 80 and 120°C. A marked decrease in performance occurs with increasing temperature. The sorbent capacity decreased to approximately one third of its value at 120°C versus 40°C. The breakthrough time and capacity correspondingly decrease at higher temperature. Similar results were found by Siriwardane in the laboratory results discussed previously (Siriwardane et al., 2005).

The last four conditions in Table 10 illustrate the effect of different inlet CO$_2$ concentration (1, 8, 16, and 40%) for the same baseline temperature (approximately 40°C). As inlet CO$_2$ concentration is raised, there is significant decrease of the breakthrough time but higher exotherms. Thus the bed becomes more quickly saturated. However, the final capacity of the sorbent appears unchanged for 8, 16, and 40% CO$_2$ (although the 1% CO$_2$ test does show lower capacity). Higher partial pressure of CO$_2$ would be expected to favor physical adsorption onto the solid, but little difference in sorbent adsorption capacity is noted for the higher CO$_2$ levels. Closer inspection of the regeneration data in Table 10 indicates that larger amounts of CO$_2$ were desorbed from the sorbent for higher inlet CO$_2$ levels. This trend is consistent with higher CO$_2$ partial pressure. However, these material balances are skewed in favor of desorption relative to adsorption (i.e., positive error in Table 10) which makes interpretation more difficult.

**Effect of regenerative sweep gas and CO$_2$ concentration**

Between the initial desorption phase (desorption in nitrogen at the initial adsorption temperature) and the thermal regeneration phase, the majority of CO$_2$ is liberated during the initial desorption phase. Since the partial pressure of CO$_2$ over the sorbent is reduced when adsorption is terminated and desorption is initiated, it was questioned whether regeneration was more affected by “swinging” CO$_2$ pressure (i.e., pressure swing adsorption) rather than “swinging” temperature by thermal regeneration. A second but related consideration involved the use of a different sweep gas. The primary objective of the zeolite study, as well as CO$_2$ capture sorbents in general, is to facilitate the separation and eventual concentration of CO$_2$ from other gas components. The use of a nitrogen sweep gas during desorption/regeneration dilutes the CO$_2$ product stream and defeats the objective. One choice for a sweep gas could be a recycled stream of the CO$_2$ offgas itself. However, it is intuitive that the required regeneration temperature would be higher due to the higher CO$_2$ partial pressure surrounding the sorbent. Another choice for a sweep gas could be water vapor, which is subsequently condensed and separated downstream of the regenerator. However, water has already been shown to have a deleterious effect on the performance of the sorbent, and therefore is not feasible.

Table 11 is a series of tests to examine the effect of CO$_2$ used as a sweep gas. Due to limitation in flow for the CO$_2$ mass flow meter/controller, it was necessary to lower the nitrogen flow in order to achieve high CO$_2$ mole fraction (85%) in the gas feed mixture. This had the effect of lowering the total gas flow rate for adsorption from 1.5 to 1 liter/min, and therefore the space velocity was proportionately reduced as well. To further maximize the CO$_2$ level and simplify the experiment, oxygen was not introduced in the adsorption gas feed, only nitrogen. Five initial
temperatures of adsorption (nominally 40, 80, 120, 200, and 350°C) were investigated. Maximum adsorption and sorbent capacity occurs at the lowest temperature (case 1), and significantly decreases with higher temperature. Comparison of case 1 with the dry baseline condition (Table 7) indicates an unexplained lower level of adsorption at 40°C for case 1. However, the exotherm is much higher for case 1 (by approximately 30°C) and the breakthrough time is cut in half (from 12 to 6 min).

At the conclusion of the adsorption, a different methodology was employed for the desorption step. Rather than terminate the CO₂ feed and desorb in nitrogen, the gas feed composition remained unchanged (85% CO₂, balance N₂) and the temperature was raised to 350°C. Thermal regeneration at this high temperature was found suitable for humidified adsorption conditions. Since the gas feed remained unchanged at 85% CO₂ and the bed was already saturated during the adsorption, liberation of CO₂ would be evident as any CO₂ measurement above 85% CO₂. However, little change was observed in the CO₂ signal during the thermal regeneration.

The next step encompassed a gas switch to pure nitrogen, the customary method of experimental regeneration, while holding temperature constant at 350°C. The CO₂ signal rapidly dropped to zero within 2–3 minutes, suggesting quick desorption of the CO₂. When the material balance for CO₂ is attempted, rather poor results are obtained. This is partly attributable to the data acquisition method. Sample data points were computer recorded at 1-min interval. Because of rapid signal change and short time period to achieve steady state, the area integration is poor, and therefore interpretation of material balance is suspect. However, based on visual interpretation of the data curve, it appears that the CO₂ is mostly evolved during the last phase (when gas composition is switched). This would suggest that the use of CO₂ as a sweep gas during temperature-swing regeneration is difficult, and the overall adsorption/desorption process is more strongly influenced by swing in pressure of CO₂. The adsorption phase is strongly influenced by initial temperature as well as CO₂ concentration.

To summarize, molecular sieve 13X demonstrated the affinity to adsorb CO₂ from simulated flue gas mixtures. Removal is most favored at lower temperature (40°C) and higher partial pressure of CO₂. The sorbent capacity ranged near 3.5 mol CO₂/kg sorbent at baseline conditions, comparable to the capacity of other NETL researchers (Siriwardane et al., 2001a, 2005). An exotherm that occurs in this larger bench-scale packed bed reactor during adsorption indicates that heat management will be a critical issue in eventual reactor design. Moisture was found to have a very negative impact on sorbent performance, which subsequently raised the required swing in temperature to maintain suitable regeneration. Competitive adsorption between CO₂ and H₂O is speculated, as later determined elsewhere (Stevens et al., 2008). Regeneration at 120°C for 3 hr is sufficient for dry adsorption conditions, but much higher conditions (350°C for 3 hr or longer) are required when moisture levels approach 2–4% in the adsorption gas. Actual flue gas from a coal-burning utility can have 6–7 vol% water, and this concentration is even greater if the flue gas needs to be cleaned beforehand in a flue gas desulfurization unit. The effectiveness of regeneration is also greatly influenced by the choice of sweep gas used during regeneration. Using a highly concentrated stream of CO₂ (85%) as a sweep gas during regeneration proved to be problematic. The higher partial pressure of CO₂ inhibited the desorption of CO₂ from the sorbent, even when a very high temperature (350°C) was employed during regeneration. However, upon switching to pure nitrogen as a sweep gas, desorption of CO₂ was greatly enhanced. It appears that a swing in CO₂ partial pressure (such as in pressure swing adsorption) is more advantageous over a regeneration methodology of temperature swing alone, although
PSA can be a costly proposition. A combination of PSA and TSA is likely the preferable mode of operation with respect to maintaining zeolitic sorbent performance. These results coupled with some of the earlier laboratory-scale results established guidelines for the 13X sorbent that would be used in the packed-bed scale-up for the modular carbon dioxide capture facility.

Table 7: Multi-cycle test of baseline condition (dry). Inlet gas composition (vol %):
16% CO₂/3.5% O₂/balance N₂

<table>
<thead>
<tr>
<th>Run Identification</th>
<th>Cycle Number</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Temperature (°C)</td>
<td></td>
<td>37</td>
<td>43</td>
<td>41</td>
<td>44</td>
<td>41</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Exotherm (°C)</td>
<td></td>
<td>54</td>
<td>48</td>
<td>50</td>
<td>47</td>
<td>49</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Breakthrough Time (min)</td>
<td></td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>CO₂ adsorbed (Liter)</td>
<td></td>
<td>5.08</td>
<td>5.31</td>
<td>4.89</td>
<td>5.91</td>
<td>4.66</td>
<td>4.95</td>
<td></td>
</tr>
<tr>
<td>Capacity (mol CO₂/kg sorbent)</td>
<td></td>
<td>3.46</td>
<td>3.62</td>
<td>3.33</td>
<td>4.03</td>
<td>3.18</td>
<td>3.37</td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endotherm (°C)</td>
<td></td>
<td>21</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td></td>
<td>4.83</td>
<td>4.81</td>
<td>4.73</td>
<td>4.75</td>
<td>5.12</td>
<td>4.94</td>
<td></td>
</tr>
<tr>
<td>Thermal Regeneration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td>300</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Time (Hr)</td>
<td></td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td></td>
<td>0.61</td>
<td>0.54</td>
<td>0.55</td>
<td>0.55</td>
<td>0.57</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Total desorbed CO₂ (Liter)</td>
<td></td>
<td>5.43</td>
<td>5.34</td>
<td>5.28</td>
<td>5.3</td>
<td>5.69</td>
<td>5.51</td>
<td></td>
</tr>
<tr>
<td>CO₂ material balance difference (%)</td>
<td></td>
<td>+6.9</td>
<td>+0.6</td>
<td>+8.0</td>
<td>-10.3</td>
<td>+22.1</td>
<td>+11.3</td>
<td></td>
</tr>
</tbody>
</table>
Table 8: Multi-cycle test results for the effect of 2% H₂O. Inlet gas composition (dry vol %): 16% CO₂/3.5% O₂/balance N₂

<table>
<thead>
<tr>
<th>Run Identification</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle Number</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Sample Number</td>
<td>7/29</td>
<td>7/30</td>
<td>7/31</td>
<td>8/4</td>
<td>8/5</td>
<td>8/6</td>
<td>8/7</td>
<td>8/11</td>
<td>8/12</td>
<td>8/13</td>
</tr>
</tbody>
</table>

Adsortion

<p>| | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Temperature (°C)</td>
<td>40</td>
<td>39</td>
<td>41</td>
<td>40</td>
<td>41</td>
<td>43</td>
<td>42</td>
<td>42</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Exotherm (°C)</td>
<td>55</td>
<td>44</td>
<td>32</td>
<td>26</td>
<td>23</td>
<td>22</td>
<td>23</td>
<td>22</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Breakthrough Time (min)</td>
<td>11</td>
<td>9</td>
<td>9</td>
<td>8</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>CO₂ adsorbed (Liter)</td>
<td>4.10</td>
<td>3.80</td>
<td>3.88</td>
<td>3.25</td>
<td>2.75</td>
<td>1.80</td>
<td>1.79</td>
<td>2.00</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>Capacity (mol CO₂/kg sorbent)</td>
<td>2.79</td>
<td>2.59</td>
<td>2.64</td>
<td>2.22</td>
<td>1.87</td>
<td>1.23</td>
<td>1.22</td>
<td>1.36</td>
<td>1.49</td>
<td></td>
</tr>
</tbody>
</table>

Desorption

<p>| | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Endotherm (°C)</td>
<td>22</td>
<td>21</td>
<td>19</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>18</td>
<td>17</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td>1.94</td>
<td>3.67</td>
<td>2.58</td>
<td>3.01</td>
<td>2.73</td>
<td>1.30</td>
<td>2.07</td>
<td>2.14</td>
<td>2.20</td>
<td></td>
</tr>
</tbody>
</table>

Thermal Regeneration

<p>| | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>300</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Time (Hr)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td>2.77</td>
<td>0.49</td>
<td>0.94</td>
<td>0.34</td>
<td>0.17</td>
<td>1.03</td>
<td>0.06</td>
<td>0.07</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Total desorbed CO₂ (Liter)</td>
<td>4.70</td>
<td>4.16</td>
<td>3.52</td>
<td>3.35</td>
<td>2.90</td>
<td>2.33</td>
<td>2.13</td>
<td>2.21</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>CO₂ material balance difference (%)</td>
<td>+14.6</td>
<td>+9.5</td>
<td>-9.3</td>
<td>+3.1</td>
<td>+5.5</td>
<td>+29.4</td>
<td>+19.0</td>
<td>+10.5</td>
<td>+4.1</td>
<td></td>
</tr>
</tbody>
</table>
Table 9: Multi-cycle test results for the effect of 4% H₂O. Inlet gas composition (dry vol %): 16% CO₂/3.5% O₂/balance N₂

<table>
<thead>
<tr>
<th>Run Identification</th>
<th>Cycle Number</th>
<th>Sample Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>9/12</td>
<td>9/23</td>
</tr>
</tbody>
</table>

**Adsorption**

<table>
<thead>
<tr>
<th></th>
<th>Cycle Number 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Temperature (°C)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>39</td>
<td>39</td>
<td>40</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Exotherm (°C)</td>
<td>54</td>
<td>14</td>
<td>10</td>
<td>32</td>
<td>47</td>
<td>54</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Breakthrough Time (min)</td>
<td>12</td>
<td>4</td>
<td>3</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CO₂ adsorbed (Liter)</td>
<td>4.61</td>
<td>0.94</td>
<td>0.77</td>
<td>2.80</td>
<td>4.01</td>
<td>4.45</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Capacity (mol CO₂/kg sorbent)</td>
<td>3.14</td>
<td>0.64</td>
<td>0.52</td>
<td>1.91</td>
<td>2.73</td>
<td>3.03</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

**Desorption**

<table>
<thead>
<tr>
<th></th>
<th>Cycle Number 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endotherm (°C)</td>
<td>21</td>
<td>9</td>
<td>8</td>
<td>20</td>
<td>22</td>
<td>21</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td>4.24</td>
<td>1.02</td>
<td>0.71</td>
<td>4.47</td>
<td>0.81</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Thermal Regeneration**

<table>
<thead>
<tr>
<th></th>
<th>Cycle Number 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>350</td>
<td>120</td>
<td>120</td>
<td>120,300</td>
<td>350</td>
<td>350</td>
<td>120</td>
<td>120,350</td>
</tr>
<tr>
<td>Time (Hr)</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>1,3</td>
<td>3</td>
<td>11</td>
<td>3</td>
<td>1,18</td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td>0.66</td>
<td>0.10</td>
<td>0.04</td>
<td>0.48</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total desorbed CO₂ (Liter)</td>
<td>4.90</td>
<td>1.12</td>
<td>0.75</td>
<td>3.08</td>
<td>3.66</td>
<td>4.96</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>CO₂ material balance difference (%)</td>
<td>+6.3</td>
<td>+19.1</td>
<td>-2.6</td>
<td>+10.0</td>
<td>-8.7</td>
<td>+11.5</td>
<td>-3.1</td>
<td></td>
</tr>
</tbody>
</table>
### Table 10: Parametric effect of adsorption temperature and CO₂ mole fraction. Baseline inlet gas composition (vol %): 16% CO₂/3.5% O₂/balance N₂

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Adsorption Temperature</th>
<th>CO₂ Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run Identification</td>
<td>10/28</td>
<td>10/30</td>
</tr>
<tr>
<td><strong>Adsorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Temperature (°C)</td>
<td>37</td>
<td>80</td>
</tr>
<tr>
<td>Initial CO₂ (%)</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Exotherm (°C)</td>
<td>56</td>
<td>39</td>
</tr>
<tr>
<td>Breakthrough Time (min)</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>CO₂ adsorbed (Liter)</td>
<td>5.13</td>
<td>3.23</td>
</tr>
<tr>
<td>Capacity (mol CO₂/kg sorbent)</td>
<td>3.50</td>
<td>2.20</td>
</tr>
<tr>
<td><strong>Desorption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endotherm (°C)</td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td>4.55</td>
<td>3.27</td>
</tr>
<tr>
<td><strong>Thermal Regeneration</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Time (Hr)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>CO₂ desorbed (Liter)</td>
<td>0.83</td>
<td>0.04</td>
</tr>
<tr>
<td>Total desorbed CO₂ (Liter)</td>
<td>5.39</td>
<td>3.31</td>
</tr>
<tr>
<td>CO₂ material balance difference (%)</td>
<td>+5.1</td>
<td>+2.5</td>
</tr>
</tbody>
</table>
Table 11: Effect of high CO\textsubscript{2} mole fraction (as a sweep gas) on regeneration temperature.
Inlet gas composition (vol %): 85\% CO\textsubscript{2}/15\% N\textsubscript{2}

<table>
<thead>
<tr>
<th>Run Identification</th>
<th>Condition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
</table>

**Adsorption**

<table>
<thead>
<tr>
<th></th>
<th>85%CO\textsubscript{2}/15%N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Temperature (°C)</td>
<td>38</td>
</tr>
<tr>
<td>Exotherm (°C)</td>
<td>81</td>
</tr>
<tr>
<td>Breakthrough Time (min)</td>
<td>6</td>
</tr>
<tr>
<td>CO\textsubscript{2} adsorbed (Liter)</td>
<td>4.08</td>
</tr>
<tr>
<td>Capacity (mol CO\textsubscript{2}/kg sorbent)</td>
<td>2.78</td>
</tr>
</tbody>
</table>

**Thermal Regeneration**

<table>
<thead>
<tr>
<th></th>
<th>85%CO\textsubscript{2}/15%N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>350</td>
</tr>
<tr>
<td>CO\textsubscript{2} desorbed (Liter)</td>
<td>1.30</td>
</tr>
</tbody>
</table>

**Thermal Regeneration**

<table>
<thead>
<tr>
<th></th>
<th>100%N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>350</td>
</tr>
<tr>
<td>CO\textsubscript{2} desorbed (Liter)</td>
<td>0.51</td>
</tr>
<tr>
<td>Total desorbed CO\textsubscript{2} (Liter)</td>
<td>1.81</td>
</tr>
<tr>
<td>CO\textsubscript{2} material balance difference (%)</td>
<td>-55.6</td>
</tr>
</tbody>
</table>

2.5 **MODULAR CARBON DIOXIDE CAPTURE FACILITY (MCCF)**

As a major step in a carbon sequestration scenario (storage being the other), the capture/separation of carbon dioxide represents a significant cost and energy penalty in the overall sequestration process. To accelerate the development of low cost capture and separation technologies, NETL was to implement the design and construction of a modular, flexible CO\textsubscript{2} capture test facility, labeled the Modular Carbon Dioxide Capture Facility (MCCF). The facility would be able to test new capture technologies on coal combustion flue gas and, additionally, on process gas from advanced fossil fuel conversion systems, such as coal gasification. Ultimately, a database for a particular capture technology would provide experimental information from which further engineering scale up decisions could be formulated. By providing a means to evaluate the most promising CO\textsubscript{2} capture/separation abatement processes, the MCCF would help DOE meet its goal of developing point source cleanup systems that are more efficient, cleaner, and less costly than established techniques proposed for implementation in existing power generation plants and advanced power generation systems, such as IGCC.

NETL has an extensive history of conducting research at the laboratory-, bench-, and pilot-scale regarding environmental control of emissions resulting from fossil fuel utilization. Included in this body of research is the use of dry scrubbing materials, such as regenerable solid sorbents, that may be employed to remove acid gas components from flue gas or fuel gas. A large pilot-
scale facility, the Life Cycle Test System (LCTS), was designed and implemented to aid in the evaluation of sorbent processes. A detailed description of the experimental apparatus comprising the LCTS is available (Pennline et al., 1995). The LCTS was primarily used in the study of a dry, regenerable sorbent for the simultaneous removal of acid gases (SO$_2$ and NO$_x$) from flue gas using the Moving-Bed Copper Oxide Process. A series of parametric tests were conducted in the LCTS at large process developmental unit (PDU) scale to help elucidate the technical and economic viability of the sorbent process (Pennline et al., 2013). Note that PDU- and pilot-scale are assumed similar in size in this section and the terms can be used interchangeably.

Dry, regenerable sorbent CO$_2$ scrubbing processes were added to the portfolio of possible carbon dioxide mitigation scenarios and hence the capability to evaluate such capture processes at PDU scale was implemented. NETL conducted a CO$_2$ capture workshop in February 2003 that essentially inaugurated the modular carbon dioxide capture facility (MCCF) for post-combustion application. The earlier NETL process developmental unit, the LCTS, was utilized in the formulation of the MCCF. Key components of the system, including the furnace and ancillary piping, were incorporated into the MCCF. Additional modifications were made to the system to facilitate evaluation of capture technologies at relatively lower process temperatures than were encountered during LCTS operation.

The evolution of the MCCF as a multipurpose, versatile experimental research facility was to offer the industrial and academic communities various opportunities to partner with NETL. Performance of a particular carbon dioxide abatement process could be optimized in the MCCF to help achieve the extremely high emissions control goals of the DOE Carbon Sequestration program at that time. Operational performance standards for CO$_2$ capture would thus be established. The MCCF would provide the ability to test capture and separation concepts on process streams that produce/simulate conventional or advanced energy conversion systems. Side by side comparison of advanced capture and separation concepts could be conducted. The MCCF could be used to investigate the impact of other gaseous components (SO$_2$, NO$_x$, H$_2$S, H$_2$O, particulates, and/or air toxics emissions) and other parameters on the particular technology. Finally, the MCCF offered industry and other sequestration stakeholders the opportunity to further develop CO$_2$ capture/separation technologies through cooperative ventures with NETL. Collaborations with CO$_2$ capture technology developers would be sought.

In the flue gas mode (post-combustion) depicted in Figure 17, the MCCF mimicked coal fired combustion processes that produce electricity. The combustor can be fired with natural gas, coal, or a combination of the two; coal burning of approximately 40 pounds of pulverized coal per hour results in a flue gas (110 scfm) laden with various pollutants. The versatility of a “black box” design permits the incorporation of a particular capture/separation technology anywhere along the flue gas path. If regeneration of the capture medium is required as part of the capture/separation process, this step could be readily integrated into the system.

In a fuel gas mode (pre-combustion), the MCCF was proposed to blend various high pressure gases (hydrogen, carbon monoxide, water, carbon dioxide, and minor components) to simulate the gas composition found in gasification processes, for example IGCC. Again, a “black-box” design was sought for a generic capture technology (see Figure 18.) Temperatures could range from those found before the hot gas desulfurization cleanup step to ambient temperature. Total pressure could be above 300 psig.
Originally, the MCCF was inaugurated to study a physical adsorbent to remove CO\textsubscript{2} from flue gas. The material, zeolite 13X, is a molecular sieve composed mainly of sodium aluminosilicate, and was chosen based partially on its commercial use, availability as a physical adsorbent for CO\textsubscript{2}, and numerous studies previously conducted by NETL (Siriwardane et al., 2001, 2001a, 2005; Hoffman et al., 2004). The intent was to establish baseline performance of the MCCF using a commercially available material. Smaller bench-scale 13X studies using a packed-bed reactor were conducted in tandem to help guide MCCF testing. (See previous section.) Results indicated favorable CO\textsubscript{2} removal with the adsorption reaction being highly exothermic. Moisture was found to negatively impact the performance of the zeolite; the sorbent material is used commercially as a desiccant. The adsorption reaction was most favored at temperatures near 40°C. Thermal regeneration can be conducted at 120°C for dry flue gas, but much higher temperature (350°C) is required for moisture laden flue gas.

![Diagram](image-url)

**CO\textsubscript{2} Capture Facility – Flue Gas**

Figure 17: MCCF in flue gas mode of operation.
Although zeolite 13X was the first sorbent technology to be investigated in the MCCF, an effort with Toshiba was to immediately follow with lithium orthosilicate sorbent. For temperature, the absorption would be between 500°C and 700°C, whereas the thermal regeneration would occur between 700°C and 850°C, depending on background gas composition. Considerable modifications to the MCCF were necessary to accommodate testing with Toshiba’s sorbent. New vessels of high grade alloy were to be used for the absorber and regenerator (Vojtko et al., 2004). The reactor vessel consisted of a pipe design of approximately 10 in diameter by 5 ft height with three zone electric heating on the outer shell. New heat exchangers upstream and downstream of the vessels were necessary to attain desired process temperature. The upstream heater would be direct-fired or electric, while the downstream heat exchanger would consist of two hair-pin, shell-in-tube, heat exchangers in series. The ability to attain vacuum during regeneration was incorporated into the system to allow pressure swing-type operation. Although the design was completed, the process system for the Toshiba sorbent was terminated. A systems analysis was performed using the technology for a post-combustion application (Ciferno et al., 2004). The system analysis revealed that the operational temperature for the sorbent along with various uncertainties with this sorbent would contribute negatively to the process and be severely detrimental to the overall cost of the process. For these reasons the projected work with Toshiba was terminated.

The concept of the MCCF was unique at the time and could have been used to further advance new technologies in the carbon dioxide capture/separation area. However, after its initial campaign with zeolite 13X (described in detail in the next section), the work with the MCCF was abandoned due to two main reasons. The first was that the CO₂ capture technologies developed up to calendar year 2004 were not sufficiently, technologically advanced to make a significant investment in. The second reason was the uncertainty in a long-term investment in the budgeting
process. It is interesting to note that the concept of the MCCF as a “user facility” has been adopted by NETL and the Carbon Sequestration Program in the form of the National Carbon Capture Center in Wilsonville, AL (Northington et al., 2012).

### 2.6 PDU-SCALE TESTING

A process flow diagram for the MCCF modified to use sorbents in a post-combustion application is given in Figure 19. The system is shown in a configuration amenable for the testing of a physical adsorbent (zeolite 13X). Other system configurations are possible to facilitate testing of various CO\textsubscript{2} capture technologies. In the flue gas mode, the MCCF can mimic coal-fired combustion processes that produce electricity. The combustor (photo shown in Figure 20) can be fired with natural gas, coal, or a combination of the two. Burning approximately 40 pounds of pulverized coal per hour, or approximately 20 pounds of natural gas per hour, results in a flue gas (110-scfm) laden with various pollutants. The combustor has a rating of 500,000 Btu/hr at full load, but can be operated at reduced load. The versatility of a “black-box” design permits the incorporation of a particular capture/separation technology anywhere along the flue gas path (Hoffman, 2005).

In the setup of the MCCF, flue gas exits the furnace and is passed through two gas coolers (#1 and #2 in Figure 19). The pipe-in-pipe heat exchangers have circulating water on the shell side and the flue gas temperature can be lowered but is maintained above its dewpoint. However, since the adsorption temperature (approximately 100°F) is below the typical dewpoint of flue gas, additional drying equipment was designed for the MCCF. A condensing shell-and-tube heat exchanger (flue gas chiller in Figure 19) was placed in the flue gas line to remove water from the flue gas. A refrigeration unit, using chilled water (near 40°F) circulated on the shell side of the condenser, lowered the moisture level in the flue gas to about 1%. An electric gas heater was installed downstream of the chiller to reheat the flue gas back to the desired adsorption temperature (near 100°F).

The existing adsorption vessel (photo shown in Figure 20) was used for the MCCF, but the mode of sorbent operation was different than that used in the past. Unlike a moving-bed of sorbent used in the previous LCTS studies (Pennline et al., 2013), the MCCF adsorber was filled with a stationary bed of zeolite with no sorbent transport. The top and bottom sorbent ports were blanked off. The bed cross section measured 8 ft high by 1 ft wide, with a horizontal bed depth of 5 inches in the direction of gas flow. The bed inventory was approximately 150 lb of zeolite when the vessel was completely filled. The vessel was originally designed in the LCTS for temperatures up to 1200°F and near atmospheric pressure (plus or minus 40 inches water).

Shown in Figure 21 are the various instrumentation ports in the sidewall of the adsorption vessel. Flue gas is expanded through a rectangular diverging entrance cone, passed horizontally through the sorbent bed, and then the gas flow is contracted through a rectangular converging exit cone before leaving the vessel. Two sorbent retention screens, consisting of vertically slotted bar screens with an aperture of 0.030 inch, were used to contain the bed of zeolite. Stainless steel materials of construction were typically used throughout the MCCF, especially for those components that were contacted by flue gas. The adsorber shell has electric heat tracing arranged into five zones, each of which has its own temperature measurement and control. Four heating zones provide coverage for the bed and the fifth heating zone heats the gas entrance section. Skin thermocouples welded to the exterior wall in the zones are used for control and monitoring.
Gas temperature is vertically profiled using a series of thermocouples horizontally extended through the sidewall of the vessel (see Figure 21). The insertion depth was adjusted so that the measurement location (thermocouple tip) corresponded near the centerline of the gas flow path. Gas temperature was measured before the sorbent bed (TE-70 through TE-75), and after exiting the bed (TE-76 through TE-81). The bed temperature was also measured with a series of thermocouples extending approximately 6 inches into the midpoint of the bed (TE-392 through TE-397). Additional ports were available to extract sorbent samples using a thief-like sampling tube with gas assist using a vacuum eductor. Although the sampling valves (ASV-392 through ASV-397) are not shown in Figure 21, their location was in close proximity to the corresponding bed thermocouples.

Various additions to the flue gas line upstream and downstream of the adsorber were made. Continuous emission monitors (CEMs) for carbon dioxide were added at both locations, and humidity probes were installed to monitor moisture levels. These instruments in conjunction with existing CEMs for SO$_2$, NO$_x$, and O$_2$ were used to characterize removal levels across the reactor vessel. Gas composition is measured at the exit of the furnace, and at the adsorber entrance and exit locations. In Figure 19, these flow stations are labeled with 0, 1, or 2 at the end of the P&ID label for each CEM, with 0 reflecting the furnace exit and 1 and 2 corresponding for the adsorber entrance and exit, respectively.

Flue gas flow is first measured by a venturi meter (FY-15 in Figure 19) located downstream of the condensing chiller and the gas reheater. This flow location represents flue gas that has been dried, and therefore the flow is approximately 10% lower than the furnace output, since the volumetric moisture level has been reduced from roughly 10% to 1%. Hence, the dried gas flow is roughly 100 SCFM instead of the customary 110 SCFM rated for moisture-laden flue gas at full furnace load.

Two gas venturi meters (FY-17 and FY-18 in Figure 19) monitored changes in flow rates across the adsorber. Since the same single vessel was intended for both adsorption and regeneration steps, gas isolation valves were installed to switch the process stream between flue gas and inert sweep gas passing through the adsorber/regenerator. The capability to bypass flue gas flow around the adsorber was an original mode of operation employed during LCTS studies. However, a new MCCF feature was designed to allow a separate gas stream to purge the adsorber once the vessel was isolated from flue gas flow. Two input streams for regeneration were incorporated, including a low flow sweep gas of 50 lb/hr and a high flow heat gas of 200 lb/hr. The sweep gas was used to desorb CO$_2$ from the sorbent, whereas the heat gas was used to affect significant changes in sorbent bed temperature. Both streams of nitrogen were electrically preheated prior to their admission into the vessel. Note in Figure 19 that only the flow of heat gas would be detected by the entrance venturi meter (FY-17), since the sweep gas was introduced downstream of the meter. The inputs of both streams were measured with flow controlling meters, with the P&ID designation of FIT-505 for the sweep gas and FY-360 for the heat gas in Figure 19.

A slip stream with gas isolation valves was added to the adsorber exit process line. The slip stream contained a smaller shell-and-tube heat exchanger with chilled water to remove moisture, followed by a gas bagmeter to quantify total gas volume sampled. The intent of the combined instrumentation was to facilitate the material balance for CO$_2$ around the adsorber while also providing the means to remove any significant quantity of moisture potentially evolved during sorbent regeneration.
Moisture levels in the gas streams were determined using three Vaisala humidity probes inserted through the pipe wall and into the centerline of the stream. Both relative humidity and temperature were simultaneously measured at the tip of the probe, and this information was used to calculate absolute moisture levels, and thus mole fraction. The probes had a maximum temperature limit near 100°C and therefore were isolated from gas flow when higher gas temperatures were encountered, particularly during sorbent regeneration.

The first humidity probe was positioned at the dried, reheated total flue gas stream (RH-1 in Figure 19) upstream of the flow venturi. This probe location provided information on the chiller efficiency to remove moisture from the flue gas. A second humidity probe was located in the adsorber exit slip stream (RH-3 in Figure 19). The third humidity probe was located further downstream of the adsorber exit (RH-4 in Figure 19), just after the venturi meter (FY-18) and gas analysis (CEM station 2). The redundancy of the two adsorber exit probes was necessary for reasons of flow and temperature limits. The bagmeter in the slip stream was sized for the flow rate associated with sweep gas employed during sorbent regeneration. It could not accommodate the higher flow rates of total flue gas or heat gas streams, and therefore RH-3 was not necessarily on-line at all times. In addition, the gas temperature exiting the adsorber could become quite high during the latter stages of sorbent regeneration, and therefore RH-4 was located sufficiently downstream to allow the gas to cool before the measurement was taken.

The MCCF was commissioned during the end of calendar year 2003 and a dry, regenerable sorbent scrubbing technique was chosen for investigation. As previously mentioned, physical adsorbent (zeolite 13X, a molecular sieve composed mainly of sodium aluminosilicate) was the first (and only) sorbent candidate to be evaluated in the MCCF. A series of parametric tests using zeolite 13X followed. Table 12 is a summary of the test conditions. Five test series were performed, each typically consisting of a one-week testing period of 24-hour per day operation. Prior to beginning a test series, the material was activated overnight by thermal regeneration at high temperature (350°C) under N₂ purge, following by cool down to adsorption temperature. Several conditions were conducted for each test series. In some instances between test series, the sorbent inventory was removed from the system and replenished with fresh zeolite material. Fresh material was charged to the system prior to the start of MCCF-05, and again prior to the start of MCCF-06. Key MCCF process parameters are listed in Table 12 and include material balances for CO₂, SO₂, and NOₓ (Hoffman, 2005).

**Generalized Mode of Operation**

Results from a typical MCCF experiment are shown in Figure 22. This particular experiment is identified as MCCF-03-1, representing the first condition of test series three. The furnace firing rate was at reduced load with a natural gas feed of 10 lb/hr with 20% excess air, resulting in a dried flue gas of approximately 200 lb/hr (approximately 43 SCFM). Various MCCF parameters are plotted versus clock time in the six plots of Figure 22. The three plots along the left column show furnace inputs and stream flowrates at various locations. The three plots along the right column show gas composition and reactor temperatures. With respect to the plot legends, the reader should refer to Figure 19 for stream location and to Figure 21 for reactor temperature identification.

Similar to the packed-bed experimental protocol found in Section 2.4 Bench-Scale Testing, a typical experiment would proceed through three phases (adsorption, desorption, and regeneration). These phases have been identified in the reactor temperature plot of Figure 22. To
enhance the visual interpretation in the plots of Figure 22, each phase was individually plotted with an expanded time scale. Figure 23 shows the adsorption phase, Figure 24 shows the desorption phase, and Figure 25 shows the regeneration phase.

Prior to the introduction of flue gas, the system was brought to a thermal equilibrium by flowing heated nitrogen through the reactor vessel. For the adsorption phase (Figure 23), flue gas was introduced to the adsorber at 17:55. Inlet flue gas temperature was held near 100°F. It took about 17 minutes before the exit CO₂ concentration began a rapid ascent, signifying the breakthrough time for the bed. The exit CO₂ concentration rose to the inlet CO₂ concentration (near 9%) after about 30 minutes, indicating the bed was saturated with respect to CO₂ adsorption.

The sorbent bed experienced a significant exotherm during adsorption. Since multiple thermocouples were utilized to characterize reactor temperatures (see Figure 21), individual temperature measurements are listed in Table 13. The adsorption exotherm was calculated by the difference in peak bed temperature and initial bed temperature for each bed thermocouple. The six bed exotherms were then averaged and reported as a single value in Table 13.

The average exotherm for MCCF-03-1 was 114°F (46°C). This is extremely consistent with values observed during bench-scale packed bed tests, where exotherms ranged near 47°C to 50°C for the same initial bed temperature of 100°F (Hoffman et al., 2004). It is also apparent in Figure 23 that after the bed thermocouples experience the exotherm, the heat is partially convected away from the bed by the flow of flue gas. The reactor gas exit thermocouples experience an exotherm that is somewhat smaller and delayed in time.

The combustion of natural gas in the furnace results in small levels of NOₓ present in the flue gas. The level of NOₓ during a test is fairly constant, but can vary among tests. Its formation is highly dependent on the combustion temperatures and fuel/air mixing, and therefore the furnace firing rate or furnace load. The NOₓ level is typically around 100–200 ppm in the flue gas. The inlet NOₓ level was near 120 ppm for MCCF-03-1. Based on the data in Figure 23, there is partial removal of NOₓ from the flue gas across the adsorber, with the outlet NOₓ value near 50 ppm.

Moisture was also monitored in the exit gas stream of the reactor. At the time of MCCF-03, only one humidity probe was available and was installed in the slip stream of gas exiting the adsorber. In Figure 19, this location is identified as RH-3 and is labeled as H₂O in the data plots of Figures 22–25. The probe also records temperature and is labeled as “Probe T” in the same plots. Prior to the start of adsorption, the probe resided off-line with no flow through the slip stream from the adsorber and no water was detected. The system had been inerted under a flow of nitrogen during regeneration of the previous cycle. After flue gas flow was initiated through the vessel and through the slip stream, a trace amount of moisture was initially detected. Based on the performance of the chiller to lower the flue gas temperature, the moisture in the flue gas entering the adsorber should have been near 1%. The exit moisture rose to about 0.6% during the first 30 minutes, during the same timeframe of CO₂ adsorption and bed exotherm. The moisture then drops to around 0.1% and remained constant for the remainder of the adsorption stage. The initial appearance of water in the exit stream could have several explanations. Some residual moisture may have been present in the system, and when the flow valves were switched, the moisture was transported to the probe location. A second explanation could be that some water was desorbed from the sorbent during the higher bed temperatures of the exotherm. The first explanation, that moisture was present in an isolated leg of the system, appears intuitively more
likely. From the H\textsubscript{2}O concentration measurements, it was concluded that moisture was being removed across the bed.

Although CO\textsubscript{2} adsorption was completed within the first 30 minutes, the adsorption phase was allowed to continue for a total of 6 hours. Several phenomena are observed, including bed temperature remaining elevated and continued adsorption of H\textsubscript{2}O and NO\textsubscript{x}. It will be shown later that the bed temperature will remain elevated until adsorption of water ceases and the bed is saturated; a return of bed temperature to the initial value follows.

The consistency and steady-state nature of the data in Figure 23 is self-evident. Flow rates, as measured by the various venturi meters at different locations (FY-15, FY-17, and FY-18), are in excellent agreement. The exit flow (FY-18) is lower than the inlet flow (FY-17) during the adsorption of CO\textsubscript{2} during the first 30 minutes, but then it is equal once bed saturation is achieved. The gas composition data (CO\textsubscript{2} and O\textsubscript{2}) for the three locations are also in good agreement. Since the system is under slight vacuum, one sign of air in-leakage is a rise in the oxygen level as the flue gas progresses downstream to subsequent measurement stations. Air in-leakage was minimal during this test.

Figure 24 shows the desorption phase for MCCF-03-1. Adsorption was terminated at 23:55 and desorption was begun immediately afterward. During this transition, the flow of flue gas is bypassed around the adsorber and a sweep flow of N\textsubscript{2} is introduced to the adsorber. The intent is to purge the reactor with minimal dilution of gas products. Normally the furnace remains operational and off-line during desorption and regeneration, but equipment malfunction was encountered during the valve switching and the furnace suffered a flameout. However, this had no effect on the desorption phase since flue gas is customarily bypassed. The furnace was reestablished approximately two hours later (near 02:00). Hence there is a pronounced disruption in natural gas and combustion air feeds to the furnace and flue gas flowrate and gas composition for CO\textsubscript{2} and O\textsubscript{2} for the furnace exit location.

A sweep flow of 50 lb/hr N\textsubscript{2} was sent through the vessel during the desorption phase. The sweep gas is electrically preheated to maintain similar process temperature in the reactor. As can be seen in the plots of Figure 24, CO\textsubscript{2} is desorbed from the zeolite and appears in the exit stream. Attempt is made to hold the reactor temperature near the same temperature during desorption, but some downward drift was encountered. Negligible traces of H\textsubscript{2}O and NO\textsubscript{x} are desorbed at these low desorption temperatures.

The thermal regeneration phase for MCCF-03-1 (see Figure 25) was begun at 03:02. The sweep gas flow of 50 lb/hr N\textsubscript{2} was discontinued and the heat gas flow of 200 lb/hr N\textsubscript{2} was initiated. The higher flowrate was discovered to be more effective in changing the sorbent temperature, but it was still very difficult and time consuming to affect changes in bed temperature for a stationary bed of material. The overall thermal goal for the regeneration phase was to achieve regeneration temperature near 660\textdegree F (350\textdegree C) for a time period of 3 hours, since these conditions were found to be suitable during bench-scale packed bed testing.

As the bed temperature enters an intermediate temperature range (approximately 250–450\textdegree F), significant desorption of NO\textsubscript{x} is observed in the exit stream. Moisture also begins to appear in the exit stream near the time of the maximum NO\textsubscript{x} level (around 05:00 in Figure 25). As the moisture probe encounters higher process temperature due to the bed heating, eventually the probe’s upper temperature limit is approached and the probe must be withdrawn from the measurement location. With disconnection of the electrical leads to the probe, the signal defaults
to the upper limit, and hence high, constant values appear in the probe’s data for the remainder of
the regeneration phase. Note that the spike in exit gas concentration around 09:30 was due to a
drift check on gas analyzers.

A curious phenomenon consistently appears in bed temperature during heat-up of the
regeneration phase. The bed suffers a cool down before resuming an increase in temperature.
This “endotherm” may be attributable to desorption of a gas in significant quantity, such as
moisture. A less likely candidate could be NO\textsubscript{3} desorption. Despite no changes made in external
electric heaters on the vessel or electric preheat of the heat gas, the phenomenon consistently
appeared and coincided with the NO\textsubscript{3} and H\textsubscript{2}O desorption. There are some MCCF process
limitations in that the electric heaters for the nitrogen heat gas cannot be activated until gas flow
is initiated, and so there is a transient in gas temperature entering the vessel until the heater
achieves maximum output.

The bed thermocouple readings are not necessarily uniform during heatup. The bottom portion of
the bed (TE-396 and TE-397) appears to lag the upper remainder of the bed. Even when the
upper steady state temperatures are approached, the bottom thermocouples may not reach the
target temperature of regeneration. Hence the effectiveness of thermal regeneration to remove
moisture for the lower bed region might be in doubt for the subsequent cycle. Also note that the
exit gas temperatures are lower but follow the same trend as the bed temperatures due to the
convective heat transfer from gas flow.

Upon completion of a 3-hour hold time at the upper regeneration temperature, the vessel heaters
are turned off and the electric preheat of the N\textsubscript{2} heat and sweep gases are de-energized. The
intent is to cool off the vessel by unheated gas throughput with maximum flow. As bed
temperatures approach the target adsorption temperature of 100°F for the next cycle, the heat gas
is discontinued and the sweep gas is again preheated. Once the vessel achieves thermal steady
state, the next adsorption cycle could commence.

**MCCF-02: Initial Tests**

To further ascertain the effect of moisture in the flue gas on the zeolite performance, experiments
of rather long time duration were conducted during MCCF-02. Shown in Figure 26 is a two-
cycle test of MCCF-02. These experiments were among the first to be conducted in the facility,
and during this time only one moisture probe was available for these tests. Output from the probe
was not electrically connected to the computerized data acquisition system, and therefore the
relative humidity and temperature data were periodically recorded by hand. The probe location in
the adsorber exit slip stream corresponds to RH-3 in Figure 19.

The adsorption phase of the first cycle (MCCF-02-1) is shown in the left-hand column of data
plots in Figure 26. Flue gas at 100°F was initiated through the adsorber at 15:37. The typical
exotherm was observed in the adsorber along with CO\textsubscript{2} breakthrough. Note that spikes in gas
composition typically correspond to periods when the gas analyzers were off-line and being
calibrated with span or zero gases. The bed temperatures passed through a maximum near 210°F
and then fell to values near 150°F but remained at an elevated plateau. The adsorption phase was
continued for nearly 18 hours. No moisture was detected in the exit stream while the bed
temperatures remained elevated near 150°F. Eventually the bed temperatures began a slow
decline and returned to 100°F. The adsorber exit gas temperatures lagged the bed temperatures
but also exhibited the similar drop in temperature. The appearance of moisture in the exit stream
corresponded to the time window when bed temperatures returned to the flue gas inlet
temperature. It appears that the bed was being heated due to exothermic adsorption of water, and once the bed reached adsorption saturation, adsorption of water ceased and began to break through the bed. The moisture level rose to values near 1%, consistent with values predicted by chiller performance.

The center column of data plots in Figure 26 shows the desorption/regeneration phases for MCCF-02-1. The low flow sweep gas of 50 lb/hr N₂ was used for the entire cycle, without the high flow rate of heat gas. Therefore the rate of change in process temperature was slower. Bed temperature was raised to values near 150°F and held for an extended period of about 18 hours. An initial “slug” of water was desorbed from the bed, having a maximum near 4% in the off-gas. Bed temperature was further increase to values ranging between 200°F to 350°F. Additional water was desorbed from the bed, as well as the appearance of NOx desorption. Although the probe temperature was rising to levels near its maximum limit of operation, it was not necessary to remove the probe from its sensing location. Less insulation of piping as well as not using heat tracing allowed the probe to remain somewhat cooler and remain on-line. Note that regeneration was not conducted at high enough temperature (near 660°F) for sufficient time (3 hr) due in part to the low flow rate of sweep gas. This had implications for the subsequent cycle of MCCF-02.

The second cycle (MCCF-02-2) is shown in the right-hand column of data plots in Figure 26. Adsorption, desorption, and regeneration phases are included on the same data plot. The second cycle experienced degraded performance in adsorption (see Table 12). The exotherm was lower (from 116°F to 63°F), and CO₂ breakthrough time was shorter (from 11 to 2 min) with corresponding lower sorbent capacity. The moisture exhibited a similar trend to the first cycle, with breakthrough corresponding to the time period when bed temperature fell from the plateau to inlet values. Desorption of water was observed in large concentration as bed temperature was raised. Note that the bed temperature was raised in a quicker fashion for the second cycle by avoiding the initial long holding period of 150°F employed for the first cycle. Desorption of NOx was again observed as bed temperature approached and exceeded 200°F.

**MCCF-03: Repetitive Testing**

The repeatability of the MCCF results was gauged by performing a four-cycle test of the same condition in MCCF-03. A lower gas velocity, or reactor space time for the adsorber, was desired to further lengthen the CO₂ breakthrough time. Hence the furnace was fired at approximately 40% of full load. A natural gas feed of 10 lb/hr with 20% excess air, resulted in a dried flue gas of approximately 200 lb/hr (approximately 43 SCFM). Note that the first cycle of MCCF-03 was previously discussed as an example of a typical MCCF test.

Figure 27 shows the initial period of adsorption for the four cycles of MCCF-03, and Figure 28 shows the desorption and regeneration phases for the four cycles of MCCF-03. Plots of gas composition and reactor temperature appear side-by-side for each cycle. Although the absolute clock time may be different among any x-axis, the plots have been time-shifted such that the start of adsorption is vertically aligned in Figure 27 and the start of desorption is vertically aligned in Figure 28. Also note that the same total windows of time (x-axis) as well as y-axis ranges are identical among the plots in Figure 27. A relatively short time window was used in Figure 27 to highlight CO₂ breakthrough and the bed exotherm. A longer total time window (x-axis) is employed in Figure 28, but again the plots have equivalent abscissas and ordinates.
To further investigate minimum regeneration conditions (temperature and time) and its effect on maintaining repeatable adsorption, the second cycle regeneration (see MCCF-03-2 in Figure 28) was performed at lower temperature for a much shorter time period. The effect was pronounced for the third adsorption cycle, particularly the bed temperature profile (see MCCF-03-3 in Figure 27). Some of the bed thermocouples did not experience the immediate exotherm. From inspection of the data listed in Table 12, the third cycle had degraded adsorption performance. The exotherm was lower (from 116°F to 98°F), and CO$_2$ breakthrough time was halved (to 9 min) with corresponding lower sorbent capacity.

Normal, but elevated, conditions of regeneration were then performed for the third cycle (see MCCF-03-3 in Figure 28). These regeneration conditions successfully returned the zeolite to the same level of performance for the fourth adsorption cycle (see MCCF-03-4 in Figure 25). Equivalent results for exotherm, CO$_2$ breakthrough time, and sorbent capacity are noted in Table 12 for the first, second, and fourth cycles. The same cycles have highly similar profiles in gas composition and reactor temperature. The adsorber inlet CO$_2$ curve (see AT-CO2-1 data for MCCF-03-2 in Figure 27) appears anomalous but is actually in error. The analyzer was mistakenly left off-line due to an incorrect position in the sampling valve and was instead sampling residual calibration span gas instead of actual flue gas. Lacking adsorber inlet CO$_2$ measurements, CO$_2$ values at the furnace location were assumed to equal the levels at the adsorber inlet in order to perform CO$_2$ material balances across the adsorber. The validity of this assumption appears reasonable since the O$_2$ measurements at the three locations are in agreement, signifying minimal air in-leakage. In addition, the other tests for MCCF-03 demonstrate that the CO$_2$ measurements at both locations are typically in good agreement under conditions of equivalent O$_2$ measurements.

**MCCF-04: Gas Residence Time Series**

The effect of gas flow rate (i.e., space velocity) was studied in MCCF-04. To maintain equivalent flue gas composition entering the adsorber, the firing rate was varied for the combustor. Three different feed rates of natural gas with 20% excess combustion air resulted in three different flow rates of flue gas (see Table 12). The furnace was operated at approximately 15%, 40%, and 100% of full load, corresponding to flue gas (dried to approximately 1% moisture content) flow rates of 16, 44, and 100 scfm, respectively. For a bed cross-sectional area of 8 ft$^2$ and bed thickness of 5 in, the superficial gas velocity would be 12.5 ft/min and the gas residence time through the bed would be 2 sec under full flow conditions of 100 scfm flue gas. These values assume that the gas is at a standard temperature of 60°F in the adsorber and would have to be corrected for the typical adsorption temperature of 100°F employed during all MCCF tests. This temperature correction factor for gas expansion is about 7.7%. The gas velocity would be proportionately lower and residence time proportionately higher for the reduced-load conditions. Thus the gas velocities (for no temperature correction) were 12.5, 5.5, and 2.0 ft/min and corresponding gas residence times were 2, 4.5, and 12.5 sec, respectively.

Figure 29 shows gas composition and temperature data for the three adsorption tests for MCCF-04. The desorption and regeneration data plots are presented in Figure 30. MCCF-04 was terminated after the third adsorption cycle, and therefore no data are shown for the third desorption/regeneration cycle. Note again that the abscissa and ordinate for all axes have the same relative scale length and the plots are vertically aligned to mark the beginning of adsorption (target of 660°F at 3 hr) were employed between each adsorption condition. Note that the
perturbation for MCCF-04-1 (around 17:45 in Figure 29) was due to shutdown of the furnace as a result of low cooling water supply. The furnace was eventually relit, but the adsorber remained off-line from flue gas flow; desorption was initiated. CO\textsubscript{2} breakthrough and bed saturation had already been reached before the furnace disruption for MCCF-04-1, and therefore comparisons among the three adsorption profiles were still possible.

The effect of lower gas flow and velocity are clearly visible in Figure 29 and Table 12. Longer time is required for CO\textsubscript{2} breakthrough at lower flue gas flow rate. The CO\textsubscript{2} breakthrough occurs in 44 min, 16 min, and 8 min respectively for 16, 44 and 100 scfm flue gas flow. The temperature profiles show a similar trend with gas flow rate. The onset of heat release is accelerated as higher flow rate of flue gas is passed through the adsorber. Despite the temporal differences in temperature, similar peak temperatures are reached and therefore the exotherms are similar for the three conditions (around 113°F). Due to the expanded time scales in the temperature plots, it is readily apparent that the heat release is first detected by the thermocouples in the bed, and then in the exit gas thermocouples, thus affirming the role of flue gas to transport heat away from the bed and into the exit gas stream.

Material balances for CO\textsubscript{2} indicate that the sorbent capacity was not influenced by the differences in rate of adsorption. Hence the total amount of CO\textsubscript{2} adsorbed onto the zeolite (i.e., sorbent capacity) is similar for the three conditions, despite the differences in CO\textsubscript{2} breakthrough. It is logically consistent that the overall sorbent capacity would be influenced by absolute partial pressure of CO\textsubscript{2} over the sorbent (see 13X isotherms of Siriwardane et al. (2001a, 2005)), rather than by differences in rate of adsorption onto the solid achieved by differences in gas velocity. The consistency in gas composition for CO\textsubscript{2} and O\textsubscript{2} at different sampling locations is again apparent and indicates minor air in-leakage occurred between the furnace and the adsorber.

The two cycles of regeneration for MCCF-04 (see Figure 30) appear very consistent. The CO\textsubscript{2} is initially desorbed during low temperature desorption. The NO\textsubscript{x} is desorbed when the bed temperature is rapidly raised during the thermal regeneration stage. Excessive time is required to swing the bed between the adsorption temperature and the regeneration temperature. The heat transfer rate within a fixed bed of material is unacceptably slow and cumbersome. The regeneration cycles did not appear influenced by the different flow rates of flue gas employed during adsorption.

**MCCF-05: Effect of SO\textsubscript{2}**

The effect of SO\textsubscript{2} added into the flue gas was examined in MCCF-05. The objective was to ascertain any potentially negative effects of flue gas contaminants on the performance of the zeolite. Fresh material was charged to the system prior to the start of MCCF-05 to eliminate potential interferences from prior test series. Full furnace load was employed to achieve maximum flow rate of flue gas, thus minimizing the breakthrough or saturation time of the bed. SO\textsubscript{2} was spiked into the flue gas to maintain approximately 2,200 ppm SO\textsubscript{2} in the gas stream entering the adsorber, and this represents the SO\textsubscript{2} found in untreated flue gas for a mid-to-high sulfur coal that would be combusted in a utility’s furnace. A three-cycle test of the same test condition was performed during MCCF-05. However, two major equipment complications were encountered. First, the main flue gas chiller was malfunctioning and unable to maintain full cooling performance, and therefore high levels of moisture (4 to 5%) were present in the flue gas entering the adsorber. A second problem was detected during post-test maintenance; the bed of sorbent had settled approximately six inches from the top, allowing flue gas to bypass or short-
circuit the bed of sorbent. Subsequent sieve analysis of the bed inventory through a Tyler #12 size mesh screen indicated 13% of the sorbent was minus 12 mesh. The original zeolite 13X material is 8 x 12 mesh, so the remaining 87% of the bed was intact or plus 12 mesh. The apparent attrition was attributed to unusually high throughput of heated nitrogen flow intended to dry and/or regenerate the inventory prior to the start of the test series.

Gas composition and temperature data for the three adsorption tests of MCCF-05 are shown in Figure 31. The abscissa and ordinate for all axes have the same relative scale length and the plots are vertically aligned to mark the beginning of adsorption in Figure 31. The effect of higher inlet moisture level, although unintended, may have had a striking effect on the heat release observed during adsorption. The exotherm was three times larger than normal (over 300°F versus 114°F). The CO₂ breakthrough time appeared similar (6–8 min) as was observed for MCCF-04-3 (8 min) for full furnace load. In addition to higher peak temperature, the shape of the exotherm was also different. During the initial phase, the temperature reached the typical peak value observed in prior tests. After maintaining a plateau in temperature, a second rapid ascent in temperature was observed and a second maximum was attained. The bimodal profile of temperature maxima suggest a process difference, due possibly to higher inlet moisture or gas bypass. It must be remembered that the maximum heat of absorption for water on 13X is near 75 KJ/mole H₂O, higher than that for CO₂, and probably is related to the temperature rise in the bed.

Although the increased exotherms seem most likely due to the higher inlet moisture in the flue gas, lower flow of flue gas through the bed (i.e., more gas bypassing the bed) would result in less convective heat transfer from the bed, thus also potentially contributing to higher bed exotherms. However, any heat transfer effect of decreased space velocity should be apparent from the onset of introducing gas flow, rather than the time delay observed for the second maximum. The temperature results for the top of the bed (TE-392) and exit gas (TE-76) are significantly lower than the other thermocouple locations, suggesting that the bed thermocouple was not immersed in the zeolite and was exposed to higher gas flow.

Since flue gas was likely bypassing or short-circuiting the bed, results for material balances may be somewhat ambiguous for MCCF-05. Results appear to suggest significant adsorption of SO₂ in levels approaching that of CO₂ adsorption capacity, despite the CO₂ outweighing the SO₂ in the inlet flue gas by roughly a factor of 40. The large deficit of SO₂ not liberated during sorbent regeneration also implies that the SO₂ adsorption may be indeed permanent.

**MCCF-06: Effect of Minor Flue Gas Components**

To better understand the effect of flue gas contaminants, MCCF-06 was conducted with some modifications in test parameters from MCCF-05. Since bed settling due to sorbent attrition was observed at the conclusion of MCCF-05, fresh material was again charged to the system prior to the start of MCCF-06. It was experimentally verified that the chiller could maintain suitable drying performance of the flue gas at reduced load (40%), so the furnace was fired at the condition corresponding to 10 lb/hr natural gas feed with 20% excess combustion air, resulting in 44 scfm of dry flue gas (having 1% moisture). The SO₂ was spiked slightly lower into the flue gas to maintain approximately 2,000 ppm SO₂ in the gas stream entering the adsorber. In addition, NOₓ was spiked into the flue gas to raise the total level to near 500 ppm, a level consistent with untreated NOₓ from a pulverized coal-fired combustor. A three-cycle test of the same condition was performed for MCCF-06 (see Table 12).
Given in Figure 32 are the data plots for the three cycles of adsorption for MCCF-06. The three-cycle desorption and regeneration data plots are presented in Figure 33. Note again that the abscissa and ordinate for all axes have the same relative scale length and the plots are vertically aligned to mark the beginning of adsorption in Figure 32 and the beginning of desorption in Figure 33.

The gas composition and temperature profiles for adsorption in Figure 32 appear similar to prior test series. However, there does appear to be slight degradation in performance with the addition of SO$_2$ and NO$_x$ spiked into the flue gas. The adsorption exotherm drops from 120°F to 102°F to 77°F for MCCF-06-1 through MCCF-06-3, respectively (see Table 12). Similarly, the CO$_2$ breakthrough time shows slight degradation, with a lower value of 10 min for the third cycle, and a correspondingly lower sorbent capacity (see Figure 32). Results for the first cycle for MCCF-06 were similar to those for the first cycles of MCCF-03 and MCCF-04 at the same test parameters, noting that MCCF-06 had spiked levels of SO$_2$ and NO$_x$.

The gas composition data plots for SO$_2$ and NO$_x$ in Figure 32 indicate nearly complete removal of both gases, despite their high initial inlet values. Apparently an extremely long period of adsorption would be required before significant breakthrough of the gases might occur. However, conducting tests of such duration were not of practical interest for the studies performed at large pilot scale. Note that the data anomaly for exit SO$_2$ level for the first cycle (at 14:09 for MCCF-06-1 in Figure 32) was due to a brief calibration check of the analyzer to confirm analyzer performance and verify that the exit concentration was indeed so low. Also note that the third cycle had a slightly lower NO$_x$ level (410 ppm instead of 500 ppm) due to an incorrect setting of the mass flow controller, but which probably had minimal effect on the results.

The performance of the chiller was confirmed with moisture measurements made in the flue gas before entering the adsorber. The probe data are in very good agreement with values predicted based on the temperature of the flue gas exiting the chiller (see Table 12). The flue gas was dried to 1–1.2% for MCCF-06, bearing in mind that the furnace was operating at reduced load.

The desorption/regeneration data plots in Figure 33 show significant evolution of SO$_2$ as the sorbent is raised in temperature. The SO$_2$ is desorbed over a higher and broader temperature range than the NO$_x$. NO$_x$ first appears, followed by SO$_2$ as the zeolite temperature is raised. Note that the absence of furnace gas composition data during the second cycle appears to suggest that the furnace was down or off-line. This was not the case, but rather a computer malfunction during data acquisition caused the furnace data file to be irretrievable. However, this had no effect on system operation since the malfunction occurred during desorption/regeneration when the flue gas is bypassing the vessel anyway.

The material balance results for SO$_2$ and NO$_x$ show large deficits in regenerated quantities, even though the data plots give the visual appearance of large levels of SO$_2$ being desorbed. Sorbent samples were retrieved at the conclusion of MCCF-06. Chemical analysis of the spent sorbent confirmed the presence of residual sulfur on the zeolite. Material balances for MCCF-06 were recalculated to incorporate solid analysis in Table 15.

Table 14 is a summary of analyses performed on zeolite samples. Fresh material and sorbent samples withdrawn at the conclusion of test series MCCF-03, MCCF-04, and MCCF-06 were submitted for physical and chemical analysis, including surface area, sulfur, and metals. Material was in a regenerated state at the conclusion of MCCF-03 and MCCF-06, but was in a spent state.
at the conclusion of MCCF-04. This is the reason that material balances for desorption and regeneration are not listed in Table 12 for MCCF-04-3 since the regeneration was not conducted for the third cycle.

Surface area was determined by two methods of analysis. The first method employed BET with nitrogen. However, the BET estimate of surface area is inaccurate when the sample contains significant amounts of micropores, which zeolite 13X does. The Langmuir method of surface area is therefore considered a better estimate for microporous materials. Sulfur was determined using a LECO system. Metals, including aluminum, magnesium, sodium, and silicon, were determined using ICP analysis. The metal levels were then converted to the corresponding metal oxide and summed to gauge the overall material balance of analysis for the sample.

The fresh zeolite had a Langmuir surface area of approximately 600 m²/g and a much lower BET surface area of approximately 385 m²/g. Negligible sulfur was found on the fresh zeolite, and the major metals found are consistent with zeolite 13X being composed of sodium aluminosilicate (Siriwardane et al., 2001a) (see Table 3 of the current report). The summation of the metal oxides yielded good closure on the ICP method of analysis for metals.

The results for MCCF-04 indicates that the spent sorbent was very similar to the fresh sorbent, and therefore showed little sign of degradation. Sulfur was again absent on the spent sorbent since no spiking of flue gas contaminants was performed during this test series. The adsorber profile did not exhibit any trends with respect to bed height and therefore no stratification is apparent in the data.

However, the results for MCCF-06 clearly demonstrate the significant effects of gas spiking with SO₂ and NOₓ. The surface areas by both methods show that the spent material has roughly half the surface area of the fresh material. In addition, large levels of residual sulfur were found on the sorbent, despite the fact that the material was left in a regenerated state at the conclusion of MCCF-06. Stratification in bed height is visible in the data. Larger amounts of residual sulfur were found near the top of the bed compared to the bottom of the bed. There also appears to be an inverse relationship between residual sulfur and surface area, suggesting that sulfur loading may be plugging pores, particularly the micropores for large reduction in surface area.

If stratification with respect to bed height is present, it is not apparent in the thermocouple measurements of temperature for the adsorber (see adsorber temperature data in Table 13). The inlet gas temperature is very uniform from top to bottom before entering the sorbent bed. The bed thermocouples reach equivalent peak temperature despite any temporal differences, and so there are very consistent values for the exotherm. Whether the gas velocity (i.e., gas hydrodynamics) is non-uniform is another consideration. Settling of bed fines towards the bottom of the bed could potentially cause preferential flow of gas towards the top of the bed, although visual inspection of sorbent samples does not reveal any differences in size or color from top to bottom.

The sulfur material balance for MCCF-06 was recalculated based on the residual sulfur observed on the zeolite. The material balance is summarized in Table 15. Since the solids analysis represents the condition of the sorbent at the conclusion of the three cycles, the material balance for each cycle was summed over the three cycles to arrive at a cumulative or total material balance. Since bed gradients with respect to sulfur levels were observed, an average sulfur balance of 2.19 wt% was calculated by averaging the six bed measurements. This value was then assumed to represent the residual sulfur residing on the entire bed inventory. As can be seen in
Table 15, much better closure for sulfur was obtained, with a deficit of about 28% still remaining as compared to the original deficits ranging from 50% to 90%. However, the results are certainly sensitive to the residual sulfur loading assumed to represent the entire bed inventory.

To summarize, the MCCF was used in the study of a physical adsorbent to remove CO\textsubscript{2} from flue gas. This material (zeolite 13X) was chosen based partially on its commercial use and availability as a physical adsorbent for CO\textsubscript{2}. The objective was to establish baseline performance of the MCCF using a commercially available material. Results from this first campaign indicated favorable CO\textsubscript{2} removal and the adsorption reaction was highly exothermic. Moisture was found to negatively impact the performance of the zeolite; the material is used commercially as a desiccant. A concern with this sorbent in future reactor design would be associated with the exothermic heat release due to both CO\textsubscript{2} and H\textsubscript{2}O adsorption. Heat management would be critical and is a concern with all CO\textsubscript{2} capture sorbents. Other flue gas contaminants, including SO\textsubscript{2} and NO\textsubscript{x}, were adsorbed onto the zeolite, with both species being irreversibly adsorbed, to an extent. The adsorption reaction was most favored at temperatures near 38°C. Thermal regeneration under a nitrogen sweep can be conducted at 120°C for dry flue gas, but a much higher temperature (350°C) is required after moisture laden flue gas is processed.
Figure 19: MCCF process flow diagram.
Figure 20: Photographs of MCCF equipment.
Figure 21: Instrumentation ports on sidewall of adsorber bed.
Table 12: Summary of zeolite tests in MCCF

<table>
<thead>
<tr>
<th>Test Series</th>
<th>MCCF-02 (Oct)</th>
<th>MCCF-03 (Jan)</th>
<th>MCCF-04 (Feb)</th>
<th>MCCF-05 (Apr)</th>
<th>MCCF-06 (Jun)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1  2</td>
<td>1  2</td>
<td>1  2</td>
<td>1  2</td>
<td>1  2</td>
</tr>
<tr>
<td>Cycle/Condition</td>
<td>1  2</td>
<td>1  2</td>
<td>1  2</td>
<td>1  2</td>
<td>1  2</td>
</tr>
<tr>
<td>Natural Gas Furnace Feed (FY-20) (lb/hr)</td>
<td>22.6  22.6</td>
<td>10  10</td>
<td>10  10</td>
<td>10  4</td>
<td>23.3</td>
</tr>
<tr>
<td>Flue Gas at Chiller Exit (TE-13) Gas Temperature (°F)</td>
<td>50  50</td>
<td>47  46  44  47</td>
<td>47  47  52</td>
<td>54  54  57</td>
<td>48  48  49</td>
</tr>
<tr>
<td>Predicted H2O Level (%)</td>
<td>1.20  1.20</td>
<td>1.07  1.03  0.95  1.07</td>
<td>1.07  1.07  1.29</td>
<td>1.39  1.39  1.55</td>
<td>1.11  1.11  1.15</td>
</tr>
<tr>
<td>Flue Gas at Reheater Exit (TE-15) Humidity Probe H2O Level (%)</td>
<td>1.7  1.3  1.3</td>
<td>4.8  4.3  4.8</td>
<td>1.2  1.0  1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue Gas into Adsorber (FY-17) (lb/hr) (scfm)</td>
<td>446  451  195  204  194  202  200  72  457</td>
<td>468  468  472  200  207  204</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Composition into Adsorber (dry)</td>
<td>CO2 (%)</td>
<td>9.3  9.3  9.1  8.8  8.6  8.8  8.7  8.5  9.2</td>
<td>9.5  9.5  9.5  8.4  8.5  8.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O2 (%)</td>
<td>4.3  4.5  5.0  5.7  5.5  5.5  5.1  5.4  4.4</td>
<td>3.9  4.3  4.2  5.5  5.9  5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOx (ppm)</td>
<td>80  100  120  200  170  190  130  90  210</td>
<td>80  120  110  510  500  410</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO2 (ppm)</td>
<td>2210  2200  2300  2000  1990  2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2 (moles)</td>
<td>Adsorption</td>
<td>119.71  23.45  94.91  88.93  52.13  89.24</td>
<td>96.03  117.31  118.89  72.17  55.24  46.30  82.08  81.16  58.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>15.32  13.04  59.70  71.79  41.43  89.25</td>
<td>128.76  127.7  na  27.38  8.22  9.57  59.88  51.89  34.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regeneration</td>
<td>9.21  7.51  61.42  20.78  47.78  8.90</td>
<td>7.64  14.71  na  0  29.08  7.49  24.52  24.02  19.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Material Balance (% error)</td>
<td>-79.5  -12.4  +27.6  +4.1  +71.1  +10.0  +42.0  +21.4  na  -62.1  -32.5  -63.2  +2.8  -6.5  -8.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbent Capacity (moles CO2/kg)</td>
<td>1.68  0.33  1.33  1.25  0.73  1.25</td>
<td>1.35  1.64  1.67  1.01  0.77  0.65  1.15  1.14  0.823</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2 Breakthrough Time (min)</td>
<td>11  2  17  20  9  18</td>
<td>16  44  8  8  6  7  13  15  10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption Exotherm (°F)</td>
<td>116  63  114  116  98  114</td>
<td>113  111  114  323  302  303  120  102  77</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 12: Summary of zeolite tests in MCCF (cont.)

<table>
<thead>
<tr>
<th>Test Series</th>
<th>MCCF-02 (Oct)</th>
<th>MCCF-03 (Jan)</th>
<th>MCCF-04 (Feb)</th>
<th>MCCF-05 (Apr)</th>
<th>MCCF-06 (Jun)</th>
<th>Test Series</th>
<th>MCCF-02 (Oct)</th>
<th>MCCF-03 (Jan)</th>
<th>MCCF-04 (Feb)</th>
<th>MCCF-05 (Apr)</th>
<th>MCCF-06 (Jun)</th>
<th>Test Series</th>
<th>MCCF-02 (Oct)</th>
<th>MCCF-03 (Jan)</th>
<th>MCCF-04 (Feb)</th>
<th>MCCF-05 (Apr)</th>
<th>MCCF-06 (Jun)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_x) (m-moles)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>7968</td>
<td>1581</td>
<td>1356</td>
<td>1033</td>
<td>718</td>
<td>1469</td>
<td>525</td>
<td>769</td>
<td>5825</td>
<td>1824</td>
<td>3880</td>
<td>1989</td>
<td>7336</td>
<td>9085</td>
<td>5477</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td>41.4</td>
<td>11.4</td>
<td>5.6</td>
<td>273</td>
<td>11.4</td>
<td>328</td>
<td>25.5</td>
<td>95.6</td>
<td>na</td>
<td>148</td>
<td>58</td>
<td>492</td>
<td>826</td>
<td>1196</td>
<td>894</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regeneration</td>
<td>434</td>
<td>551</td>
<td>1139</td>
<td>153</td>
<td>777</td>
<td>40.9</td>
<td>468</td>
<td>594</td>
<td>na</td>
<td>803</td>
<td>138</td>
<td>1145</td>
<td>738</td>
<td>866</td>
<td>1325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material Balance (% error)</td>
<td>-94.0</td>
<td>-64.4</td>
<td>-15.6</td>
<td>-58.8</td>
<td>+9.8</td>
<td>-74.9</td>
<td>-6.1</td>
<td>-10.3</td>
<td>na</td>
<td>-47.9</td>
<td>-94.9</td>
<td>-17.7</td>
<td>-78.7</td>
<td>-77.3</td>
<td>-59.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_2) (moles)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>51.55</td>
<td>54.48</td>
<td>37.70</td>
<td>31.41</td>
<td>42.44</td>
<td>37.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td>3.06</td>
<td>0.89</td>
<td>2.69</td>
<td>0</td>
<td>5.54</td>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regeneration</td>
<td>0.09</td>
<td>5.07</td>
<td>3.26</td>
<td>2.56</td>
<td>4.43</td>
<td>18.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material Balance (% error)</td>
<td>-93.9</td>
<td>-89.6</td>
<td>-84.2</td>
<td>-91.8</td>
<td>-76.5</td>
<td>-48.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 22: Adsorption, desorption, and regeneration results during a typical test (MCCF-03-1).
Figure 23: MCCF-03-1 adsorption data.
Figure 24: MCCF-03-1 desorption data.
Figure 25: MCCF-03-1 regeneration data.
### Table 13: Adsorber temperature data

<table>
<thead>
<tr>
<th>Test Series</th>
<th>MCCF-02 (Oct)</th>
<th>MCCF-03 (Jan)</th>
<th>MCCF-04 (Feb)</th>
<th>MCCF-05 (Apr)</th>
<th>MCCF-06 (Jun)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle/Condition</td>
<td>1  2</td>
<td>1  2  3  4</td>
<td>1  2  3</td>
<td>1  2  3</td>
<td>1  2  3</td>
</tr>
<tr>
<td>Natural Gas Furnace Feed (FY-20) (lb/hr)</td>
<td>22.6 22.6</td>
<td>10 10 10 10</td>
<td>10 4 23.3</td>
<td>23.3 23.3 23.3</td>
<td>10 10 10</td>
</tr>
<tr>
<td>Flue Gas into Adsorber (FY-17) (lb/hr) (scfm)</td>
<td>446 451</td>
<td>195 204 194 202</td>
<td>200 72 457</td>
<td>54 54 57</td>
<td>200 207 204</td>
</tr>
<tr>
<td>Initial Bed Temperature (°F)</td>
<td>92 96</td>
<td>111 106 103</td>
<td>96 97 97</td>
<td>76 99 106</td>
<td>87 94 92</td>
</tr>
<tr>
<td>Peak Bed Temperature (°F)</td>
<td>212 169 218</td>
<td>222 210 219</td>
<td>213 211 214</td>
<td>413 367 235</td>
<td>224 202 183</td>
</tr>
<tr>
<td>Bed Exotherm (°F)</td>
<td>117 61 114</td>
<td>102 87 108</td>
<td>113 109 113</td>
<td>317 258 128</td>
<td>113 96 75</td>
</tr>
<tr>
<td>Average Exotherm (°F)</td>
<td>116 63 114</td>
<td>116 98 114</td>
<td>113 111 114</td>
<td>323 302 303</td>
<td>120 102 77</td>
</tr>
</tbody>
</table>
Figure 26: Effect of moisture in flue gas on adsorption and regeneration for MCCF-02.
Figure 27: Four-cycle adsorption test for MCCF-03.
Figure 28: Four-cycle desorption/regeneration test for MCCF-03.
Figure 29: Effect of flue gas flowrate on adsorption for MCCF-04.
Figure 30: Desorption/regeneration cycles for MCCF-04.
Figure 31: Effect of SO$_2$ spiking on three-cycle adsorption test for MCCF-05.
Figure 32: Effect of SO$_2$ and NO$_x$ spiking on three-cycle adsorption test for MCCF-06.
Figure 33: Three-cycle desorption/regeneration test for MCCF-06.
<table>
<thead>
<tr>
<th>Test Series</th>
<th>Sample Location</th>
<th>Surface Area (m²/g)</th>
<th>Sulfur (wt%)</th>
<th>Aluminum (wt%)</th>
<th>Magnesium (wt%)</th>
<th>Sodium (wt%)</th>
<th>Silicon (wt%)</th>
<th>Total Oxides (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Sorbent</td>
<td>Drum</td>
<td>386.5</td>
<td>598.8</td>
<td>0.09</td>
<td>14.4</td>
<td>27.3</td>
<td>1.19</td>
<td>1.98</td>
</tr>
<tr>
<td>MCCF-03 (Jan)</td>
<td>(Top) ASV-Top</td>
<td>349.7</td>
<td>543.9</td>
<td>0.03</td>
<td>12.8</td>
<td>24.3</td>
<td>1.05</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>(Bottom) ASV-Bot</td>
<td>286.0</td>
<td>445.2</td>
<td>0.04</td>
<td>14.3</td>
<td>26.9</td>
<td>1.18</td>
<td>1.95</td>
</tr>
<tr>
<td>MCCF-04 (Feb)</td>
<td>(Top) ASV-392A</td>
<td>373.8</td>
<td>577.1</td>
<td>0.05</td>
<td>12.5</td>
<td>23.5</td>
<td>1.02</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>(Top) ASV-392B</td>
<td>381.0</td>
<td>588.9</td>
<td>0.02</td>
<td>13.0</td>
<td>24.5</td>
<td>1.06</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>ASV-393</td>
<td>300.8</td>
<td>466.6</td>
<td>0.09</td>
<td>12.6</td>
<td>23.7</td>
<td>1.03</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>ASV-394</td>
<td>324.9</td>
<td>503.9</td>
<td>0.02</td>
<td>13.0</td>
<td>24.6</td>
<td>1.07</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>ASV-395</td>
<td>395.8</td>
<td>612.9</td>
<td>0.04</td>
<td>11.6</td>
<td>22.0</td>
<td>0.955</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>ASV-396</td>
<td>371.1</td>
<td>573.1</td>
<td>0.01</td>
<td>12.6</td>
<td>23.8</td>
<td>1.05</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>(Bottom) ASV-397</td>
<td>360.8</td>
<td>558.5</td>
<td>0.05</td>
<td>13.3</td>
<td>25.1</td>
<td>1.09</td>
<td>1.81</td>
</tr>
<tr>
<td>MCCF-06 (Jun)</td>
<td>(Top) ASV-392</td>
<td>193.4</td>
<td>304.6</td>
<td>2.62</td>
<td>13.5</td>
<td>25.5</td>
<td>1.10</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>ASV-393</td>
<td>94.3</td>
<td>153.9</td>
<td>2.92</td>
<td>12.9</td>
<td>24.3</td>
<td>1.05</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>ASV-394</td>
<td>100.2</td>
<td>167.7</td>
<td>2.89</td>
<td>14.0</td>
<td>26.5</td>
<td>1.15</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>ASV-395</td>
<td>187.3</td>
<td>299.5</td>
<td>1.90</td>
<td>13.7</td>
<td>25.9</td>
<td>1.12</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>ASV-396</td>
<td>213.0</td>
<td>336.2</td>
<td>1.48</td>
<td>14.9</td>
<td>28.2</td>
<td>1.24</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>(Bottom) ASV-397</td>
<td>252.3</td>
<td>395.0</td>
<td>1.30</td>
<td>13.9</td>
<td>26.3</td>
<td>1.14</td>
<td>1.90</td>
</tr>
</tbody>
</table>
Table 15: Cumulative material balance for MCCF-06, adjusted for residual sulfur on zeolite

<table>
<thead>
<tr>
<th>Test Series</th>
<th>MCCF-06 (Jun)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle/Condition</td>
<td>1</td>
</tr>
<tr>
<td>Natural Gas Furnace Feed (FY-20) (lb/hr)</td>
<td>10</td>
</tr>
<tr>
<td>Flue Gas at Chiller Exit (TE-13)</td>
<td></td>
</tr>
<tr>
<td>Gas Temperature (°F)</td>
<td>48</td>
</tr>
<tr>
<td>Predicted H₂O Level (%)</td>
<td>1.11</td>
</tr>
<tr>
<td>Flue Gas at Reheater Exit (TE-15)</td>
<td></td>
</tr>
<tr>
<td>Humidity Probe H₂O Level (%)</td>
<td>1.2</td>
</tr>
<tr>
<td>Flue Gas into Adsorber (FY-17) (lb/hr)</td>
<td>200</td>
</tr>
<tr>
<td>(scfm)</td>
<td>44</td>
</tr>
<tr>
<td>Gas Composition into Adsorber (dry)</td>
<td></td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>8.4</td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>5.5</td>
</tr>
<tr>
<td>NOₓ (ppm)</td>
<td>510</td>
</tr>
<tr>
<td>SO₂ (ppm)</td>
<td>2000</td>
</tr>
<tr>
<td>CO₂ (moles)</td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>82.0</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Desorption</td>
<td>59.8</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Regeneration</td>
<td>24.5</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Material Balance (% error)</td>
<td>+2.8</td>
</tr>
<tr>
<td>Sorbent Capacity (moles CO₂/kg)</td>
<td>1.15</td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CO₂ Breakthrough Time (min)</td>
<td>13</td>
</tr>
<tr>
<td>Adsorption Exotherm (°F)</td>
<td>120</td>
</tr>
<tr>
<td>NOₓ (m-moles)</td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>7336</td>
</tr>
<tr>
<td>Desorption</td>
<td>826</td>
</tr>
<tr>
<td>Regeneration</td>
<td>738</td>
</tr>
<tr>
<td>Material Balance (% error)</td>
<td>-78.7</td>
</tr>
<tr>
<td>SO₂ (moles)</td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>31.4</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Desorption</td>
<td>0</td>
</tr>
<tr>
<td>6.45</td>
<td></td>
</tr>
<tr>
<td>Regeneration</td>
<td>2.56</td>
</tr>
<tr>
<td>25.57</td>
<td>8</td>
</tr>
<tr>
<td>Residual (2.19 average wt% S on sorbent)</td>
<td></td>
</tr>
<tr>
<td>Material Balance (% error)</td>
<td></td>
</tr>
<tr>
<td>48.71</td>
<td></td>
</tr>
<tr>
<td>-27.8</td>
<td></td>
</tr>
</tbody>
</table>
2.7 CURRENT PRE-COMBUSTION AND POST-COMBUSTION ZEOLITIC SCHEMES

Pre-Combustion

From the previous studies, zeolites showed excellent performance at removing CO$_2$ from gas streams. Although most of the work involved removal of CO$_2$ at low temperatures, processes employing high/moderate temperature CO$_2$ removal with zeolites could hold certain advantages, especially when applied to pre-combustion situations. CO$_2$ removal from an IGCC system is the most energy efficient if the removal occurs at elevated temperature along with the removals of other pollutants. The efficiency of the power cycle is improved as compared to the current commercial CO$_2$ removal process (Selexol) that requires fuel gas cooling, which decreases thermal efficiency (Pennline et al., 2008). In addition, regenerating the sorbent at high pressure minimizes the compression cost required for eventual CO$_2$ sequestration. A process that involves high pressure adsorption of CO$_2$ in the presence of steam at 120–150°C and high pressure regeneration in the presence of CO$_2$ at 300–350°C has been proposed (Fisher et al., 2011).

High pressure and temperature tests were conducted with Zeolite 13X (Sud-Chemie) in a bench-scale flow reactor with a diameter of 1 in and bed height of 3 in. The zeolite was pretreated by increasing the temperature to 350°C in nitrogen for 2 h to remove absorbed water and then reducing the temperature to 150°C. CO$_2$ capture was then initiated by introducing a CO$_2$-rich gas mixture containing 28% CO$_2$, 7%H$_2$O, and balance helium with a space velocity of 500 h$^{-1}$. The gas mixture was introduced until the outlet gas composition reached 28% CO$_2$. After adsorption of CO$_2$ and H$_2$O at 150°C, the reactor was purged with N$_2$ at 150°C until the outlet CO$_2$ and H$_2$O from the reactor was less than 5,000 ppm. The temperature programmed desorption (TPD) study was subsequently initiated by ramping the reactor temperature from 150 to 350°C at a rate of 2°C/min. The CO$_2$ and H$_2$O effluent concentrations in the reactor were continuously monitored by a Pfeiffer OmniStar mass spectrometer (MS). The zeolite sample was subsequently cooled to 150°C, and another adsorption cycle was conducted.

Prior to capture, the CO$_2$ concentration was at 28 vol%, while the feed gas bypassed the reactor with the zeolite bed. Capture was initiated by switching the reactor online, which redirected the feed gas into the reactor/zeolite bed. After capture was initiated, the CO$_2$ concentration in the reactor effluent decreased for nearly 11 min; afterward, the CO$_2$ concentration profile steadily increased, a breakthrough, indicating the zeolite was saturated with CO$_2$. A total of 3.19 mols of CO$_2$ per kg of zeolite was captured (see Table 16). Following regeneration at 350°C and 280 psig, a second capture cycle was performed that captured 2.85 mole of CO$_2$ per kg of zeolite, indicating the zeolite is regenerable at 280 psig. During the temperature programmed desorption with N$_2$ on the CO$_2$-saturated zeolite, the switch from CO$_2$-rich gas to N$_2$ prior to the temperature ramp produced a significant release of CO$_2$, suggesting a portion of the CO$_2$ was weakly bound, as found at lower temperature applications (Stevens et al., 2008). The increase in temperature led to an increase in the MS CO$_2$ profile intensity. However, per kg of zeolite, only 0.24 mole of CO$_2$ was released, suggesting a majority of the CO$_2$ was released during the switch from CO$_2$-rich capture gas to N$_2$-purge gas at 150°C. This indicates 2.95 of the 3.19 mole of CO$_2$ per kg of sorbent were released during the gas switch. Further heating resulted in an increase in the H$_2$O intensity, which peaked at 326°C, and a total of 1.11 mole of H$_2$O per kg of zeolite was released, indicating that heating the zeolite to 350°C is necessary for removal of adsorbed H$_2$O.
Table 16: Sorption capacities over Zeolite 13X sorbent during bench-scale flow reactor testing with CO$_2$ and 7% H$_2$O and balance N$_2$ at a GHSV of 500 h$^{-1}$

<table>
<thead>
<tr>
<th>Cycle</th>
<th>T (°C)</th>
<th>P (psig)</th>
<th>Inlet CO$_2$ vol%</th>
<th>Capacity (mol/kg)</th>
<th>T (°C)</th>
<th>P (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>280</td>
<td>28.7</td>
<td>3.19</td>
<td>350</td>
<td>280</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>280</td>
<td>28.7</td>
<td>2.85</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>1</td>
<td>350</td>
<td>280</td>
<td>90</td>
<td>0.01</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

In an ideal case, regeneration of the zeolite would be carried out at 350°C in a hot CO$_2$ atmosphere. For this to be feasible, the zeolite must have a very low sorption capacity at 350°C. To ensure this occurs, a third CO$_2$ capture cycle was conducted at 350°C, 280 psig, and 90% CO$_2$ to investigate the zeolite’s ability to be regenerated in the presence of high pressure and temperature CO$_2$. Under these conditions, only 0.01 mole of CO$_2$ per kg of zeolite was captured, as seen in Table 16. Because the adsorption of CO$_2$ at 350°C is very low at high pressure, these results suggest that a gas stream of high pressure CO$_2$ can be used to regenerate the zeolite, yielding a concentrated CO$_2$ stream at high pressure for sequestration.

Figure 34: CO$_2$ capture process with zeolite sorbent for IGCC systems.
Based on the previous experimental results, a pre-combustion process for CO₂ capture was proposed and is given in Figure 34. A continuous flow of sorbent between two reactors—the absorber and regenerator—would be needed. The absorber unit is maintained at 150°C, while the regenerator is maintained at 350°C. A detailed explanation of the streams can be found elsewhere (Fisher et al., 2011). The advantages of this system include low regeneration energy, high pressure regeneration that prepares the high pressure CO₂ gas stream for compression and subsequent sequestration, and removal of CO₂ from the IGCC system without significant syngas cooling.

Using this scheme, material and energy balances were determined for a baseline EPRI IGCC plant. From these balances, certain conclusions could be drawn. The thermal efficiency of the IGCC plant was calculated based on a higher heating value (HHV) of an Illinois #6 coal and with the proposed CO₂ separation process was determined to be 36.5%, which is similar to 37% for the Selexol process used in the EPRI report for CO₂ removal. If other warm gas contaminant removal technologies are utilized for removal of pollutants, for example H₂S, HCl, etc., in conjunction with warm gas CO₂ cleanup, several percent of improvement in the IGCC thermal efficiency might be realized, bringing the HHV efficiency up to or greater than that of the Selexol process. Maintaining the thermal energy of the streams within the IGCC plant is essential for maximizing plant efficiency. The proposed process is insensitive to water; whereas, typical solvent-based processes, such as Selexol, require an energy-intensive drying step upstream of the CO₂ capture unit. The process also results in a purified CO₂ stream at 280 psig, which significantly reduces the compression ratio and corresponding energy required for the CO₂ sequestration. The advantages outlined for this process encourages the use of zeolites in a pre-combustion application.

**Post-Combustion**

Development of efficient CO₂ removal sorbents from flue gas is very critical for achieving successful processes for CO₂ emission control from existing coal combustion power plants. However, as has been seen in most of the previous studies, whether laboratory-, bench-, or pilot-scale, the moisture content of the power plant’s flue gas is an issue for many types of sorbents used for CO₂ separation because the sites which attract the CO₂, also attract H₂O. Zeolitic materials, such as 13X, have shown promise for CO₂ capture with acceptable CO₂ capture capacities, relatively low heat of reactions, and low sensible heats, all of which contribute to a lower energy penalty for CO₂ removal. However, when moisture is present in the gas stream, a high temperature is required to regenerate the strongly adsorbed H₂O molecules on the zeolite making the process more energy intensive.

A more recent study had been undertaken to find a cost effective method for removing the moisture from the flue gas stream so that the sorbents can be used primarily for CO₂ separation (Fisher et al., 2013). Molecular sieve 4A from Van Air Industries has shown great promise for moisture removal in this study with a capacity over 11 moles of H₂O per kilogram of sorbent (mol H₂O/kg). However, to achieve this high capacity requires high regeneration temperatures reducing the overall efficiency of the power plant. In order to reduce the energy consumption, a partial regeneration was performed by heating the sorbent to 120°C, and this procedure resulted in an acceptable H₂O capture capacity of 4 mol H₂O/kg. Furthermore, removing the moisture from the gas stream allows an effective use of a sorbent like zeolite13X for CO₂ capture. Preliminary energetic calculations indicate this process will be at least equal to, and potentially lower in energy consumption than current processes modeled in NETL’s baseline study.
Although this work is in its initial stage, the benefits could be significant since prior research indicates that 13X is an excellent candidate for flue gas temperature CO$_2$ capture in a dry environment.
3. **ALKALI/ALKALINE EARTH SORBENTS**

3.1 **INTRODUCTION**

Solid sorbents can have applicability in either a post-combustion (for example, a conventional power generation scheme) or a pre-combustion application (an IGCC situation). A unique approach for CO\(_2\) capture employs dry scrubbing – a process that includes chemical absorption with a sorbent. A dry, regenerable sorbent process is cyclic in the sense that the sorbent can remove the carbon dioxide, be regenerated (and in this step yields a concentrated stream of CO\(_2\)), and thus be reused. The process can be economically advantageous over commercially available wet scrubbing technologies. Although the process can be used in flue gas separations, it can also be used to capture CO\(_2\) from gasification streams, preferably at elevated temperatures. The surroundings of the sorbent, most notably the oxidizing or reducing gas composition, and the temperature, have the most significant impact on the performance towards CO\(_2\) capture. Depending on the type of sorbent and the bonding of the CO\(_2\) to the sorbent, regeneration can be accomplished with a temperature swing, a pressure swing, or a combination of the two. The sorbents can be envisioned within a stationary reactor bed that is periodically switched between the absorption and regeneration modes of operation, such as those found in traditional pressure swing adsorption. Other reactor configurations, for example entrained reactors, fluidized beds, and moving beds, can continuously transport the sorbent between the absorption/regeneration steps (Pennline et al., 2005).

As previously mentioned, dry scrubbing uses a solid instead of a liquid scrubbing medium. The system involves regenerable gas/solid interactions. Depending on the nature of the gas/solid interactions, the CO\(_2\) may be physically adsorbed or chemically absorbed. In the case of chemical absorption, CO\(_2\) undergoes a chemical reaction with an active compound present on the solid to form a new product, such as a carbonate or bicarbonate. Hence, chemical absorption involves heterogeneous gas/solid chemical reactions (White et al., 2003). The reaction of CO\(_2\) with alkali/alkaline earth materials falls in this category.

With respect to an IGCC process, the CO\(_2\) absorption reactor could be integrated into one of several IGCC process locations. The site of integration would depend on the nominal operating parameters (i.e., temperature, etc.) required for the particular sorbent of interest. For instance, alkali metal carbonates/bicarbonates (“low temperature”) are more suitable for the absorber being placed near the end of the process near the stack. The alkaline-earth oxides/carbonates and some alkali metals (“high temperature”) are potentially more adaptable for use in pre-combustion removal where the absorber would be located upstream of the gas combustion turbine. The fuel/synthesis gas location represents a highly-reducing atmosphere whereas the stack gas location represents a more traditional flue gas location, containing oxygen. These substantial differences in gas surroundings need to be considered when integrating a CO\(_2\) capture process into the IGCC system. However, depending on the sorbent, thermodynamic calculations indicate that the dry, regenerable process can be situated at more than one location within the IGCC process.

For chemical absorption of CO\(_2\) onto a solid, a heterogeneous reaction occurs on the surface of the solid to form a new chemical species. Because CO\(_2\) is an acid gas, reaction often involves neutralization of the CO\(_2\) with a base compound on or within the solid. Such acid/base neutralization reactions are commonly employed in commercial wet scrubbing of CO\(_2\) using basic solvents, including alkanolamines, NH\(_3\), hot K\(_2\)CO\(_3\), and so on. Hence, analogous reactions
can be extended to a gas/solid system in place of the liquid scrubbing medium (White et al., 2003).

Compounds of alkali and alkaline earth metals can be employed in chemical reactions with CO₂. As an example, an alkali metal carbonate can react with CO₂ and H₂O to form an alkali metal bicarbonate:

\[ X_2CO_3 + CO_2 + H_2O \leftrightarrow 2XHCO_3 \]

\((X = Li, Na, K, \text{etc.})\)

Another class of reactions involves alkaline earth metals, whereby an alkaline earth metal oxide can react with CO₂ to form an alkaline earth metal carbonate:

\[ XO + CO_2 \leftrightarrow XCO_3 \]

\((X = Mg, Ca, \text{etc.})\)

A different type of reaction involves substitution of metals to form a metal carbonate, for example, in the case of Li and Zr:

\[ Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2 \]

Carbonate/bicarbonate reactions using alkali metals are projected to occur at temperatures less than 100–200°C and can be applicable to flue gas temperatures. The alkaline earth metal reactions, depending on the specific metal, can occur over a wide and elevated range of temperature (approximately 500–900°C). The high-temperature materials may have application suitable for CO₂ capture in process streams at elevated temperature, such as in IGCC or other advanced power systems. Regarding temperatures for suitable operation, it is difficult to generalize any one group of reactions, but rather, a specific reaction should be considered in its entirety.

Projections were determined from thermodynamic analyses used to identify ranges of temperature for absorption and regeneration for a particular reaction (Hoffman and Pennline, 2000). Enthalpy and free energy changes are calculated for both absorption (forward) and regeneration (reverse) reactions, and equilibrium constants are determined over a range of temperatures. Materials of general interest primarily included alkali and alkaline earth metal compounds. Thermophysical properties of candidate compounds were obtained from CRC Handbook of Chemistry and Physics and Perry’s Chemical Engineers’ Handbook. However, it must be noted that equilibrium calculations do not yield information regarding the rate of reaction (kinetics), but rather the final equilibrium chemical state. A reaction may be
thermodynamically favorable but may require a very long time to achieve its final chemical state. Reactions should have sufficiently fast kinetics to have practical application in a CO₂ chemical absorption process employing solids as the scrubbing medium. The effect of other gaseous components in the mixture on the absorbent reactivity with CO₂ must also be considered.

Several considerations, or constraints, were taken into account in order for a metal compound to be a potential, feasible sorbent. First, the state of phase of the compound dictates that the reactive material impregnated (as a solid) within a support and its products must remain a solid during absorption and regeneration. Otherwise, the active material would be lost after the first cycle and would not be reusable. Thus the process temperature of absorption and regeneration must remain below the melting point of the reactant or product. Second, in order to achieve high absorption conversion of CO₂, the forward (absorption) reaction must be more favorable over the reverse reaction. This is reflected in the equilibrium constant at a particular temperature. A turnover temperature can be defined as the temperature where the forward and reverse reaction rate constants are equal. And since the equilibrium constant is defined as the ratio of the reaction rate constants, then the turnover temperature is the temperature where the equilibrium constant equals unity. Thus the absorption process temperature should be lower than the turnover temperature, and the regeneration process temperature should be greater than the turnover temperature.

Calculated thermodynamic values for the reactions of consideration are given in Table 17. The thermophysical properties from the various handbooks were used to calculate the energy changes of reaction and the equilibrium constant. The equilibrium constant was calculated at temperatures above standard conditions by assuming that the enthalpy change of reaction was independent of temperature, leading to a simpler method of calculation. The equilibrium turnover temperature, where the equilibrium constant equals unity, was calculated and included in Table 17.
Sorbent Research for the Capture of Carbon Dioxide

Table 17: Calculated thermodynamic properties of reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>Enthalpy Change of Reaction @ 25°C (Kcal/mole)</th>
<th>Free Energy Change of Reaction @ 25°C (Kcal/mole)</th>
<th>Equilibrium Constant of Reaction @ 25°C</th>
<th>Equilibrium Turnover Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XOH + CO₂ → XHCO₃</td>
<td>Li</td>
<td>-20.47</td>
<td>-10.28</td>
<td>3.47E07</td>
<td>326</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>-29.99</td>
<td>-17.8</td>
<td>1.14E13</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>-33.73</td>
<td>-21.53</td>
<td>6.18E15</td>
<td>551</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>-21.36</td>
<td>-1.90</td>
<td>2.41E01</td>
<td>54</td>
</tr>
<tr>
<td>X₂CO₃ + CO₂ + H₂O → 2XHCO₃</td>
<td>Li</td>
<td>-20.65</td>
<td>-3.26</td>
<td>2.46E02</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>-30.69</td>
<td>-6.87</td>
<td>1.09E05</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>-33.74</td>
<td>-9.7</td>
<td>1.30E07</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>-30.75</td>
<td>-5.40</td>
<td>9.13E03</td>
<td>88</td>
</tr>
<tr>
<td>X(OH)₂ + CO₂ → XCO₃+H₂O</td>
<td>Mg</td>
<td>-3.55</td>
<td>-1.91</td>
<td>8.54E10</td>
<td>-366</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>-17.67</td>
<td>-17.28</td>
<td>4.72E12</td>
<td>1077</td>
</tr>
<tr>
<td>XO + CO₂ → XCO₃</td>
<td>Mg</td>
<td>-23.81</td>
<td>-11.27</td>
<td>1.84E08</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>-43.75</td>
<td>-32.24</td>
<td>4.43E23</td>
<td>860</td>
</tr>
</tbody>
</table>

By invoking the sorbent constraints with respect to state of phase and favorable thermodynamics, suggested ranges of temperature were identified in order for absorption and regeneration to be feasible (Hoffman and Pennline, 2000). These quantities are included in Table 18. Note that some of the reactions (involving metal hydroxides) do not appear feasible as solid sorbents based on the thermodynamic analysis. This rudimentary thermodynamic analysis was used as a gauge to further test various alkali/alkaline earth materials as capture sorbents in the early stages of development at NETL.

Table 18: Temperature ranges of reactions for absorption and regeneration

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>Absorption Temp (°C)</th>
<th>Regeneration Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XOH + CO₂ → XHCO₃</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>X₂CO₃ + CO₂ + H₂O → 2XHCO₃</td>
<td>Na</td>
<td>&lt;111</td>
<td>111–270</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>&lt;145</td>
<td>145–200</td>
</tr>
<tr>
<td>X(OH)₂ + CO₂ → XCO₃+H₂O</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>XO + CO₂ → XCO₃</td>
<td>Mg</td>
<td>&lt;293</td>
<td>293–350</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>&lt;860</td>
<td>860–1339</td>
</tr>
</tbody>
</table>
A more elegant technique for predicting the identity of applicable CO$_2$ sorbents has been recently developed (Duan and Sorescu, 2010). In this study, analysis is applied based on calculation of the thermodynamic data using first-principles density functional theory (DFT) and lattice phonon dynamics to screen a large number of alkaline earth metal oxides, hydroxides, and their corresponding composites, and to explore their CO$_2$ capture properties systematically.

Predictions are compared with the available thermodynamic data to assess the accuracy of the approach and to outline a general screening scheme that can be used to predict the CO$_2$ capture properties of the new types of materials for which thermodynamic data might not be available.

The methodology or computational hierarchy for screening a large number of candidates for suitability as CO$_2$ sorbents for either pre-combustion or post-combustion capture applications has been established. It has been shown that the predicted heats of reactions from DFT-only calculations are higher than the experimental measured values by about 20–30 kJ/mol at low temperatures and that the curvature of the corresponding curves as a function of temperature is often not consistent with the experimental one. Along a wide range of temperatures, the DFT-only predicted chemical potentials of the reactions are also higher than either the experimental data or the results predicted using both the DFT and the phonon free energy calculations. Phonon dispersion calculations have to be performed with large supercells and this step is computationally intensive. In order to speed up the screening process, it is reasonable to use the DFT-only energies only as a prescreening tool with appropriate error bars. In particular, the CaO system has been taken as a reference capture reaction. If the calculated heat of reaction for a test material is lower than the heat of reaction for the reference system, then this solid is included in the list of so-called “good” candidates. In this way, a large number of reactions can rapidly be eliminated at minimal computational cost. The screening process can then be further refined by performing phonon calculations for materials belonging only to the list of good candidates. A schematic of the search mechanism is presented in Figure 25. This scheme is based on a set of computational filters that are summarized elsewhere (Duan and Sorescu, 2010).
From some of these studies, it was concluded that although pure Li$_2$O can absorb CO$_2$ efficiently, it is not a good solid sorbent for CO$_2$ capture applications because the reverse reaction, corresponding to Li$_2$CO$_3$ releasing CO$_2$, can only occur at very low CO$_2$ pressure or at very high temperature when Li$_2$CO$_3$ is in liquid phase (Duan and Sorescu, 2009). These predicted results are in very good agreement with experimental measurements. The same computational methodology had been extended to describe the phase diagrams of M–C–O–H (M=Li,Na,K) systems, where Na$_2$CO$_3$/NaHCO$_3$ and K$_2$CO$_3$/KHCO$_3$ were identified as promising candidates for both pre-combustion and post-combustion capture, in agreement with previous experimental findings. Additionally, the thermodynamic properties of CO$_2$ absorption/desorption reactions with alkaline earth metal oxides MO and hydroxides M(OH)$_2$, where M=Be,Mg,Ca,Sr,Ba, were analyzed. The heats of reaction and the chemical potential changes of these solids upon CO$_2$ capture reactions were calculated and used to evaluate the energy costs. Relative to CaO, a widely used system in practical applications, MgO and Mg(OH)$_2$ systems were found to be better candidates for CO$_2$ sorbent applications due to their lower operating temperatures (600–700 K). In the presence of H$_2$O, MgCO$_3$ can be regenerated into Mg(OH)$_2$ at low temperatures or into MgO at high temperatures. This transition temperature depends not only on the CO$_2$ pressure but also on the H$_2$O pressure.

Results from the preliminary thermodynamics calculations and the more elegant DFT-type of calculations can be used as indicators for the use of the sorbents in a power generation scheme (Duan and Parlinski, 2011; Duan et al., 2012; Duan, 2013). For the alkali/alkaline earth materials, their use in a pre-combustion application is probably more feasible. Although predictions have directed the use of the materials in a post-combustion application, post-combustion systems analysis studies (Ciferno et al., 2004; Fisher and Keller, 2006) reveal that the regenerative heat duties for some of the materials are quite large, in part due to the large heat of reaction. This significantly impacts the overall heat duty of the sorbent and makes the process
energetically inferior when compared to the post-combustion benchmark technology of monoethanolamine scrubbing.

3.2 POTASSIUM-BASED SORBENTS

Some of the initial investigations at NETL began with potassium-based sorbents. From the literature, at least one research group (Hayashi et al., 1998) studied potassium carbonate supported on an activated carbon substrate material. This material was deemed a good candidate for carbon dioxide capture. Earlier work at NASA utilized potassium carbonate as a regenerative material that could absorb CO$_2$ and H$_2$O (Onischak and Baker, 1978). The purpose was to develop life support systems to scrub breathing air during space travel. From the thermodynamic study that was previously described, potassium carbonate was chosen as a valid candidate. Due to its temperature constraints, it was envisioned that the sorbent would be used in a lower temperature post-combustion application, with the absorption temperature less than 145°C.

The approach undertaken in the potassium carbonate study was to investigate sorbents using two reactor systems; a thermogravimetric analyzer (TGA) and a bench-scale packed bed reactor. (Hoffman and Pennline, 2000). For the TGA system, change in sample weight was recorded as the sorbent was exposed to gases under conditions representative of absorption and regeneration. The extent of chemical reaction was linked to sample weight change, from which kinetic rate parameters could be estimated. In the bench-scale packed bed reactor system, process gases were flowed through a stationary bed of sorbent. The effluent from the reactor was fed to continuous emission monitors (CEM), facilitating on-line measurement of gas composition, including CO$_2$, and thus the breakthrough curve.
Experiments were performed using a microbalance assembly consisting of a Cahn TG-131 Thermogravimetric Analyzer (TGA) (see Figure 36). Gas composition that approximately simulates flue gas was created by blending high purity gases using mass flow controllers (Brooks model 5850E controller and Brooks model 5878 instrument readout). Carbon dioxide of stock gas grade (99.99%) was supplied by a gas cylinder with pressure regulator, and a house supply of dry nitrogen was utilized. The gas stream was humidified using a sparger vessel. Gas relative humidity was verified using a Vaisala HMP-36 humidity/temperature probe and a Vaisala HMI-32 instrument readout. Moisture-laden gas streams were heat-traced with electrical heating tapes and controlled by variable autotransformers (Variac). A heated section had one heating tape with one thermocouple mounted on the external surface. The electrical power to the tape was manually governed by Variac setting to achieve a temperature readout in excess of the dew point to prevent condensation. A circulating bath (Haake) of ethylene glycol/water was used to provide fine temperature control of the gas mixture prior to the gas entering the reactor.

Approximately 200 mg of sample was placed in a quartz cylindrical sample pan. Slotted apertures in the bottom and side wall of the sample pan help mitigate gas diffusional resistance. Sample temperature was measured and controlled with a type K thermocouple placed immediately below the suspended sample pan. Total gas flow rate was held constant at 140 cc/min. For the typical baseline condition during CO₂ absorption, the gas inlet composition (vol%) was typically 10% CO₂, 10% H₂O, and 80% N₂, at a TGA reactor temperature of 60°C.
After charging the sorbent to the TGA, the sample was preconditioned and dried in nitrogen by elevating the reactor temperature to 150°C for approximately 4 hours. This preheating near the thermal regeneration temperature assured that the initial chemical state of the sample contained only reactant material (potassium carbonate) and no product material (potassium bicarbonate). The sample was then cooled to the desired absorption temperature and allowed to come to steady state, both thermally and gravimetrically.

The sample was then preconditioned with humidified gas by switching the sparger in-line, whereby nitrogen was flowed through the heated reservoir of water in the sparger. The ability of the sparger to achieve saturation of the nitrogen gas was verified with a sampling probe measuring relative humidity and gas temperature. The humidity probe was independently calibrated against several standards including saturated salt solutions.

Once the sample achieved steady state under humidified conditions, carbon dioxide was added to the water/nitrogen mixture. Nitrogen gas flows were adjusted so that the sample was exposed to the same level of moisture (10%) and total flow rate (140 cc/min) prior to the introduction of CO₂. The CO₂ absorption stage was allowed to proceed until a steady-state weight gain was achieved.

The sequence of gas switching was then reversed. First CO₂ was turned off, eventually followed by a termination of the humidification. The motivation for observing the sample during CO₂ isolation was to verify what fraction of the weight gain during absorption was indeed permanent weight gain by chemical reaction to form bicarbonate. Some of the weight gain was due to physical sorption of CO₂, most likely onto the alumina substrate. Once the sample was exposed to a gas lacking carbon dioxide (i.e., moist N₂), sorbed CO₂ would then desorb from the substrate, resulting in sample weight loss. This difference in the initial and final sample weight under humidified conditions represented chemical CO₂ uptake by the sorbent, from which an overall sorbent utilization was calculated based on the metal loading and theoretical weight gain due to bicarbonate formation.

Experiments were conducted at larger scale in a bench-scale packed bed reactor, as seen in Figure 37, to supplement the information obtained during TGA testing (Hoffman and Pennline, 2000). The reactor is comprised of a quartz tube measuring 40 mm internal diameter by 450 mm length. [NOTE: Description and schematics of reactor systems may appear to be repetitive. For example, the bench-scale system described here was used in the previously described zeolite work in Section 2 and also used in the soon-to-be-described amine-enriched sorbent study in Section 4. However, subtle differences in sample sizes, flow rates, and operational procedures, as well as modifications/improvements to the system, make the repetition valuable in further understanding the experimental results.] Sorbent sample was placed on a fritted filter in the center of the quartz tube, and then positioned at the center of a 400 mm clam-shell furnace. The furnace has a heating zone of 300 mm length and is controlled by a linear programmable controller. Bed temperature was measured and controlled through the use of a dual type J thermocouple located in the sample bed. A sample charge of 75 grams of sorbent resulted in a bed height of about 3 inches, and the thermocouple was positioned at approximately the 1-inch bed height, corresponding to the bottom third of the inventory. Secondary temperature controls for heater tapes along the gas inlet path served to control the temperatures of several gas mixing chambers and a water humidification chamber. A superficial gas contact time of 3.7 seconds was provided based on total gas flowrate (1.5 liter/min at STP) and sample bulk density. Gas composition was blended from gas cylinders using thermal mass flow controllers, and water was metered using a variable flow dispensing pump. The packed-bed system is configured with gas analyzers for continuous monitoring of flue gas components (SO₂, NO₂, O₂, hydrocarbons, etc.), but for this study, only a
CO₂ gas analyzer was required to monitor gas composition. The process gas is passed through a Perma Pure drying tube to remove moisture prior to the stream entering the gas analysis train.

![Figure 37: Schematic of bench-scale packed-bed reactor.](image)

The experimental procedure and test conditions employed for the bench-scale packed bed tests were similar to those used for the TGA tests. Gas composition and reactor temperatures were chosen to replicate the TGA test conditions. For the typical baseline condition during CO₂ absorption, the gas inlet composition (vol%) was typically 10% CO₂, 10% H₂O, and 80% N₂, at a reactor temperature of 60°C. Once the sample was charged to the system, it was dried under nitrogen, then humidified, and then exposed to CO₂ during the absorption step. Once CO₂ breakthrough was complete and the exit gas reached the inlet CO₂ level, the reactor was isolated (i.e., gas bypass) and the gas analyzer was recalibrated. The reactor was then brought back on-line and thermal regeneration was initiated by raising the bed temperature. However, the rate of temperature ramping was much slower in the packed-bed tests, due to larger thermal inertia, as compared to the TGA tests. Therefore, it is difficult to assign a singular temperature for the condition of regeneration, although a target regeneration temperature of 150°C was eventually achieved. The same sample was used repetitively in the initial testing and was not removed from the reactor after each test, but instead remained within the reactor as the sample was cycled between absorption and regeneration for various test conditions. Baseline conditions were re-tested periodically to check for degradation in system performance.
Materials were acquired to fabricate the sorbent of interest in this study, namely potassium carbonate on alumina. A high surface area activated alumina (approximately 360 m$^2$/g) was obtained gratis from Alcoa Industrial Chemicals Division based in Vidalia, LA. The material (LD-350) has a nominal diameter of 1/16 inch and a bulk density of 40 lb/ft$^3$. Potassium carbonate (ACS reagent grade, 99+% K$_2$CO$_3$) was impregnated onto the alumina. Potassium bicarbonate (ACS reagent grade, +99.7% KHCO$_3$), a product of CO$_2$ absorption, and potassium carbonate sesquihydrate (ACS reagent grade, 99% K$_2$CO$_3$·1.5H$_2$O) were obtained to aid in characterizing reaction products and whether the sorbent contained hydrated water. All three materials were obtained from Aldrich Chemical and were similar in appearance (white powder).

Several batches of sorbent were prepared for use in this study. Properties of the sorbent batches and of the alumina substrate can be found elsewhere (Hoffman and Pennline, 2000). Samples were routinely dried at temperatures in excess of 100°C prior to performing the chemical analysis. Batches #1 and #2 were prepared for TGA testing, while Batch #3 was prepared in larger quantity for testing in the bench-scale packed bed reactor.

For the first batch, anhydrous potassium carbonate (8 g) was added to 50 ml of de-ionized water and mixed for approximately 1-hour with a magnetic stirrer. Activated alumina (20 g) was added to the solution and allowed to soak for 18 hours. The mixture was then vacuum-filtered through a Buchner funnel for approximately 10 minutes. The sorbent was transferred to a glass dish and air-dried for approximately 3 hours. The sorbent was further dried in an oven at 100–110°C for 18 hours. A sample of the sorbent was analyzed for metals (potassium and aluminum). The average composition (by weight percent) was found to be 12.2% K$_2$CO$_3$ and 84.4% Al$_2$O$_3$.

A second batch of sorbent was prepared with the goal of achieving approximately double the amount of impregnated potassium. Anhydrous potassium carbonate (16 g) was added to 50 ml of de-ionized water and mixed for approximately 2.5 hour with a magnetic stirrer. Activated alumina (20 g) was added to the solution and allowed to soak overnight for 18 hours. The mixture was vacuum filtered through a Buchner funnel for approximately 10 minutes. The sorbent was transferred to a glass dish and air-dried for approximately 3 hours. The sorbent was further dried in an oven at 100–110°C for 24 hours. A sample of the sorbent was analyzed for metals (potassium and aluminum). The average composition (by weight percent) was found to be 17.1% K$_2$CO$_3$ and 77.8% Al$_2$O$_3$. Hence, as compared to the first batch, the potassium loading on the sorbent was increased by almost 50% by doubling the amount of potassium carbonate in the impregnation solution.

A third batch of sorbent was prepared in large quantity for the purpose of conducting tests in a packed bed reactor. The recipe used to prepare Batch #1 was scaled-up to achieve a similar metal loading for Batch #3. For Batch #3, anhydrous potassium carbonate (48 g) was added to 300 ml of de-ionized water and mixed for approximately 1 hour with magnetic stirrer. Alumina (120 g) was added to the solution and allowed to soak overnight for 18 hours. The mixture was vacuum filtered through a Buchner funnel for approximately 10 minutes. The sorbent was transferred to a glass dish and air-dried for approximately 3-hours. The sorbent was further dried in an oven at 100–110°C for 66 hours. A sample of the sorbent was analyzed for metals (potassium and aluminum). The average composition (by weight percent) was found to be 11.5% K$_2$CO$_3$ and 75.9% Al$_2$O$_3$. An analysis for sulfur was also performed and indicated minute trace levels (less than 0.005wt% S).
Materials were analyzed using various analytical techniques. For metal analysis, ICP emission spectroscopy was performed. Sorbent from batches 1, 2, and 3 had potassium loadings (as potassium carbonate) of 12.2, 17.1, and 11.5 weight percent, respectively. Materials were additionally characterized for BET surface area (via nitrogen), pore volume (nitrogen adsorption), and average pore radius. Analyses indicated approximately one-third of the surface area of the alumina was lost upon impregnation of the metal. To check on the uniformity of the impregnation of potassium carbonate within the sphere, representative samples from three sets of spheres were analyzed with x-ray photoelectron spectroscopy (XPS). In order to image the cross section of the potassium-containing spheres, the spheres were cleaved in half with a razor blade. This produced a relatively smooth cross section to image. Analysis of samples from the different batches indicated that the potassium is near uniformly distributed throughout the spheres.

### 3.2.1 TGA Results

Experiments were undertaken in the TGA to evaluate the CO$_2$ capture of potassium-based sorbents (Hoffman and Pennline, 2000). Major parameters investigated included metal loading, temperature (absorption and regeneration), and gas composition. The reactor system was also evaluated with respect to characterizing flow dynamics within the TGA. Efforts included minimizing gas diffusion, measuring gas buoyancy forces due to changes in gas composition, and evaluating the effects of pure alumina substrate lacking potassium impregnation.

A typical weight/time curve for a TGA experiment is shown in Figure 38. This particular experiment used Batch #1 sorbent which was evaluated at an absorption temperature of 80°C. The sample is dried at 150°C in nitrogen, followed by humidification, and then CO$_2$ absorption. Some CO$_2$ is desorbed (physical sorption) upon removal of CO$_2$ as an input, and then humidification of the sample is ceased, resulting in additional weight loss as moisture desorbs from the sample. Considerable time is required for the sample to achieve steady state during each particular phase of the experiment. This particular experiment lasted almost four days.
Figure 38: Typical TGA experiment (Batch #1 sorbent at 80°C absorption).

The sorbent capacity is based on the difference in weight, under humidified conditions, of the sorbent after all CO$_2$ which was physically sorbed has been desorbed. In the example of Figure 38, the weight gain (forming potassium bicarbonate) equaled 26 percent of the theoretical weight gain if all of the potassium carbonate was converted to potassium bicarbonate. Hence the sorbent capacity (i.e., utilization) is reported as 26%.

TGA experiments were typically conducted using a gas composition (vol%) of 10% CO$_2$, 10% H$_2$O, with balance N$_2$. TGA results indicate CO$_2$ capture is favored at low absorption temperature (50–60°C), with sorbent utilization strongly decreasing with higher absorption temperature (80–100°C). Higher potassium loading on the sorbent did not provide additional benefit for CO$_2$ capture, as evidenced by lower sorbent utilization for the higher loaded sorbent. The sorbent was thermally regenerated at 150°C, which is consistent with the predicted temperature based on thermodynamic analysis. The alumina substrate, when tested individually, does exhibit an affinity to sorb CO$_2$. In the TGA tests, some of the CO$_2$ is presumably desorbed (as observed as sample weight loss) as the sample is exposed to nitrogen following CO$_2$ absorption.

The TGA data were analyzed in greater detail in an attempt to extract kinetic rate information. The weight/time data of the TGA during absorption can be interpreted to obtain this kinetic information. The effect of temperature on the reaction rate was studied, and an apparent activation energy was determined (Hoffman and Pennline, 2001). Chemical reaction is assumed to be the rate limiting step, and diffusion is assumed to be a minor resistance. Derivatives of the weight/time data
were calculated, from which the maximum and average derivatives were then related to reaction rate law expressions. Data were fitted to a first order Arrhenius rate law, and the regression line coefficients were used to calculate the overall activation energy and pre-exponential term. It must be noted that some limitations in the data did periodically make interpretation of the results difficult. For the reaction of CO\textsubscript{2} absorption using potassium carbonate, the activation energy was estimated at approximately 4 kcal/mole and the pre-exponential term was approximately 10\textsuperscript{3}/hr. A comparison was made to an analogous gas-solid absorption reaction that had previously been investigated at NETL (Yeh et al., 1987). The reaction of SO\textsubscript{2} with an alumina supported copper oxide sorbent had been used in regenerable processes to remove SO\textsubscript{2} from flue gas. The copper oxide absorption reaction had a similar activation energy (approximately 5 kcal/mole), but the pre-exponential term (approximately 10\textsuperscript{44}/hr) is vastly larger by many orders of magnitude than the CO\textsubscript{2} absorption reaction. Hence the CO\textsubscript{2} absorption reaction appears considerably slow in comparison to an SO\textsubscript{2} removal system. Although the reactions have different optimal reaction temperatures and process conditions, concentration levels, etc., the comparison does yield qualitative insight into the slow nature of the CO\textsubscript{2} absorption reaction using the potassium carbonate sorbent.

3.2.2 Bench-Scale Packed Bed Results

Additional experiments were performed at larger scale in a packed-bed reactor (Hoffman and Pennline, 2000). The major benefit of performing the experiments in a bench-scale packed bed reactor versus TGA was obtaining species composition information (CO\textsubscript{2}) of the gas stream exiting the reactor. Test conditions were chosen to best replicate experiments performed in the TGA study. Using Batch #3 sorbent, parametric scans were conducted for absorption temperature (60, 80, 100°C), inlet CO\textsubscript{2} level (2, 5, 10%), inlet H\textsubscript{2}O level (0, 2, 5, 10%), repeats of the baseline condition, and the effect of the alumina substrate. All regenerations were performed by raising the bed temperature to 150°C, although the thermal ramping was slow due to large thermal inertia of the system. Also included is a calculated quantity of sorbed CO\textsubscript{2} during the absorption stage, and desorbed or liberated CO\textsubscript{2} during the thermal regeneration stage. The quantities were obtained via simple integration of the CO\textsubscript{2} breakthrough curves. The same sample was used repetitively within the reactor as the sample was cycled between absorption and regeneration for various test conditions. Only the last condition utilized different starting material (i.e., alumina substrate).

Figure 39 is a typical CO\textsubscript{2} breakthrough curve for the packed bed unit. By using this curve, the amount of CO\textsubscript{2} adsorbed can be determined. Of additional interest is the exotherm that occurs during the test that causes a temperature rise within the bed. In Figure 39, the effect of varying the inlet CO\textsubscript{2} level to the reactor is depicted. Considerable differences in the breakthrough curves are obvious, with lower inlet CO\textsubscript{2} levels exhibiting longer times necessary to breakthrough the reactor. There are also discernible differences in the temperature profiles. The exotherm is earlier and more elevated for the higher inlet CO\textsubscript{2} experiments, consistent with the earlier onset of breakthrough for the higher CO\textsubscript{2} concentration experiments.
Figure 39: Effect of inlet CO$_2$ level on CO$_2$ breakthrough.

Packed-bed results provided the additional benefit of measuring changes in exit gas composition as well as changes in bed temperature due to exothermic reaction. Breakthrough of CO$_2$ through the bed was strongly influenced by higher inlet CO$_2$ levels. The onset of bed temperature rise was noted to coincide with the breakthrough of CO$_2$, with earlier CO$_2$ breakthrough characterized by earlier temperature rise within the bed. Minor differences in the breakthrough curve were noted for absorption temperatures ranging between 60–100°C, contrary to the TGA results. Moisture difference was found to have little influence on the breakthrough curve. Sorption of moisture onto the sample, in the absence of CO$_2$, did not result in bed temperature rise. Absorption after multi-cycling of the sorbent between absorption and regeneration results in equivalent CO$_2$ breakthrough curves and thus indicates that negligible sorbent degradation is occurring. By stopping and starting the CO$_2$ feed, it was established that some of the CO$_2$ uptake on the sorbent was due to physical sorption, probably on the alumina sorbent. Additionally in the packed-bed tests, the CO$_2$ breakthrough curve for the substrate occurs in approximately half the time as for the sorbent (alumina plus potassium carbonate). In addition, a temperature rise does occur for the substrate when exposed to CO$_2$, indicating that the substrate does participate in the capture of CO$_2$.

The results with the two reactor systems impacted the research direction with potassium. One issue with the sorbent was the overall utilization of the potassium on the substrate indicating that the absorptive capacity was low and thus the working capacity of the sorbent would be low. As seen in
regenerative energy calculations for post-combustion sorbents (see Section 4.3), the low working capacity would significantly impact the heat duty for the sorbent. Monoethanolamine scrubbing has a higher capacity than this potassium sorbent, thus seriously impacting the overall energetics of the system. Another significant issue was with the kinetics of the sorbent. TGA information revealed that the reaction with this sorbent was relatively slow. The kinetic model indicated that the rate was very slow compared to other gas-solid reactions. Although the thermodynamics estimated that the carbonation of potassium carbonate was feasible, operational problems would occur because of the poor kinetics. Due to the above issues, the work with potassium was abandoned.

### 3.3 CALCIUM-BASED SORBENTS

Some of the initial work at NETL in the chemical absorption area also involved investigations with calcium oxide. As seen in the introduction for the Alkali/Alkaline Earth Sorbents Section, the thermodynamic analysis of carbonation of calcium oxide indicates that the reaction has potential application for systems at relatively high temperature. Based on the calculated equilibrium constants, the forward and reverse reaction rate constants become equal at approximately 860°C. Hence the CO₂ absorption (forward) reaction appears more favorable between 750–860°C, while thermal regeneration (decomposition or the reverse reaction) is attainable at temperatures higher than 860°C (near 1000°C). Due to the high temperature of operation for this sorbent, a post-combustion application was not feasible. Difficulties were envisioned: modification of the ductwork upstream of the preheater appeared complex in existing pulverized coal fired utilities; the volume of flue gas that needed to be processed at the extremely high temperature was excessive; and the potential permanent deactivation of the calcium sorbent due to poisoning with flue gas contaminants, i.e. sulfur dioxide and nitric oxides – acid rain precursors – appeared problematic. For this type of sorbent, a pre-combustion application was assumed more appropriate.

The research with the calcium sorbent can be divided into testing with calcium oxide and calcium carbonate powders and then testing with supported calcium on silica or on alumina or on a zirconia support. The pure reagent compounds were calcium oxide (98%) and calcium carbonate (99+%) (Aldrich catalog No. 24,856-8 and No. 25,650-1 respectively) and were obtained in powdered form. The silica, Type XS 16080 from Norton Chemical, consisted of 1/8 inch diameter cylindrical pellets. The original extrudates were cleaved with a razor blade to yield pellets whose length approximated its diameter, and thus a similar aspect ratio. The silica has a medium surface area (117 m²/g) with a packing density of 40.5 lb/ft³ and a crush strength of 14.4 lb. The total pore volume was 0.8 cc/g and the median pore diameter was 393 Angstroms.

Calcium nitrate tetrahydrate [ACS reagent grade, 99% Ca(NO₃)₂•4H₂O] from Aldrich Chemical was used to deposit the calcium onto the silica. Acetone [ACS reagent grade, 99.6%] from Mallinckrodt Chemical was the solution medium in which the wet impregnation occurred. Calcination of the impregnated silica at 400°C under nitrogen for 48 hours converted the calcium nitrate tetrahydrate into calcium oxide on the silica. Six batches of sorbent were prepared for use in the study. For a batch, silica was added to a specific solution, soaked for 18 hours, dried at 100-110°C for approximately three hours, and then calcined. Chemical analysis was performed using two sample preparation methods. Preparation parameters were varied and calcium loadings on the six sorbent batches intentionally varied from about 2 to 9 wt%. Properties of the sorbent batches and of the silica substrate itself can be found elsewhere (Hoffman and Pennline, 2001).
For the activated alumina and zirconia supports, both microporous and mesoporous substrates were chosen to explore the effect of pore size and surface area. A high-surface area activated alumina (designated Ga-200L having approximately 200 m$^2$/g) containing a modifier (lanthanum) was obtained gratis from Alcoa Industrial Chemicals Division based in Vidalia, LA. The lanthanum modifier (approximately 3 wt% lanthanum) is added to impart high temperature stability to the alumina. Ga-200L was commercially available as a fine powder, but was extruded by the manufacturer into cylindrical pellets of various lengths. The alumina has a nominal diameter of 1/16 inch and was cleaved to lengths similar to the diameter. (Hoffman et al., 2002)

Two mesoporous zirconia catalyst supports (Type A and Type B) were obtained from Alfa Aesar. The zirconium oxide substrates are 1/8 inch diameter and have larger pore size and smaller surface area relative to the Ga-200L alumina. Both zirconia supports have a bimodal distribution of pore diameter. Type A has approximately double the surface area of Type B (90 versus 51 m$^2$/g), with Type A having correspondingly smaller pore size for both maximums of the pore size distribution.

The sorbents composed of calcium deposited on a substrate were prepared in similar fashion to the silica-based sorbent. Reagent grade calcium nitrate tetrahydrate was dissolved in a suitable solvent (acetone) and mixed thoroughly with a magnetic stirrer for approximately an hour. Substrate material (either spherical or cylindrical extrudates), were cleaved, when necessary, to suitable length size with a razor blade such that its length approximated its diameter and thus had an aspect ratio near unity. The substrate was then oven dried at 100–110°C and sieved to remove fines. The substrate was added to the solution of dissolved metal compound and soaked overnight at room temperature. The mixture was then vacuum-filtered through a Buchner funnel for approximately 10 minutes. The sorbent was transferred to a glass dish and air-dried for several hours. The impregnated material was additionally dried (calcined) at 400°C in a muffle furnace for up to 48 hours. The calcination step converted the metal complex (calcium nitrate tetrahydrate) into metal oxide distributed throughout the substrate. (Hoffman et al., 2002)

Chemical analysis of the sorbents revealed that higher levels of impregnated calcium (approximately 10 wt% Ca) were achieved for the alumina substrate versus the zirconia substrates, which have roughly half the level of impregnated calcium. This is likely attributable to the mesoporous nature of the zirconia having significantly less surface area than the alumina (51 and 90 m$^2$/g versus 215 m$^2$/g, respectively). Type A zirconia had slightly higher calcium loading than Type B zirconia (4.8 versus 4.3 wt% Ca), also consistent with Type A having slightly higher surface area (90 versus 51 m$^2$/g). Additionally, scanning electron microscopy with energy-dispersive X-ray methods verified the uniformity of calcium deposition throughout the cross section of a pellet and thus validated the impregnation technique. (Hoffman et al., 2002)

Experiments were performed using a microbalance assembly consisting of a Cahn TG-131 Thermogravimetric Analyzer (TGA) whose setup was described in the previous section. (See Figure 36.) Approximately 200 mg of sample was placed in a quartz cylindrical sample pan. Slotted apertures in the bottom and side wall of the sample pan help mitigate gas diffusional resistance. Total gas flow rate was held constant at 140 cc/min. After charging the sorbent to the TGA, the sample was preconditioned and dried in nitrogen by elevating the reactor temperature to 150°C for a short period, followed by additional heating to achieve the absorption temperature of interest (typically 500–750°C). The sample was then allowed to come to steady state, both thermally and gravimetrically. Once the sample achieved steady state under dry nitrogen conditions, carbon dioxide was switched in-line and nitrogen flow was ceased, while the total
flow rate remained the same (140 cc/min). The CO₂ absorption stage was allowed to proceed until a steady-state weight gain was achieved, or was otherwise halted if an excessive duration of time was required to reach steady state. The sequence of gas switching was then reversed. CO₂ flow was turned off and N₂ flow was re-established. The motivation for observing the sample during CO₂ isolation was to verify what fraction of the weight gain during absorption was indeed permanent weight gain by chemical reaction to form carbonate. Some of the weight gain was possibly due to physical sorption of CO₂, most likely onto the substrate. Once the sample was exposed to a gas lacking carbon dioxide (i.e., dry N₂), sorbed CO₂ would then desorb from the substrate, resulting in sample weight loss. This difference in the initial and final sample weight under dry N₂ conditions represented chemical CO₂ uptake by the sorbent, from which an overall sorbent conversion was calculated based on the metal loading and theoretical weight gain due to carbonate formation.

3.3.1 Calcium-Based Reagent

Calcium oxide and calcium carbonate reagents were tested in the TGA as described previously (Hoffman and Pennline, 2000). The CO₂ absorption reaction was observed to be initially very quick, followed by a regime of much slower reaction. The CO₂ absorption reaction appears favorable between 750–850°C, while regeneration (decomposition or the reverse reaction) is attainable at 1000°C. The absorption reaction is initially very fast (perhaps 50% conversion after an hour), followed by a much slower rate, due most likely to diffusional limitations from formation of a product layer of CaCO₃. It must be noted that a powder was charged to the TGA for reagent tests. By raising the temperature from 850°C to 1000°C (see Figure 40), the sample can be rapidly regenerated within approximately fifteen minutes. Extended CO₂ absorption experiments were conducted over several days duration, and it appears that high reaction conversion can be eventually achieved (Hoffman et al., 2002; Fauth et al., 2004).
The preceding temperature ranges were conducted for reagent exposed to a pure CO$_2$ gas atmosphere. The thermal regeneration of the product (i.e., decomposition of CaCO$_3$ to CaO) is strongly dependent on the background gas composition. By switching the feed gas from pure CO$_2$ to pure N$_2$, the carbonated product, depending on the temperature, can be observed to lose weight, thus exhibiting the reverse reaction back to CaO. In pure N$_2$, the regimes of temperature suitable for regeneration are significantly lower than in pure CO$_2$. Calcium carbonate begins to decompose at 650°C in pure nitrogen but is stable in pure carbon dioxide at temperatures up to 900–950°C. By raising the temperature from 950°C to 1000°C, only then does the product begin to lose weight in a CO$_2$ atmosphere, signifying decomposition.

A calcium carbonate reagent test was conducted where absorption and regeneration was examined at 550°C, 650°C, and 750°C. Reagent results indicate that absorption can be conducted anywhere from as low as 500°C to as high as 750–850°C. However, once the sorbent is removed from the pure CO$_2$ atmosphere and subjected to a nitrogen background, the sorbent will begin to regenerate (decompose) at temperatures above 650°C. At lower temperature (550°C), the calcium carbonate product is stable in pure N$_2$ and does not lose sample weight. It should be emphasized that the recommended temperature regimes for absorption and regeneration are influenced by the actual gas composition of the stream from which CO$_2$ is to be sequestered as well as the gas composition under which the sample is to be regenerated.

A multi-cycle test of calcium carbonate reagent sample with repeated absorption and regeneration stages was conducted at 750°C (see Figure 41). Gas composition was switched between carbon dioxide (absorption) and nitrogen (regeneration) at 30 min increments, resulting in 1 hr intervals for a complete cycle. Although the cycles appear very similar, a slight
degradation in performance is apparent. For equivalent cycle times, the CO$_2$ capture (conversion to calcium carbonate) decreased by approximately two percentage points, from 36% to 34% to 32% over 3 cycles. This observation of slight degradation can also be found in other research efforts with calcium (Fauth et al., 2003).

![Cycling test with calcium carbonate reagent at 750°C absorption.](image)

**Figure 41:** Cycling test with calcium carbonate reagent at 750°C absorption.

### 3.3.2 Calcium/Silica Sorbent

Silica was the first candidate support for calcium. Although the amounts of calcium deposited onto the substrate ranged up to 9 weight percent, the initial TGA results with this sorbent indicated an extremely poor reactivity of the sorbent with CO$_2$, as seen in Figure 42. These initial sorbent studies with calcium deposited on silica substrate were unsuccessful due to side reaction of the calcium with the substrate support at elevated temperature (Hoffman and Pennline, 2001a). Chemical analysis of the fabricated sorbent indicated that the formation of calcium silicate inactivated the sorbent and prevented the calcium oxide from reacting with CO$_2$ in a carbonation reaction. It was because of the initial poor results with this sorbent that testing was discontinued.
3.3.3 Calcium/Lanthanum/Alumina Sorbent

TGA tests were conducted using the prepared Batch #1 sorbent composed of calcium oxide impregnated onto lanthanum-doped alumina substrate. The alumina substrate, when tested individually in the temperature range of 650–850°C while exposed to pure carbon dioxide, did not exhibit any appreciable affinity to sorb CO$_2$. Therefore, the substrate can be considered inert with respect to CO$_2$ absorption. TGA absorption tests with Batch #1 sorbent were conducted by exposing the sorbent to pure CO$_2$ at temperatures between 550–750°C (see Figure 43). As with the pure reagent tests, the initial rate of reaction is very fast, achieving perhaps 15–20% sorbent conversion. However, the reaction then slows significantly and enters a regime characterized by very long residence time required to achieve minimal increase in sorbent conversion. This regime is partially attributed to increased gas diffusional resistance through a product layer of calcium carbonate. The regeneration of the sorbent was also examined over the same temperature range at 550, 650, and 750°C in Figure 43. Once the absorption reaction had progressed into the slow kinetics regime, the temperature was held constant and the gas feed was switched from pure CO$_2$ to pure N$_2$. In all three temperature cases, the sorbent lost the majority of its absorption weight gain, and therefore the decomposition of calcium carbonate was occurring. At 650 and 750°C, this result is consistent with the calcium carbonate reagent tests. The reagent test at 550°C showed that calcium carbonate is stable in pure nitrogen and did not exhibit weight loss. However, the sorbent test at 550°C in the figure shows significant decomposition once the gas was switched. This observation cannot be attributed to physical absorption/desorption since the
substrate was found to be inert. Better dispersion of the active reagent on the support could play a role in this result (Hoffman et al., 2002).

The overall behavior of the sorbent was concluded to be unsatisfactory with respect to CO$_2$ capture. The sorbent conversion is much lower in the case of the sorbent versus the pure reagent. Also, the captured CO$_2$ is not permanently sequestered onto the sorbent, as characterized by significant weight loss after gas switching. High conversion, in the case of the sorbent, does not appear attainable even with a significantly longer time on stream. Pore pluggage due to calcium carbonate layer formation appears to be a plausible cause (Fauth et al., 2004).

3.3.4 Calcium/Zirconia Sorbent

TGA experiments were conducted using calcium deposited on zirconium oxide substrate. The zirconia support was mesoporous with larger pore diameter but lower surface area compared to the lanthanum alumina substrate. Type A and Type B zirconia substrates, with no calcium deposition, were examined at 500°C in pure CO$_2$. Both substrates showed slight weight gain, indicating some CO$_2$ absorption was achieved. However, upon gas switching from pure CO$_2$ to pure N$_2$, the substrates lost all of the gained weight. Since calcium carbonate reagent tests have shown the product to be stable in pure N$_2$ at 500°C, it is assumed that the captured CO$_2$ was not due to chemical reaction to form carbonate, but rather another mechanism, possibly physical/chemisorption. In either case, the amount of captured CO$_2$ is minimal and not
permanent. Although the substrates contain no calcium, if one assumes a calcium loading identical to the respectively fabricated sorbents, the weight gain corresponds to approximately 8% and 4% reaction conversion (out of 100% theoretical) to produce calcium carbonate for Type A and Type B zirconia, respectively. The higher conversion for Type A is also consistent with the higher surface area of Type A versus Type B (90 versus 51 m$^2$/g).

TGA absorption tests were conducted at 500°C for both sorbents by exposing the materials to pure CO$_2$. A test with Type A sorbent is presented in Figure 44. Consistent with the reagent tests and the alumina sorbent tests, the absorption reaction is initially very quick and then enters a slower kinetic regime. However, the zirconia sorbents perform much better, as characterized by the much higher conversion that can be attained versus the alumina-based sorbent. Conversion ranging from approximately 50–75% was observed for the calcium/zirconia sorbents versus approximately 15–20% conversion for the calcium/alumina sorbent. One explanation for the improved conversion is the pore size differential between mesoporous zirconia and microporous lanthanum-alumina. Even though the alumina has much higher surface area, pore pluggage and/or increased diffusional resistance through the calcium carbonate product layer appears a plausible cause for the calcium/alumina sorbent (Hoffman et al., 2002; Fauth et al., 2004).

![Figure 44: TGA test with type A Ca/Zirconia sorbent at 500°C absorption.](image)

The permanence of the sequestered CO$_2$ onto the calcium/zirconia sorbent was also in stark contrast to the alumina-based sorbents. When gas switching from pure CO$_2$ to pure N$_2$ at the end of the absorption stage at 500°C, the zirconia exhibited significantly less weight loss and retained a larger fraction of the absorbed CO$_2$. Approximately 70–80% of the sorbed CO$_2$ remained with the sorbent for the Type B zirconia, and roughly half of the sorbed CO$_2$ remained with the
sorbent for the Type A zirconia (see Figure 44). It is noteworthy that Type B zirconia sorbent, with larger pore size and smaller surface area, retained a larger proportion of the sorbed CO$_2$ versus Type A zirconia sorbent. Regeneration of the zirconia sorbents was quickly achieved by raising the temperature from 500 to 750°C under nitrogen.

### 3.3.5 Systems Analysis

During the experimentation with the calcium sorbents, a rudimentary systems analysis was performed through the Gasification Program, where the interest was in the pre-combustion removal of carbon dioxide (Klett and Rutkowski, 2001). Some of the background material that was used in the systems analysis was the initial work with the calcium silicate sorbent system. Additionally, it was envisioned that the reactor system that would be used for the sorbent system was a moving-bed type where sorbent is continually transported between the absorber and the regenerator (Pennline and Hoffman, 2002).

It was assumed that the sorbent system could be incorporated into two power generation systems. The first was an integrated gasification combined-cycle (IGCC) system and the second was a pressurized fluidized-bed combustion (PFBC) system, where coal is pyrolyzed followed by combustion of the char and combustion of the syngas in a gas turbine. Block diagrams for the two generation systems were prepared and depicted the location where the calcium-based process could be incorporated. Upon review of the removal sites, the high absorption temperature of the calcium oxide/carbonate system limits its application to the gasifier exit for the IGCC or the carbonizer exit for the PFBC (1600°F to 1900°F). A systems analysis was then performed using various assumptions including utilization of the sorbent, calcium loading on the substrate, moving bed design, etc. From this study, the following conclusions were made:

- In view of the slow kinetics associated with potassium sorbents, the focus of the analysis was shifted to the calcium oxide/carbonate system.
- The high absorption temperature of the calcium oxide/carbonate systems limits its application to the gasifier exit for the IGCC or the carbonizer exit for the PFBC. These applications would not capture the CO$_2$ associated with the CO in the syngas. If all CO$_2$ is removed from the raw gas exiting the gasifier, 80 percent of the carbon (as CO and CH$_4$) remains in the syngas.
- Regeneration temperatures are above any temperature in these systems. Regeneration temperatures (near 2000°F) for calcium carbonate are above any temperature in these systems. Additional fuel is required to heat the sorbent for regeneration, making a sole temperature-swing regeneration impractical. Thus, if possible, a pressure swing regeneration would be more appropriate to avoid the use of additional fuel for regeneration.
- The absorption reactor design is unique in that a cross-flow moving-bed configuration is utilized. Carbon dioxide-laden gas flows horizontally through the reactor, where the sorbent removes CO$_2$. Similarly, the sorbent flows continuously vertically through the reactor.
- The CO$_2$ sorbent was assumed to be pure CaO for the study. The NETL sorbent contained only 10 percent CaO, which would require 10 times as much solids circulation, making the process impractical. A higher loading of CaO is need for the sorbent.
• Lower temperature solid absorbents need to be developed to open up the applications to low-temperature options.

The systems analysis was one of the first forays by NETL into the area of integrating the sorbent research into practical designs of power generation systems. It was apparent that in any sorbent system, large quantities of materials will be needed. Not mentioned was the impact of other constituents in the fuel (synthesis) gas on the sorbent. The calcium sorbent work did progress significantly after the calcium/silicate research was performed and used in the systems analysis. However, due to the findings of the systems analysis and the overwhelming inherent problems with the calcium sorbent system, (particularly the fact that the sorbent’s high absorption temperature in an IGCC plant scheme equates to only about 20% capture of the theoretical carbon content), work in this area was suspended.

3.4 LITHIUM-BASED SORBENTS

Research with lithium-based sorbents at NETL commenced for several reasons, but the prime one was that of the sorbent work done to date at that time, the lithium sorbents evolved from some of the most advanced investigations. Research scientists at Toshiba Corporation had been extensively studying lithium compounds for CO\textsubscript{2} capture. Initial work focused on lithium zirconate (Li\textsubscript{2}ZrO\textsubscript{3}) powder (Ohashi et al., 2000; Nakagawa and Ohashi, 1998a, 1998b) and demonstrated fast absorption of CO\textsubscript{2} at temperatures near 500°C.

\[
\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{ZrO}_2 \quad H_{298} = -160 \text{ kJ/mol}
\]

With its excellent CO\textsubscript{2} sorption characteristics (large CO\textsubscript{2} sorption capacity, small morphological change during sorption/desorption), Li\textsubscript{2}ZrO\textsubscript{3} was considered a promising candidate material for CO\textsubscript{2} separation from post shift reactor-derived fuel gas at high temperature. Improvement in the CO\textsubscript{2} sorption rate was important for the practical application and for the design and development of a dry, regenerable sorbent for CO\textsubscript{2} separation under operating conditions prevailing in IGCC processes. Research under the Japanese effort also investigated the effect of potassium carbonate added to the lithium zirconate sorbent (Ohashi and Nakagawa, 1999). Results pointed out the absorption reaction kinetics were accelerated due to the formation of a eutectic carbonate composed of Li\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3}.

Toshiba also investigated lithium silicate for application as a high temperature CO\textsubscript{2} absorbent. (Kato et al., 2001; Kato et al., 2002). Tests showed lithium orthosilicate (Li\textsubscript{4}SiO\textsubscript{4}) absorbs CO\textsubscript{2} at a rate 30 times faster than lithium zirconate and other lithium metal oxide predecessors. Tests conducted in 20% CO\textsubscript{2} at 500°C showed 1g of Li\textsubscript{4}SiO\textsubscript{4} can absorb 62 mg of CO\textsubscript{2} within several minutes upon exposure.

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3 \quad H_{298} = -143 \text{ kJ/mol}
\]

Additionally, NETL was to operate the flexible Modular CO\textsubscript{2} Capture Facility (MCCF) that was to evaluate the ability of various non-liquid capture technologies to separate and capture CO\textsubscript{2} from both fuel and flue gas. (See Zeolite Section 2.5 for a better description of the MCCF.) In
2003, Toshiba Corporation entered into a collaborative agreement with NETL to test the corporation’s lithium silicate sorbent. Lithium silicate potentially offered improved absorption capacity, temperature range for absorption, and production cost. Preliminary TGA results at NETL indicated Toshiba’s Li₄SiO₄ sorbent had favorable kinetics for CO₂ capture.

3.4.1 Lithium Zirconate

A series of microbalance tests were conducted using lithium as the active metal for the capture of carbon dioxide (Hoffman, 2002; Fauth et al., 2005). Lithium zirconate powdered reagent (Aldrich catalog No. 40,092-0; -80 mesh) was obtained and examined in the Cahn TGA. (See Section 3.2: Potassium-Based Sorbents for a detailed description of the TGA.) In Figure 45, the absorption reaction of lithium zirconate reagent was studied at a temperature near 500°C, while the regeneration was examined at higher temperature (600°C–700°C). The absorption reaction continues steadily with conversion and does not appear to enter a regime of significantly lower kinetics at high conversion. This observation is in contrast with the calcium-based reagents where initial fast reaction was followed by slower kinetics speculated to be attributed to carbonate product layer inhibition.

The regeneration of the lithium carbonate product was found to occur at higher temperature. The lithium carbonate product is stable at 500°C, even after switching the gas composition from pure CO₂ to pure N₂. By raising the temperature to 600°C, the carbonate product can be regenerated in pure N₂, and much faster regeneration can be achieved at 700°C (see Figure 45). In qualitative terms, the calcium reagent system appears to have a faster initial reaction rate, but the lithium reagent system gradually approaches high conversion without any significant slowdown in kinetics from its initial rate (Hoffman, 2002a).
The use of a potassium doping agent, added to the lithium zirconate reagent, was explored as a means of enhancing the reaction kinetics. The technique was initially employed by researchers at Toshiba (Ohashi and Nakagawa, 1999), and was explored by Lin (2002) as a means to improve CO2 sorption rate of Li2ZrO3 sorbent. The overall purpose was to cause the formation of a eutectic compound whereby the production of a liquid interface within the solid matrix would occur. It was speculated that the presence of the liquid interface should lessen the diffusional resistance of CO2 and enhance the reaction kinetics.

Using the fabrication procedure described (Lin, 2002), an equimolar mixture of potassium carbonate and lithium carbonate powdered reagents was added to lithium zirconate reagent such that the resulting 3-component mixture was 90 wt% lithium zirconate. The eutectic mixture was exposed to pure CO2 in a TGA experiment at 500°C. The results of lithium zirconate with and without the doping agent can be seen in Figure 46. Results of the testing were transposed from sample weight to fractional conversion to normalize any differences in initial sample weight and metal loading. The conversion data are presented in the figure. When compared against the TGA results for pure lithium zirconate, the eutectic mixture was roughly twice as fast in achieving a given conversion. The results suggest some enhancement with the addition of potassium, but greater improvement in kinetics was expected. The work by Lin indicated the eutectic complex to be 40 times faster than pure Li2ZrO3 (Lin, 2002).
The electronic structural and phonon properties of Li$_2$ZrO$_3$, Li$_6$Zr$_2$O$_7$, and monoclinic phase ZrO$_2$ were later investigated by density functional theory and phonon dynamics (Duan, 2011a). (Methodology for this computational modeling endeavor was detailed in the Introduction to this section.) The electrochemical properties and the thermodynamic properties of CO$_2$ absorption/desorption are analyzed. The optimized structures and calculated bulk modulus and cohesive energy are in good agreement with experimental measurements. The phonon dispersions and phonon density of states for Li$_2$ZrO$_3$ and Li$_6$Zr$_2$O$_7$ were calculated by the direct method. Based on the phonon dispersion, the phonon free energy, the internal energy, and the entropy of these solids were evaluated within the harmonic approximation and were used to analyze the chemical potentials of the reactions of CO$_2$ capture by these two lithium zirconates. From the calculated thermodynamic properties of these two lithium zirconates reacting with CO$_2$, it was found that the overall performance of Li$_2$ZrO$_3$ capturing CO$_2$ is better than that of Li$_6$Zr$_2$O$_7$. In the first half cycle for the sorbent to absorb CO$_2$ to form lithium carbonate, Li$_6$Zr$_2$O$_7$ is better than Li$_2$ZrO$_3$ because the former reaction releases more heat of reaction and has a lower Gibbs free energy and a higher CO$_2$ capture capacity. However, during the second half cycle to regenerate the sorbent from carbonate and zirconia and to release CO$_2$, instead of forming Li$_6$Zr$_2$O$_7$, the main product is the thermodynamically favorable Li$_2$ZrO$_3$. Therefore, compared with Li$_2$ZrO$_3$, there is no advantage for using Li$_6$Zr$_2$O$_7$ as the CO$_2$ active sorbent. Although this computational study was performed years after the experimental study, it did give some credibility to the initial pursuit of the lithium zirconate sorbent.
Experimental results from the initial testing with lithium zirconate with and without the potassium doping agent led to additional testing with variations of this sorbent. Results are reported for the identification and evaluation of a number of binary and ternary eutectic salt-promoted Li$_2$ZrO$_3$ sorbents for high temperature CO$_2$ capture (Fauth et al., 2005). Specifically, combinations of alkali (Li, K and Na) carbonate and carbonate/halide eutectics along with alkali/alkaline earth (K, Mg) carbonate eutectics were investigated. This information could define a research strategy to achieve higher CO$_2$ absorption capacities with eutectic salt-promoted Li$_2$ZrO$_3$ sorbents. Again, CO$_2$ absorption capacity was examined utilizing the Cahn TGA. Scanning electron microscopy and X-ray diffraction analyses were used to characterize modified Li$_2$ZrO$_3$ sorbents and carbonation products. In addition, the effect of temperature, a major process parameter on the direct carbonation of Li$_2$ZrO$_3$, was studied in the TGA with pure CO$_2$ under isothermal conditions. Improvements in both the CO$_2$ sorption rate and CO$_2$ sorption capacity are seen vital for its practical application in the design and development of dry, regenerable sorbent materials for CO$_2$ capture under operating conditions prevailing in IGCC processes.

Approximately 100 mg of Li$_2$ZrO$_3$ was charged into a platinum cylindrical sample pan for testing. High purity Li$_2$ZrO$_3$ procured from Sigma-Aldrich (Lot # 20004PR) was used as the primary substrate. For binary and ternary eutectic-containing Li$_2$ZrO$_3$ samples, 20% by weight of carbonate (or carbonate/halide or carbonate/hydroxide) salt was initially admixed with 100 mg Li$_2$ZrO$_3$ prior to placing the sample into the TGA instrument. The modified Li$_2$ZrO$_3$ samples were prepared by fusion of finely ground alkali salt mixtures having compositions corresponding to the eutectic temperatures. The eutectic mixtures were heated in N$_2$ at temperatures greater than reported eutectic values. Table 19 shows the composition and melting point temperatures of the binary and ternary eutectic mixtures used in the study.

Prior to CO$_2$ sorption testing, samples were pre-conditioned and dried in nitrogen by elevating the reactor temperature (at 10°C/min) to the absorption temperature of interest (500, 600 and 700°C) and held for 30 min. Upon completion of this step in reaching steady state, the surrounding stream of N$_2$ gas was switched to pure CO$_2$ while maintaining a flow rate of 140 cc/min. CO$_2$ sorption testing was conducted at three different temperatures, namely 500, 600 and 700°C. The highest temperature was kept below 723°C, the melting point temperature of pure Li$_2$CO$_3$. The change in sample weight with time was recorded during the absorption–desorption process, upon which the conversion of Li$_2$ZrO$_3$ to Li$_2$CO$_3$ was calculated from the increasing weight. Complete regeneration of the Li$_2$ZrO$_3$ sample was performed by switching the feed gas back to N$_2$ after raising the temperature to 800°C in a 100% CO$_2$ flow. Upon changing to N$_2$, the temperature was cooled at 10°C/min to a final temperature of 750°C. To determine changes in the material during testing, samples were analyzed using X-ray diffraction and scanning electron microscopy.
Table 19: Composition and eutectic temperatures of binary and ternary eutectic mixtures studied in the TGA

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Eutectic Salt Composition (mol%)</th>
<th>Melting Point (°C)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>K2CO3 38%, Li2CO3 62%</td>
<td>488</td>
</tr>
<tr>
<td>B2</td>
<td>K2CO3 57.3%, Li2CO3 42.7%</td>
<td>498</td>
</tr>
<tr>
<td>B3</td>
<td>Na2CO3 48%, Li2CO3 52%</td>
<td>500</td>
</tr>
<tr>
<td>B4</td>
<td>KF 38%, Li2CO3 62%</td>
<td>n/a</td>
</tr>
<tr>
<td>B5</td>
<td>K2CO3 57%, MgCO3 43%</td>
<td>460</td>
</tr>
<tr>
<td>T1</td>
<td>K2CO3 26.8%, Na2CO3 30.6%, Li2CO3 42.5%</td>
<td>393</td>
</tr>
<tr>
<td>T2</td>
<td>K2CO3 16.4%, Li2CO3 26.4%, LiOH 57.1%</td>
<td>372</td>
</tr>
<tr>
<td>T3</td>
<td>KCl 36.8%, NaCl 36.2%, Na2CO3 27.0%</td>
<td>560</td>
</tr>
<tr>
<td>T4</td>
<td>K2CO3 42%, NaF 32%, Na2CO3 26%</td>
<td>562</td>
</tr>
<tr>
<td>T5</td>
<td>NaCl 31%, Na2CO3 54%, NaF 15%</td>
<td>575</td>
</tr>
</tbody>
</table>

¹ Physical properties data compilation relevant to energy storage

To understand the influence of eutectic salt mixtures of alkali carbonate and alkali/alkaline earth carbonates on the CO2 sorption performance of the modified Li2ZrO3 powders, reactivity studies for six eutectic salt-containing Li2ZrO3 samples were carried out at 500°C under a CO2 gas flow of atmospheric pressure. Illustrative CO2 absorption profiles for the modified Li2ZrO3 samples together with the pure Li2ZrO3 sample are shown in Figure 47. It should be noted that no attempt was made in preparation to optimize the dispersion of the eutectic salt mixtures onto the Aldrich Li2ZrO3 powder. The results validate the initial conclusions of others (Nakagawa and Ohashi, 1998b) that addition of binary alkali carbonate constituents to pure Li2ZrO3 significantly improves the sorption kinetics at 500°C. From the information, the Na2CO3/Li2CO3-containing sample absorbed over 10 wt% of CO2 of its sample weight after only 60 min upon switching to pure CO2. Compared to the pure Li2ZrO3 sample, the CO2 uptake rate for this sample was quantitatively determined to be roughly 26 times faster. The K2CO3/Li2CO3-containing Li2ZrO3 samples (B1 and B2) also demonstrated a much faster rate (29 times faster) of CO2 uptake in comparison to the pure Li2ZrO3 powder.
The K₂CO₃/MgCO₃ eutectic has a melting point of 460°C, which is nearly 40°C lower than the binary alkali carbonate eutectics that were tested. For this sample, the CO₂ uptake rate and absorption capacity was again found to be superior relative to the pure Li₂ZrO₃ sample under a 100% CO₂ flow. The sample absorbed nearly 13 wt% CO₂ per its sample weight, corresponding to a fractional conversion of 44.4% of its theoretical maximum. Substitution of a halide constituent, KF, for K₂CO₃ also resulted in a high rate of carbonation of Li₂ZrO₃. The KF/Li₂CO₃-containing sample gave the fastest rate (32.5 times faster) of CO₂ uptake in comparison to the pure, unmodified Li₂ZrO₃ sample. It is anticipated under an IGCC scenario that reaction kinetics for the binary-type Li₂ZrO₃ samples will only improve due to higher CO₂ partial pressures (Fauth et al., 2005).

The percent weight change obtained for the Li₂ZrO₃ powder containing the ternary K₂CO₃/Li₂CO₃/LiOH-containing eutectic under pure CO₂ at 450, 500 and 600°C is illustrated in Figure 48. During initial CO₂ absorption testing, the sample established an increase in weight due to the chemical reaction between Li₂ZrO₃ and CO₂; however, the absorption rate was very much dependent on the reaction temperature. Furthermore, the destruction of the integrity of the ternary eutectic salt mixture after successive high temperature regeneration cycles and its irreversibility also played a major factor in determining its kinetic rate. For this study, the initial CO₂ absorption cycle at 450°C attained a relatively slow rate of CO₂ sorption after 60 min of contact with the reactant gas. The ternary K₂CO₃/Li₂CO₃/LiOH-containing sample entrapped only 3.6 wt% of CO₂ of its sample weight. This result corresponds to a sorbent conversion of only 12.5% of its theoretical maximum. Limited release of CO₂ ensued after the temperature was raised to 800°C in CO₂. Complete regeneration and release of CO₂ from the ternary alkali carbonate/hydroxide-containing sample was successfully conducted by switching the feed gas back to N₂ at 750°C. This regeneration temperature reflects a temperature greater than 723°C, the melting point of pure lithium carbonate. During the second CO₂ absorption cycle at 500°C, the sample significantly improved its absorption performance, achieving roughly 11.2 wt% CO₂
of its sample weight corresponding to a 38.9% conversion. The sample was regenerated identical to that in the first cycle in pure N\(_2\), thus completing a second regeneration cycle. By the end of the third CO\(_2\) absorption cycle at 600\(^\circ\)C, the profile reached a strikingly slower CO\(_2\) uptake rate (and lower CO\(_2\) sorption capacity) in comparison to the second CO\(_2\) absorption profile obtained at 500\(^\circ\)C. The absolute weight percent change was significantly reduced from ~11 wt% to ~7 wt% CO\(_2\) absorbed. In this case, thermal decomposition of the LiOH component within the eutectic salt mixture to Li\(_2\)O (LiOH thermally decomposes to Li\(_2\)O above 477\(^\circ\)C) destroyed the integrity of the eutectic salt, which resulted in a probable solid film coating of some combination of K\(_2\)CO\(_3\) and Li\(_2\)CO\(_3\) on the outer surface of the Li\(_2\)ZrO\(_3\) particles. This hypothesized product layer prevented further exposure of the unreacted Li\(_2\)ZrO\(_3\) located in the particle core to the surrounding CO\(_2\) for further carbonation. The mixed alkali carbonate/hydroxide combination, having a lower melting point (for example, 372\(^\circ\)C), was found to be unstable after a series of consecutive sorption-regeneration cycles at elevated temperature. Based on these results, it seemed reasonable to conclude any additional testing using the ternary alkali carbonate/hydroxide mixture (Fauth et al., 2005).

Figure 48: CO\(_2\) Sorption profiles of ternary lithium zirconate sorbent. Effect of temperature on CO\(_2\) absorption rate and CO\(_2\) capacity.

To summarize the eutectic work, the CO\(_2\) uptake rate on pure CO\(_2\) sorption performances of both binary and ternary eutectic salt-modified Li\(_2\)ZrO\(_3\) sorbents at 500, 600 and 700\(^\circ\)C showed very favorable reaction kinetics for CO\(_2\) capture in comparison to pure lithium zirconate. Binary K\(_2\)CO\(_3\)/MgCO\(_3\)- and KF/Li\(_2\)CO\(_3\)-containing Li\(_2\)ZrO\(_3\) powders produced the fastest CO\(_2\) uptake rate at 500\(^\circ\)C with respect to the unmodified Li\(_2\)ZrO\(_3\) sample. The addition of NaF in combination with K\(_2\)CO\(_3\) and Na\(_2\)CO\(_3\) produced a modified Li\(_2\)ZrO\(_3\) powder, which provided the highest CO\(_2\) sorption capacity and fastest CO\(_2\) uptake rate at both 600 and 700\(^\circ\)C. Eutectic mixtures containing the hydroxide constituent were found unstable due to the destruction of the integrity of the ternary eutectic salt mixture, and its irreversibility played a major factor in reducing its kinetic rate. Although the eutectic work showed a vast improvement in only the
Li$_2$ZrO$_3$ sorbent, work was concluded with this sorbent. One issue was that the temperature of absorption with these materials was still extremely high and impractical for power generation facilities. It appeared that eutectic mixtures could not lower the temperature of absorption and regeneration significantly. Additionally, preliminary work with lithium silicate yielded significant improvements in reactivity and conversion as compared to lithium zirconate sorbent.

### 3.4.2 Lithium Silicate

Lithium silicates had been investigated as a high-temperature CO$_2$ sorbent by Japanese researchers at Toshiba (Kato and Nakagawa, 2001; Kato et al., 2002). Several reactions are possible between Li$_4$SiO$_4$ and CO$_2$. Based on Toshiba’s experience, the reaction mechanism for CO$_2$ absorption is thought to proceed to an intermediate product, lithium metasilicate (Li$_2$SiO$_3$) via:

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3
\]  

Reaction 1 has a maximum weight gain of 36.8 wt% at complete reaction conversion. Lithium metasilicate can additionally react with CO$_2$ as described by Reaction 2:

\[
\text{Li}_2\text{SiO}_3 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{SiO}_2
\]  

Reaction 2 has a maximum weight gain of 48.9 wt% at complete reaction conversion. The sum of Reactions 1 and 2 is given by Reaction 3, having an overall weight gain of 73.5 wt% at completion.

\[
\text{Li}_4\text{SiO}_4 + 2\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{SiO}_2
\]

Based on thermodynamic calculations by Toshiba, the equilibrium temperature, at which reaction of CO$_2$ absorption apparently stops, was calculated to be 710°C for Reaction 1, 250°C for Reaction 2, and 445°C for Reaction 3. In the Japanese work, absorption of CO$_2$ was studied in the 500–700°C temperature range, and therefore Reaction 2 did not proceed in the forward direction. Regeneration was studied at temperatures up to 850°C, and complete regeneration was achieved during multi-cycle tests (White et al., 2003; Hoffman, 2002a).

Through a cooperative agreement with Toshiba, sorbent was obtained and tested by NETL; it was intended for use as a dry, regenerable solid for the capture of carbon dioxide present in a gas stream (Hoffman, 2002a). Lithium orthosilicate (Li$_4$SiO$_4$) fabricated into pellets was examined. The cylindrical extrudates were approximately 1/8-inch diameter of varying length and were white in appearance. Shorter length extrudates (1/8- to 1/4-inch) were chosen from the sample stock for study. The approach undertaken in the study was to investigate sorbents using a thermogravimetric analyzer (TGA). For the TGA system, change in sample weight was recorded as the sorbent was exposed to gases representative of absorption and regeneration. The extent of chemical reaction was linked to sample weight change, from which kinetic rate parameters could
be estimated. The Cahn TG-131 TGA is capable of evaluating samples up to 1100°C at atmospheric pressure. Gas composition was created by blending high purity gases using mass flow controllers (Brooks model 5850E controller and Brooks model 5878 instrument readout). Carbon dioxide of stock gas grade (99.99%) was supplied by a gas cylinder and a pressure regulator, and a house supply of dry nitrogen was utilized. A more detailed description of the TGA can be found in Section 3.2: Potassium-Based Sorbents.

Approximately 200 mg of sample was placed in a quartz cylindrical sample pan. Slotted apertures in the bottom and side wall of the sample pan help mitigate gas diffusional resistance. Sample temperature was measured and controlled with a type K thermocouple placed immediately below the suspended sample pan. Total gas flow rate was held constant at 140 cc/min. After charging the sorbent to the TGA, the sample was preconditioned and dried in nitrogen by elevating the reactor temperature to 150°C for a short period, followed by additional heating to achieve the absorption temperature of interest (typically 500–750°C). The sample was then allowed to come to steady state, both thermally and gravimetrically. Once the sample achieved steady state under dry nitrogen conditions, carbon dioxide was switched in-line and nitrogen flow was ceased, while the total flow rate remained the same (140 cc/min). The CO₂ absorption stage was allowed to proceed until a steady-state weight gain was achieved; it was otherwise halted if excessive duration of time was required to reach steady state.

The sequence of gas switching was then reversed. CO₂ flow was turned off and N₂ flow was reestablished. The motivation for observing the sample during CO₂ isolation was to verify what fraction of the weight gain during absorption was indeed permanent weight gain by chemical reaction to form carbonate. For sorbents supported on a substrate (unlike the Toshiba materials), some of the weight gain can be due to physical sorption of CO₂, most likely onto the substrate. Once the sample was exposed to a gas lacking carbon dioxide (i.e., dry N₂), sorbed CO₂ could then desorb from the substrate, resulting in sample weight loss. This difference in the initial and final sample weight under dry N₂ conditions represented chemical CO₂ uptake by the sorbent, from which an overall sorbent conversion can be calculated based on the metal loading and theoretical weight gain due to carbonate formation.

Figure 49 shows the results of a TGA experiment with Li₄SiO₄ sorbent. The fractional weight gain had been plotted versus time. The sorbent was charged to the system and temperature was raised to 500°C under N₂ flow. Once the sample was dried and maintained a steady-state weight, gas flow was switched from N₂ to CO₂ to initiate an absorption stage. The absorption kinetics were surprisingly slow at 500°C in comparison to Toshiba’s published results. After achieving approximately 50% conversion, the absorption was halted by switching the gas flow from CO₂ to N₂, thus initiating a period of regeneration at 500°C. The regeneration was very slow at this temperature, and the temperature was raised to 600°C and held constant for one hour, and then raised to 700°C. Thermal regeneration was greatly enhanced at elevated temperature as the sample weight decreased to its initial weight, and thus an absorption/desorption cycle was next studied at 700°C (Hoffman, 2002a).
Upon gas switching from N\textsubscript{2} to CO\textsubscript{2} flow at 700\textdegree C, the sample rapidly achieved over 90\% conversion within 2 minutes, and approached almost 95\% conversion within 30 minutes. The absorption kinetics are exceedingly fast at these conditions. Gas was switched back to N\textsubscript{2} flow to begin regeneration, and the sample was regenerated to 20\% absorption conversion within 30 minutes. Regeneration kinetics do not appear to be as fast as the absorption kinetics under the same temperature (700\textdegree C), but regeneration does appear favorably achieved within a reasonable time period (1–2 hr).

A second absorption cycle was begun at 700\textdegree C, and again achieved over 90\% conversion within two minutes. For the next phase of testing, regeneration was studied under CO\textsubscript{2} flow and not N\textsubscript{2} flow. The temperature was raised in 25\textdegree C increments from 700\textdegree C to 850\textdegree C, with a holding period of 2 hours at each level. The regeneration was exceedingly slow and incomplete under a CO\textsubscript{2} flow. At the end of the 2-hour increment for 850\textdegree C, the sample had regenerated only halfway, as indicated by a remainder of approximately 45\% absorbed CO\textsubscript{2}. CO\textsubscript{2} flow was ceased and the sample was further regenerated under N\textsubscript{2} flow while lowering the temperature to 700\textdegree C.
Two subsequent cycles of absorption and regeneration were conducted at 700°C, but the absorption kinetics had greatly changed. Only 20–25% conversion was achieved during the absorption stage. Suspecting incomplete regeneration, a 30-min period of regeneration under N₂ flow was conducted at much higher temperature (950°C) between the cycles, but little enhancement was observed. Fearing degradation of the sample, the reactor was cooled to ambient conditions and the experiment was terminated.

Upon reactor disassembly and sample inspection, a white film was discovered on the walls of the quartz sample bucket, and the remaining sample pellets had appeared to fuse together. It was initially speculated that the sample may have melted due to exposure at high temperature. After consultation with Toshiba during their site visit to NETL in September 2002, it was later surmised that the lithium carbonate had reacted with the silicon dioxide in the quartz container via reaction (2). Toshiba had avoided quartz contact with sorbent in their experimentation and used platinum containers in their TGA investigations with lithium silicate sorbents.

Unbeknownst of the materials compatibility problem with quartz during the TGA tests, a second experiment using a different quartz sample container was initiated. The quartz sample container is commercially available from Cahn Instruments (part number 12516-01), the TGA manufacturer. It is larger, cylindrically shaped with a round bottom bowl. It does not have slotted apertures in the sidewall and bottom, unlike the quartz container used for the first experiment. Therefore, gas diffusional resistance may be more prevalent, but the container was the only substitute available during testing.

Figure 50 is a plot of a second experiment using fresh Li₄SiO₄ loaded into the new sample container. Plot parameters are similar to the previous figure. A multi-cycle test of absorption and regeneration was conducted at 700°C, a nominal temperature identified during the first sample test.
The first absorption cycle attained high conversion (over 90%) within several (2) minutes, again consistent with the results of Figures 50. Regeneration was conducted for over 3 hours and returned the sample to a state characterized by approximately 10% absorption conversion. The second absorption cycle achieved very similar performance (again over 90% conversion), but was perhaps slightly lower by about 1% in conversion. During the second regeneration cycle, a computer malfunction occurred and briefly interrupted the data acquisition. The system was quickly reinitialized and the experiment brought back online. Since a transient had occurred in temperature, the temperature was raised to 850°C and held for approximately an hour to accelerate the regeneration, and then lowered to 700°C. The sample was regenerated to within less than 5% absorption conversion, indicating nearly complete regeneration.

The third absorption cycle achieved markedly less sorbent conversion (75–80%) than the first two cycles. A plausible cause for decreased conversion is the higher regeneration temperature (850°C) used after the second absorption cycle. The third regeneration cycle was initiated while both simultaneously ramping temperature from 700°C to 850°C and gas switching, but no significant differences were noted for the third regeneration cycle. The experiment was then halted near the completion of regeneration.

Figure 50: TGA experiment with Toshiba lithium silicate sorbent at 700°C absorption.
Inspection of the quartz sample bowl indicated white spots on the inner wall where the pellets were in contact with the quartz wall. This was consistent with the first test, although the degree of fouling was not nearly as extensive as found in the first test. The first test was characterized by nearly complete film coverage over the entire bucket versus localized spotting of the bowl in the second test. Attempts had been made to remove the white discoloration using progressively stronger acids (first HCl, and then HF), but the quartz containers appeared permanently altered. The HF is sufficiently strong and will attack the quartz as well as the contaminant, and so the use of the two quartz containers in the TGA were discontinued.

Preliminary results indicated that Li₄SiO₄ had very favorable kinetics for CO₂ capture. Based on the observed weight gain and calculated reaction conversion using reaction (1), it does appear reasonable to assume that reaction (1) governs the reaction mechanism, and nearly complete conversion for reaction (1) was observed. Additional capture of CO₂ is described by reaction (2), which would increase the capture efficiency of the sorbent, but further study was warranted to examine its feasibility.

### 3.4.3 Systems Analysis

At the time, use of lithium silicate in a capture process appeared to be a more mature sorbent technology, and the use of lithium silicate over the lithium zirconate was advantageous. As mentioned earlier in this section, NETL entered into a cooperative agreement with Toshiba to use their sorbent in an eventual test on NETL’s Modular Carbon Dioxide Capture Facility. Although the facility was to have been built for both a pre-combustion and post-combustion application, the post-combustion application was the first to be available for immediate operation. For the lithium silicate sorbent, operation in a post-combustion mode would have been a major investment with respect to materials of vessel construction and operating ranges required for this sorbent. However, the newly formed Systems Analysis Group at NETL was commissioned to perform a technical and cost analysis for the Toshiba sorbent system. The detailed techno-economic study would be a benchmark in sorbent technology, provide the investigators with some research guidance, and ultimately decide the fate of the lithium silicate technology.

A preliminary engineering analysis, consisting of mass and energy balances for a conceptual process using Toshiba’s Li₄SiO₄ sorbent, was carried out (Ciferno et al., 2004). The main focus of the study was CO₂ capture from a shifted syngas from an E-Gas (Destec) integrated gasification combined cycle (IGCC) power system, but a comparison study for a conventional pulverized coal (PC) power plant was also carried out. Data to support the CO₂ capture process studies were obtained from several reports generated by the in-house research effort and by Toshiba. The following cases were evaluated.

**Integrated Gasification Combined Cycle Cases:**

- **Case 1:** Current, at that time, IGCC technology with water-gas shift and CO₂ capture via a physical solvent (Selexol)
- **Case 2:** Current IGCC technology with water-gas shift and CO₂ capture via Li₄SiO₄ using a moving bed reactor with natural gas combustion providing the regeneration heat
- **Case 3:** Current IGCC technology with water-gas shift and CO₂ capture via Li₄SiO₄ using a fluidized bed reactor with natural gas combustion providing the regeneration heat
• Case 4: Current IGCC technology with water-gas shift and CO₂ capture via Li₄SiO₄ using a fluidized bed reactor with syngas combustion providing the regeneration heat

• Case 5: Current IGCC technology with water-gas shift and CO₂ capture via an advanced Li₄SiO₄ sorbent using a fluidized bed reactor with syngas combustion providing the regeneration heat

**Pulverized Coal Combustion Cases:**

• Case 6: Current pulverized coal combustion technology with CO₂ capture via an amine wet scrubbing process

• Case 7: Current pulverized coal combustion technology with CO₂ capture via Li₄SiO₄ using a fluidized bed reactor with steam providing the regeneration heat

The cases all assume 90 percent CO₂ removal, since this is about the realistic upper limit for the CO₂ removal processes considered (Selexol, monoethanolamine, and Li₄SiO₄), and are sized to 400 MW net output.

The major parasitic energy losses and power plant performance results for the IGCC cases are shown in Table 20. Table 21 is an economic summary. In the analysis of Case 7, it quickly became apparent that using Li₄SiO₄ sorbent to capture CO₂ from flue gas was not a viable option; and, therefore, the results for the PC cases are not included here.
Table 20: Parasitic power loss and performance summary

<table>
<thead>
<tr>
<th>Component</th>
<th>Base Plant(^a)</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Case 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) Removal Process</td>
<td>None</td>
<td>Selexol</td>
<td>Li(_4)SiO(_4)</td>
<td>Li(_4)SiO(_4)</td>
<td>Li(_4)SiO(_4)</td>
<td>Li(_4)SiO(_4) (^g)</td>
</tr>
<tr>
<td>Total Gross Power, MW</td>
<td>443</td>
<td>487</td>
<td>427</td>
<td>430</td>
<td>445</td>
<td>444</td>
</tr>
<tr>
<td><strong>Auxiliary Power, MW</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base Plant Load</td>
<td>13.1</td>
<td>15.2</td>
<td>13.3</td>
<td>13.5</td>
<td>19.0</td>
<td>17.4</td>
</tr>
<tr>
<td>ASU</td>
<td>26.5</td>
<td>31.1</td>
<td>27.3</td>
<td>46.1</td>
<td>51.9</td>
<td>40.3</td>
</tr>
<tr>
<td>CO(_2) Capture</td>
<td>-</td>
<td>7.7</td>
<td>-26.2</td>
<td>-42.8</td>
<td>-43.0</td>
<td>-28.8</td>
</tr>
<tr>
<td>CO(_2) Compression &amp; Drying</td>
<td>-</td>
<td>25.5</td>
<td>3.3</td>
<td>4.0</td>
<td>4.8</td>
<td>4.1</td>
</tr>
<tr>
<td>H(_2)S Cleanup</td>
<td>3.5</td>
<td>1.1</td>
<td>3.6</td>
<td>3.6</td>
<td>5.0</td>
<td>4.4</td>
</tr>
<tr>
<td>CO(_2) Transportation(^b)</td>
<td>-</td>
<td>3.8</td>
<td>3.5</td>
<td>4.2</td>
<td>5.0</td>
<td>4.3</td>
</tr>
<tr>
<td>CO(_2) Storage</td>
<td>-</td>
<td>2.0</td>
<td>1.8</td>
<td>2.2</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Other</td>
<td>-</td>
<td>-</td>
<td>Natural Gas(^c)</td>
<td>Natural Gas(^c)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total Auxiliary Load, MW</td>
<td>43</td>
<td>87</td>
<td>27</td>
<td>30</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>Net Power, MW</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td><strong>Power Plant Performance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal Flow Rate, ton/day</td>
<td>3,200</td>
<td>3,800</td>
<td>3,300</td>
<td>3,400</td>
<td>4,700</td>
<td>4,100</td>
</tr>
<tr>
<td>CO(_2) Captured, ton/day</td>
<td>-</td>
<td>7,428</td>
<td>6,750</td>
<td>8,142(^f)</td>
<td>9,692</td>
<td>8,243</td>
</tr>
<tr>
<td>CO(_2) Emissions, kg/kWh</td>
<td>0.663</td>
<td>0.078</td>
<td>0.071</td>
<td>0.090</td>
<td>0.102</td>
<td>0.087</td>
</tr>
<tr>
<td>Gross Turbine Heat Rate, Btu/kWh</td>
<td>7,088</td>
<td>7,591</td>
<td>7,591</td>
<td>7,591</td>
<td>10,244</td>
<td>8,920</td>
</tr>
<tr>
<td>Net Power Plant Heat Rate, Btu/kWh</td>
<td>7,850</td>
<td>9,233</td>
<td>11,400(^d)</td>
<td>10,500</td>
<td>11,408</td>
<td>9,896</td>
</tr>
<tr>
<td>Efficiency, % (HHV)</td>
<td>43%</td>
<td>37%</td>
<td>30%</td>
<td>32%</td>
<td>30%</td>
<td>34%</td>
</tr>
</tbody>
</table>

\(^a\) The base plant is a 400 MW net IGCC unit without WGS and CO\(_2\) capture
\(^b\) 50 mile pipeline
\(^c\) 60,600 lb/hr of natural gas, equivalent to a 200 MW conventional NGCC plant
\(^d\) Includes energy in natural gas used for regeneration
\(^e\) Includes a 130 MW penalty for NG regeneration
\(^f\) Includes recovery of CO\(_2\) from NG combustion
\(^g\) Advanced sorbent
Table 21: Summary of economic results

<table>
<thead>
<tr>
<th></th>
<th>Base Plant</th>
<th>Case 1</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Case 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gross Power (MW)</strong></td>
<td>443</td>
<td>487</td>
<td>430</td>
<td>445</td>
<td>444</td>
</tr>
<tr>
<td><strong>Power Plant (Including CO₂ Capture) Costs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Power Plant Capital, $/kW</td>
<td>1,430</td>
<td>1,707</td>
<td>2,081</td>
<td>2,500</td>
<td>2,310</td>
</tr>
<tr>
<td>COE (Capital), c/kWh</td>
<td>3.73</td>
<td>4.43</td>
<td>5.41</td>
<td>6.49</td>
<td>6.00</td>
</tr>
<tr>
<td>COE (Variable Costs), c/kWh</td>
<td>1.78</td>
<td>2.07</td>
<td>3.45</td>
<td>3.37</td>
<td>3.11</td>
</tr>
<tr>
<td>Total COE, c/kWh</td>
<td>5.51</td>
<td>6.50</td>
<td>8.85</td>
<td>9.86</td>
<td>9.12</td>
</tr>
<tr>
<td>$/tonne CO₂ Avoided</td>
<td>-</td>
<td>17</td>
<td>74</td>
<td>77</td>
<td>63</td>
</tr>
<tr>
<td><strong>Power Plant (Including CO₂ Capture, Transport, and Storage) Costs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Capital, $/kW</td>
<td>1,430</td>
<td>1,839</td>
<td>2,221</td>
<td>2,660</td>
<td>2,450</td>
</tr>
<tr>
<td>Total $/tonne CO₂ avoided</td>
<td>23</td>
<td>81</td>
<td>86</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Total COE, c/kWh</td>
<td>5.51</td>
<td>6.87</td>
<td>9.25</td>
<td>10.31</td>
<td>9.51</td>
</tr>
<tr>
<td>Increase in COE over Base, %</td>
<td>-</td>
<td>25</td>
<td>68</td>
<td>87</td>
<td>73</td>
</tr>
</tbody>
</table>

The basic conclusion from these results is that the Toshiba Li₄SiO₄ regenerable sorbent, developed to capture CO₂ from either an IGCC or a PC power plant, is not competitive with Selexol and amine wet scrubbing technologies, respectively (Ciferno et al., 2004).

- The quantity of Li₄SiO₄ sorbent that must be circulated for 90% CO₂ capture, even if parallel systems are used, presents a significant technical challenge, especially since these solids have to be transported at high temperature.

- Although little integration and practically no optimization of heat recovery were attempted in this analysis, an effort was made to recover as much energy as possible. However, improvements in parasitic power loads and heat recovery could occur with further study. Nevertheless, any system that removes heat from a high temperature environment (932°F) and transfers that heat to an even higher temperature environment (1,562°F) has large inherent inefficiencies.

- Supplying regeneration (CO₂ desorption) energy by means of a secondary fossil fuel, such as natural gas, is really not a viable option, since for consistency the system should be entirely coal based. Although some power was recovered through steam production by heat recovery from the flue gas from the natural gas combusted for regeneration, more power would be produced if the natural gas were fed directly to a natural gas combined cycle power plant.

- Case 4, which uses syngas for sorbent regeneration, resulted in the most promising design from an engineering point of view to compete with the Selexol process. However, Case 4 has a 50 percent higher COE and three times higher costs per tonne of CO₂ avoided compared to Case 1.
• Even using very optimistic assumptions concerning sorbent properties (lower temperature absorption and regeneration), Case 5 still results in a 20 percent increase in COE and a 100 percent increase in the cost per tonne of CO₂ avoided compared to Case 1.

• Based on initial findings with regard to the large quantity of high value steam required for sorbent regeneration when recovering CO₂ from the flue gas from a pulverized coal power plant, further engineering and economic analysis is not warranted. It is simply not economically feasible (and does not make sense) to double the size of the boiler and fuel input to the PC plant just to generate the steam required for the CO₂ capture process (Ciferno et al., 2004).

Although this study indicates that it may be technically feasible to develop a CO₂ capture process based on using Li₄SiO₄ as a solid sorbent, it appears to be very unlikely that this system will prove to be economically feasible. This analysis shows that the relatively high heat of reaction, combined with high absorption and regeneration temperatures, associated with CO₂ capture using Li₄SiO₄ result in an increase in parasitic load and the cost of electricity compared to existing CO₂ removal technologies, such as Selexol or amine-based systems. The large amount of solid sorbent that must be circulated and the high temperatures involved present formidable barriers to successful implementation. Developing an absorption technology to recover CO₂ from flue gas will always be difficult because of the low CO₂ partial pressure involved. There is more hope for IGCC systems, where the CO₂ partial pressure is high, but to compete with Selexol, the regeneration system should require only low level heat. (In addition, a later publication indicated that lithium silicate may be deleteriously impacted by the presence of steam, which is unavoidable in either pre-combustion or post-combustion applications (Ochoa-Fernandez et al., 2009). It was concluded that this particular sorbent is not a potential candidate for commercial use and, therefore, further investigation into engineering scale-up issues beyond this preliminary analysis was not warranted.

3.5 SODIUM-CONTAINING SORBENTS

The MATRIC Study, which was conducted about six years after the sorbent research effort began at NETL, contributed significantly towards the development of targets for post-combustion sorbents thereafter (Fisher and Keller, 2006). One criteria for post-combustion sorbents was to improve the regenerative heat duty by decreasing it 30 to 50 percent as compared to conventional monoethanolamine (MEA) scrubbing. As explained in the target establishment Section 4.3, the heat duty consists of various terms with the two having the most impact being the heat of reaction for the regeneration and the sensible heat required to heat the sorbent to the regeneration temperature. For post-combustion sodium-based sorbents, Research Triangle Institute had a process that operated after the desulfurization scrubbing system in a coal-fired utility (Liang et al., 2004); the Korean Institute of Energy Research had a similar process (Seo et al., 2007). Sodium carbonate was used as the CO₂ capture sorbent, reacting with CO₂ and moisture to form the bicarbonate. However, the issue with sodium carbonate is the high heat of reaction required to regenerate the sorbent (135-KJ/mole CO₂ or 1,320-Btu/lb CO₂). In MEA scrubbing the heat duty had been generally accepted as 1,500 Btu/lb CO₂, and improvements to the MEA process will drive this number down. With the high heat of reaction of the sodium sorbent, it is extremely doubtful that heat integration in a post-combustion application would be significant enough to decrease the overall heat duty so that it would be 30–50% better than that of the MEA process. Therefore, with respect to sodium-containing compounds and, in general
alkali/alkaline earth sorbents, their use in post-combustion applications is extremely doubtful. A better use of these sorbents would be in pre-combustion schemes.

Capture sorbents that operate at 315°C would be better suited for use in IGCC (pre-combustion) applications. Here, the water-gas shift reactor converts CO and H₂O in the fuel gas to CO₂ and H₂ at 200–350°C. A pure hot H₂ stream can be obtained if CO₂ is removed at 315°C. With removal of other contaminants at this temperature, the hydrogen rich stream could be fed directly into the gas turbine for high overall thermal efficiency for the power cycle. Several sodium-based sorbents were initially prepared at NETL and were tested in an atmospheric microreactor (see ensuing discussion for detailed description) at 315°C with simulated Texaco gasification gas and with simulated shift reactor gas. Regeneration was conducted at 700°C. A ten-cycle test conducted with the sodium-based sorbent indicated that the sorbent had a very high CO₂ capture capacity (4 to 6 moles/kg). These novel sorbents offered promise for IGCC applications, since their high capacities could contribute to a low regeneration cost and small vessel size. However, the regeneration at 700°C is energy intensive, and one of the research objectives was to modify the sorbent to lower the regeneration temperature (Siriwardane et al., 2004).

Further investigative studies with sodium-containing sorbents have been conducted. A novel sodium-based sorbent that can capture CO₂ from ambient to 600°C was developed at NETL (Siriwardane, 2008). The sorbent contains a mixture of sodium hydroxide and calcium oxide. These sorbents are regenerable at 700°C. The capture process with these novel warm gas CO₂-removal sorbents involves a chemical reaction. The novel sorbent had a very high CO₂-sorption capacity at 200–400°C, which is considerably higher than that of the commercial Selexol process. The reactions involved in the sorption process are described in Equation 1.

\[
2\text{NaOH (s) + CO}_2 (g) \rightarrow \text{Na}_2\text{CO}_3 (s) + \text{H}_2\text{O} \tag{1}
\]

The carbonate product can be thermally decomposed to release carbon dioxide and regenerate the sodium hydroxide sorbent according to the reverse of Reaction 1 as described in Equation 2.

\[
\text{Na}_2\text{CO}_3 (s) + \text{H}_2\text{O} \rightarrow 2\text{NaOH (s) + CO}_2 \tag{2}
\]

Reaction 2 may occur in two reaction steps, as shown in Equations 3 and 4.

\[
\text{Na}_2\text{CO}_3 (s) \rightarrow \text{Na}_2\text{O (s) + CO}_2 \tag{3}
\]

\[
\text{Na}_2\text{O (s) + H}_2\text{O} \rightarrow 2\text{NaOH} \tag{4}
\]

The decomposition temperature of pure sodium carbonate is 800°C. However, when sodium hydroxide is mixed with calcium oxide, the carbon dioxide can be recovered at 700°C.
Multicycle flow reactor studies, X-ray diffraction studies, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry were conducted to understand the CO₂-capture capacity and reaction mechanisms of NaOH/CaO (Siriwardane et al., 2007). Additionally, in a later study, temperature program desorption (TPD) and X-ray photoelectron spectroscopy (XPS) were used to elucidate the impact of additives on the regeneration of the sorbent (Siriwardane et al., 2011).

### 3.5.1 Absorption Study

During the absorption study, sorbents were prepared by solid-state mixing of sodium hydroxide with calcium oxide. The sorbents with various weight proportions of NaOH/CaO were prepared. For a solid mixture with a total of 60 g of solid, 5 ml of water was used to form granules. The wet granules were heated in an oven at 100°C for 1 h and calcined in the oven at 700°C for 1 h. Some sorbent samples were prepared using various binders. These binders included bentonite, sodium orthosilicate, and calcium aluminate. A total of 5 g of the binder was used with 60 g of total solid mixture (Siriwardane et al., 2007).

Competitive gas adsorption and desorption studies were conducted in a laboratory-scale fixed-bed reactor (Micromeritics Autochem 2910 atmospheric flow reactor) at 14.7 psi using gas mixtures with compositions of 12% CO₂, 35.9% CO, 27.1% H₂, and 25% He, saturated with water to simulate a coal gasification fuel gas stream. The outlet gas stream was analyzed using a Pfeiffer Vacuum Thermostar mass spectrometer. The samples (1.7 x 10⁻³ liter) were pretreated at 315°C for 1 h in the flow reactor, under helium saturated with water vapor at 25°C, prior to exposure to the gas mixtures. Regeneration was conducted with helium at a flow rate of 50 cm³/min. After regeneration, the solid granules were cooled in air saturated with water vapor. Heats of sorption measurements were conducted with a Setaram DSC 111 differential scanning calorimeter. The NaOH/CaO samples were heated to 315°C in helium prior to the introduction of CO₂ at a flow rate of 15 cm³/min during the measurements. Then, CO₂ was introduced, and the heat of reaction was calculated using the software provided by Setaram instruments.

The TGA analysis was conducted using a TAQ-50 analyzer from TA instruments, Inc. NaOH/CaO samples were heated to the desired reaction temperature (315 and 500°C) under N₂ immediately prior to the adsorption of CO₂. There was a loss of weight during the initial heating period. After the weight was stabilized, a gas mixture containing 100% CO₂ was introduced at 315°C and weight gain was recorded as a function of time.

A volumetric adsorption apparatus was used to obtain adsorption isotherms at 315°C of pure CO₂ (99.5%, Jackson Welding Supply Co.), on the five sorbents, up to an equilibrium pressure of about 300 psi. Approximately 10 ml of the sorbent material was placed in the sample chamber and evacuated to about 5 x 10⁻⁵ Torr prior to sorption measurements. The amount of CO₂ adsorbed was calculated using the pressure measurements before and after exposure of the sample chamber to CO₂.

X-ray diffraction measurements were conducted with a Phillips PW 1800 X-ray diffractometer. FTIR studies were conducted with a Thermo Nicolet Nexus 670 equipped with a diffuse reflectance cell. The NaOH/CaO (1:4 wt ratio) sorbent was placed in the diffuse reflectance cell and heated to 800°C with nitrogen, followed by cooling under nitrogen saturated with moisture at room temperature. Then, the sample was heated to 315°C and exposed to CO₂. The FTIR
spectra were taken at 15 and 30 min. These spectra were normalized to the background spectrum obtained with nitrogen immediately prior to the CO$_2$ exposure.

Results from the atmospheric flow reactor are shown in Figure 51. The initial concentration of CO$_2$ was 12% vol, and when sorbent (NaOH/CaO weight ratio of 1:2) was introduced to the gas stream at 315°C, the CO$_2$ concentration decreased to a ppm level and remained at that level until breakthrough (1% CO$_2$). This indicated that the sorbent can achieve 99% CO$_2$ removal.

![Figure 51: Sorption of CO$_2$ from a simulated IGCC gas stream (12% CO$_2$, 35.9% CO, 27.1% H$_2$, and 25% He, saturated with H$_2$O, at 5 cm$^3$/min) on a NaOH/CaO sorbent at 315°C, 1 atm, and cycle 1.](image)

The amount of CO$_2$ captured by the sorbent is about 2.5 mol/kg. Because the sorbent had a very high CO$_2$ capture capacity, multicycle tests were conducted after regenerating at 700°C to evaluate whether the sorbent could retain this high CO$_2$ capture capacity after successive regenerations. The results of the seven-cycle test are shown in Figure 52. There was a decrease in the capacity during cycles 1 and 3. However, the capacity continued to increase after the third cycle. During regeneration at 700°C, sodium carbonate is converted to sodium oxide. The sodium oxide is converted to sodium hydroxide because of the reaction with water vapor during the cooling process. The extent of hydroxylation could not be controlled during the multicycle tests. The CO$_2$ sorption capacity during the subsequent cycles depends upon the degree of rehydroxylation. Sodium hydroxide is the major contributor to the CO$_2$ capture process. The amount of CO$_2$ absorbed at the seventh CO$_2$ sorption cycle is significantly higher than that observed during the first cycle. The sorbent contains a 1:2 wt ratio of NaOH/CaO. For 1 kg of the sorbent, it should contain about 8.25 mol of NaOH. If NaOH reacts with CO$_2$ according to
reaction 1, then the theoretical capacity of the sorbent should be 4.12 mol/kg of material. During the first cycle, the observed CO₂-sorption capacity is about 2.5 mol/kg. This is about half of the theoretical capacity of the sorbent. The capacity of the sorbent increased as the number of cycles increased. At the seventh cycle, the sorbent had the CO₂ sorption capacity close to the theoretical capacity based on the reaction with NaOH. For comparison, pure CaO was also tested at 315°C and 1 atm. The breakthrough time for the reaction was less than 5 minutes which revealed that the reactivity was very low with pure CaO at 315°C. This indicates that in a mixture, the NaOH is the main contributor to the reaction.

The decomposition temperature of sodium carbonate is 800°C. However, in the presence of CaO, the sorbent can be regenerated at 700°C. All regenerations during the seven-cycle test were performed at 700°C, and complete regeneration can be achieved at 700°C. If calcium carbonate is formed during the reaction, it has to be decomposed at 900°C. The regeneration at 700°C indicates that the formation of CaCO₃ may not be taking place. Additionally, the rehydroxylation process is very important after regeneration and is more favorable at lower temperatures. When the water vapor was not introduced to the sorbent after regenerating at 700°C, the reactivity during the subsequent cycle was very low. Thus, rehydroxylation is critical for retaining the reactivity during cyclic tests.
TGA tests with pure CO$_2$ were conducted to measure the rate of sorption. Steam was not present because the weight gain values would be complicated by the presence of steam, and true CO$_2$ uptake cannot be obtained. TGA data for the sorbent containing NaOH/CaO (1:4 wt ratio) during the reaction with pure CO$_2$ at 315°C indicated that the CO$_2$ uptake was very rapid initially, but there was a slow uptake after that. A similar observation was made at 500°C. BET nitrogen surface area of the NaOH/CaO (1:4) sorbent was about 2 m$^2$/g, which is very low. The high CO$_2$ sorption capacities indicate that the reaction is not limited to the surface, but the bulk of the sorbent participates in the reaction. Therefore, both the product layer and pore diffusion should play an important role in determining the global rate of the reaction specifically at higher coverage.

Volumetric gas sorption was conducted with NaOH/CaO (1:4 wt ratio) at 315°C using pure CO$_2$ up to about 300 psi. The isotherms obtained at 315°C are shown in Figure 53. The sorbent capacity increased from about 1 to 2 mol/kg when the sorption pressure increased from 50 to 300 psi. This indicated that the pressure has some effect on the reaction. The sorption isotherm can be better described by the Freundlich isotherm equation

$$Q = kP^{1/n}$$

where $Q$ is the amount of gas adsorbed (in kg of CO$_2$/kg of adsorbent), $P$ is the pressure of CO$_2$ (in kPa), and $k$ and $n$ are Freundlich constants. Freundlich constants for NaOH/CaO were calculated from the data shown in Figure 53. The average of $1/n$ values calculated from the three isotherms was 0.31, and the average $k$ value was 0.008. For NaOH/CaO (1:4), the amount of NaOH available for the reaction is 5 mol/kg. If all of the NaOH reacted with CO$_2$ according to Equation 1, the amount of CO$_2$ reacted would be 2.5 mol/kg. This indicated that, at 300 psi, the amount of CO$_2$ captured approached the theoretical capacity of the sorbent based on only NaOH participating in the reaction.
Analytical results indicated that the NaOH plays a major role in the carbonation reaction. Heats of sorption of CO$_2$ with sodium oxide (Na$_2$O) and sodium hydroxide (NaOH) were computed assuming temperature-independent heat capacities of reactants and products. The calculated heat of reaction of Na$_2$O with CO$_2$ at 315°C is -76.8 kcal per gmol of CO$_2$. The calculated heat of reaction for the reaction of NaOH with CO$_2$ is -30.57 kcal per gmol of CO$_2$. The heat of reaction between the solid sorbent and CO$_2$ was experimentally determined using a DSC 111 differential scanning calorimeter. The measured heat of reaction was -32.2 kcal per gmol of CO$_2$, which is very close to the calculated value (-30.57 kcal per gmol of CO$_2$) for the reaction of NaOH with CO$_2$. This confirms that the reaction of CO$_2$ at 315°C during the first cycle is with NaOH and that NaOH did not convert to Na$_2$O at 315°C. The melting point of NaOH is 318.8°C. At these reaction conditions, NaOH may be in the liquid form imbedded in the CaO matrix and participates in the reaction with CO$_2$ as NaOH. Experimental evidence from the fixed bed flow reactor cycling tests at 315°C revealed that when the sorbent was at the 1:2 ratio of NaOH/CaO, leaching of the quartz reactor occurred, most likely related to liquid NaOH present. X-ray diffraction results were difficult to conclusively interpret due to the non-crystalline nature of the sorbent.

To summarize, the novel CO$_2$-absorption sorbent containing NaOH and CaO showed excellent performance at 315°C and was regenerable at 700°C. The sorbent demonstrated a very high capture capacity in the presence of steam, and the capacity improved during a multicycle test conducted in an atmospheric reactor. The rehydroxylation process after the regeneration is critical to the performance of the sorbent during subsequent cycles. The heat of reaction data indicated that the reaction during the first cycle was primarily due to the reaction with NaOH.
The sorbent can also capture CO$_2$ at a wide range of temperatures from ambient to 500°C. The addition of binders did not affect the performance of the sorbent, and the pellets prepared with sodium orthosilicate had the best strength. The TGA data showed the decrease of rates with increasing fractional coverage of the sorbent. The volumetric gas sorption studies showed that the isotherms were similar to the Freundlich isotherms. The regeneration temperature of 700°C was rather high and this led to further investigations of the sodium-containing sorbent with the hopes of reducing the temperature and understanding the regeneration mechanism (Siriwardane et al., 2007).

3.5.2 Regeneration Study

Removal of CO$_2$ with alkali oxides and salts involves a chemical reaction that results in the formation of alkali carbonates. Regeneration of these materials requires high temperatures because it involves the decomposition of the alkali carbonates formed during absorption. The high regeneration energies of these sorbents in a pre-combustion application would result in significant loss in thermal system efficiency. Therefore, low regenerative energy would aid in adopting CO$_2$ removal sorbents for use in advanced power systems. Incorporation of various additives may result in the decomposition of alkali carbonate at lower temperatures, and a research investigation focused on understanding the effect of additives on the decomposition of sodium carbonate (Siriwardane et al., 2011).

The experimental equipment that was used in the investigation was similar to that describe previously in the absorption study, although some modifications were made to the procedures. TPD studies were conducted in a laboratory-scale fixed-bed flow reactor (Micromeritics Autochem 2910 atmospheric flow reactor) at 14.7 psi. The outlet gas stream was analyzed using a Pfeiffer Vacuum Thermostar mass spectrometer. In the TPD studies, N$_2$ was introduced to the samples (1.7 x 10$^{-3}$ liter) at a flow rate of 10 cm$^3$/min and the temperature was increased at a rate of 10°C/min while measuring the CO$_2$ concentration with the mass spectrometer. For comparison, in some TPD studies, a nitrogen flow rate of 50 cm$^3$/min and heating rates of 5 and 25°C/min were used. TGA experiments were conducted on a TA Instruments model 2050 thermogravimetric analyzer. Samples (90 mg) were heated to 850°C under N$_2$, and weight gain was recorded isothermally as a function of time. N$_2$ was introduced at a flow rate of 90 cm$^3$/min, and the temperature was increased at a rate of 10°C/min up to 850°C and held isothermally for 120 min.

High-temperature in situ X-ray diffraction (XRD) studies were carried out using an Anton Paar HTK 1200N high-temperature stage connected to an Anton Paar TCU-1000N temperature control unit. The high temperature stage was interfaced to a Panalytical PW 3040 X-Pert Pro XRD system. The in situ high-temperature studies were conducted in ambient air, with data analysis carried out using X’Pert Highscore Plus software supplied by Panalytical. For comparative purposes, in addition to the Na$_2$CO$_3$-CaO sample, in situ temperature studies were also carried out with a CaO sample from ambient temperature (21°C) to 400°C and with a Na$_2$CO$_3$ sample from ambient temperature to 650°C.

X-ray photoelectron spectroscopy (XPS) was carried out using a Physical Electronics (PHI) model 3057 X-ray photoelectron spectroscopy subsystem with a spherical capacitance analyzer and a model 04-548 X-ray source. The system consists of separately pumped preparation and detection chambers that are routinely operated within the pressure range of 10$^{-8}$ to 10$^{-10}$ Torr. The spectrometer sample holder is resistively heated and capable of withstanding temperatures up to
The sample preparation chamber is separated from the main analysis chamber by a gate valve. The samples were placed in the preparation chamber, evacuated, and then heated. After the preparation chamber reached the desired pressure, the sample was transferred to the analyzing chamber for data acquisition. The sample was maintained at the desired temperature throughout the experiment, including data acquisition. The data were analyzed with analysis software developed by RBD Instruments.

The chemicals used in these series of experiments were obtained from Alfa Aesar (Johnson Matthey). The sodium carbonate used in the TPD, TGA, and XRD studies was monohydrated (Na$_2$CO$_3$·H$_2$O). The calcium oxide and calcium carbonate used were anhydrous. The sodium carbonate used in the XPS studies was also anhydrous.

The impact of various experimental parameters (for example, sorbent composition, purge gas flow rate, and heating rate) on sorbent performance was investigated in the TPD experiments. The measured CO$_2$ concentration and corresponding temperature data as a function of time during TPD measurements of Na$_2$CO$_3$·H$_2$O/CaO mixtures with varying compositions are shown in Figure 54. For pure Na$_2$CO$_3$·H$_2$O, the increase in the CO$_2$ concentration initiates around 780°C and the CO$_2$ maximum occurs around 850°C, with a narrow CO$_2$ peak. When Na$_2$CO$_3$·H$_2$O was mixed with CaO in the ratio of 1:3-Na$_2$CO$_3$·H$_2$O/CaO, the increase in the CO$_2$ concentration initiated at around 550°C, a temperature that is significantly lower than that of pure Na$_2$CO$_3$·H$_2$O. The CO$_2$ curve was also broader than that of pure Na$_2$CO$_3$·H$_2$O, indicating not only that CO$_2$ decomposition initiates around 550°C but also that it continues at a wide range of temperatures. When the Na$_2$CO$_3$·H$_2$O concentration was further decreased to 1:4-Na$_2$CO$_3$·H$_2$O/CaO, CO$_2$ was initially observed around 520°C because of the decomposition of carbonate, with more CO$_2$ being observed in the 520°C temperature range than that observed with the Na$_2$CO$_3$·H$_2$O/CaO (1:3) sample. The CO$_2$ curve for the Na$_2$CO$_3$·H$_2$O/CaO (1:6) sample was similar to that of the 1:4 sample. For these three Na$_2$CO$_3$/CaO systems, an increase in the CaO concentration in the Na$_2$CO$_3$·H$_2$O/CaO mixture results in a decrease in the decomposition temperature of Na$_2$CO$_3$, with an optimum CaO concentration beyond which the decomposition temperature of Na$_2$CO$_3$ is not affected.
The effect of the addition of Ca(OH)$_2$ in lieu of CaO was also investigated. After the addition of Ca(OH)$_2$, the initial decomposition temperature of Na$_2$CO$_3$ decreased from 785 to 550°C, similar to the observations with CaO. The addition of Ca(OH)$_2$ appears to be more effective than the addition of CaO in lowering the decomposition temperature of Na$_2$CO$_3$. When CaCO$_3$ was added to Na$_2$CO$_3$*H$_2$O, the temperature of decomposition did not initiate at 550°C, as was observed with CaO and Ca(OH)$_2$. Similarly, when Na$_2$CO$_3$*H$_2$O was mixed with Al$_2$O$_3$ and SiO$_2$, lower decomposition temperatures were not observed. Thus, CaO and Ca(OH)$_2$ have a unique ability to affect the decomposition temperature of Na$_2$CO$_3$. Additionally, the effect of the N$_2$ flow rate and the heating rate on the decomposition of Na$_2$CO$_3$*H$_2$O/CaO (1:4) were also investigated in the TPD study. The data suggest that higher flow rates may facilitate a lower carbonate decomposition temperature through the increased removal of CO$_2$ from the gas stream. Subsequently, a lower heating rate appeared to facilitate Na$_2$CO$_3$ decomposition at a lower temperature (Siriwardane et al., 2011).

XRD in situ temperature studies on the Na$_2$CO$_3$*H$_2$O/CaO (1:3 ratio) sample were carried out from ambient temperature (21°C) to 800°C. Analysis of the Na$_2$CO$_3$*H$_2$O/CaO (1:3) sample at ambient temperature showed the sample to be composed primarily of CaO and Ca(OH)$_2$ with a small concentration of Na$_2$CO$_3$*H$_2$O. The definitive presence of Na$_2$CO$_3$ was not observed at any temperature ranging from 100 to 800°C, indicating that the Na$_2$CO$_3$ material was disordered and not entirely crystalline. No presence of any other Na-based compound could be identified from 300 to 800°C.

In situ high-temperature XPS analysis was conducted on Na$_2$CO$_3$ and a mixture (1:3) of Na$_2$CO$_3$/CaO. The sample was heated in the sample preparation chamber to the desired temperature, with a standing pressure of 10$^{-6}$ to 10$^{-7}$ Torr, and was transferred to the analysis...
chamber for data acquisition while maintaining temperature. On the basis of the XPS spectroscopic data, the decomposition of pure Na$_2$CO$_3$ initiated around 398°C, while for the Na$_2$CO$_3$/CaO mixture (1:3), the decomposition initiated at 300°C. This observation indicates that the presence of CaO lowers the decomposition temperature of Na$_2$CO$_3$, which is consistent with the TPD data. However, it must be noted that these decomposition temperatures are significantly lower than those observed during decomposition at atmospheric pressure, because XPS analysis was conducted in vacuum as opposed to atmospheric pressure.

To summarize this regeneration study, the presence of CaO or Ca(OH)$_2$ in Na$_2$CO$_3$*H$_2$O lowered the decomposition temperature of Na$_2$CO$_3$, while the presence of SiO$_2$, Al$_2$O$_3$, and CaCO$_3$ did not show any effect. Ca(OH)$_2$ had a more pronounced effect than that of CaO, with the concentration, flow rate of sweep gas, and heating rate all affecting the decomposition temperature of Na$_2$CO$_3$. The formation of crystalline phases between CaO and Na$_2$CO$_3$ were not observed during heating in XRD, but the formation of CaCO$_3$-type species were observed. XPS studies also confirmed that the presence of CaO lowered the decomposition temperature of Na$_2$CO$_3$, with the formation of Ca$_x$CO$_{2x}$-type species observed during heating. The formation of carbonate-type species with CaO and Na$_2$CO$_3$ may have facilitated the decomposition of Na$_2$CO$_3$ (Siriwardane et al., 2011).

The research effort with the sodium/calcium mixture has lowered the regeneration temperature for sodium carbonate. However, the applicability of the sorbent system incorporated into a pre-combustion scheme is still in question. Although the temperature of regeneration can be less than 700°C, the sensible heat to heat the sorbent between the absorption and regeneration temperatures can still be appreciable. If the systems analysis that was performed for the lithium silicate work is reviewed (see Ciferno et al. 2004 in Section 3.4.3), the sodium system is not too different from the lithium-based sorbents, and issues are similar for the sodium-based system. No current work is occurring with the sodium-based sorbents.

### 3.6 Magnesium-Containing Sorbents

The more recent work at NETL with alkali/alkaline earth-based sorbents encompasses the use of magnesium hydroxide. Similar to that concluded with sodium-containing sorbents in the previous section, the use of magnesium-based sorbent in a post-combustion application is not realistic due to its optimum temperature range of absorption (200–315°C). As envisioned in a temperature swing scheme, the regeneration is near 375–400°C, and thus the absorption and regeneration conditions make this sorbent more applicable in a pre-combustion situation. This sorbent is more operable than the previous sorbents discussed in relation to an IGCC design since the sensible heat in the regenerative heat duty will be much less because of the lower difference in temperature between the absorption and regeneration steps. Additionally, in a temperature swing scheme, the pressure of the carbon dioxide will remain at that of the removal process and this is a significant advantage, since the energy for the concentrated CO$_2$ to be compressed to the transport pipeline will be much less as compared to a capture pressure-swing scheme (see Section 1: Introduction).

This novel magnesium hydroxide-based sorbent, that can capture CO$_2$ at 200–315°C and is regenerable near 375°C, was developed and patented by NETL (Siriwardane et al., 2007a; Siriwardane, 2008; Siriwardane and Stevens, 2009). The capture process with this warm-gas CO$_2$ removal sorbent involves the chemical reaction:
\[
\text{Mg(OH)}_2(s) + \text{CO}_2(g) \rightarrow \text{MgCO}_3(s) + \text{H}_2\text{O}
\] (1)

The sorbent has a very high CO\textsubscript{2} sorption capacity at 200–315°C, which is considerably higher than that of the commercial Selexol process (i.e., 3–4 mol of CO\textsubscript{2}/kg for the sorbent as compared to 0.3 mol of CO\textsubscript{2}/kg solvent for Selexol with a CO\textsubscript{2} partial pressure of 0.3 MPa). The carbonate formed during the absorption reaction can be thermally decomposed to release carbon dioxide and regenerate at 375–400°C as described in Reaction 2:

\[
\text{MgCO}_3(s) + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2(s) + \text{CO}_2
\] (2)

Reaction 2 can also occur in two reaction steps as shown below:

\[
\text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g)
\] (3)

\[
\text{MgO}(s) + \text{H}_2\text{O}(g) \rightarrow \text{Mg(OH)}_2(s)
\] (4)

According to these reactions, Mg(OH)\textsubscript{2} can be a potential regenerable sorbent for CO\textsubscript{2} capture from gas streams at warm gas temperatures (those temperatures near that exiting the water-gas shift reactor in an IGCC scheme). Therefore, both thermodynamic analysis and experiments were conducted to evaluate whether the Mg(OH)\textsubscript{2} sorbent can be utilized for CO\textsubscript{2} capture and regeneration (Siriwardane and Stevens, 2009).

Thermodynamic analysis was conducted to understand the favorable range of temperatures and pressures for the sorption, regeneration, and rehydroxylation reactions. One mole of Mg(OH)\textsubscript{2}, 1 mol of CO\textsubscript{2}, and 1 mol of water were equilibrated at 30 atm (simulating the removal conditions in an IGCC application), and the resulting products are shown in Figure 55. The figure indicates that, at 30 atm, formation of MgCO\textsubscript{3} can take place up to 400°C, which is slightly greater than if the total pressure was 1 atm. Thus, the formation of MgCO\textsubscript{3} appears to be favored at elevated pressures.
Figure 55: Thermodynamic equilibrium analysis as a function of temperature for a system of 1 mol of CO₂, 1 mol of Mg(OH)₂, 1 mol of H₂O, and 0.1 mol of N₂ at a pressure of 30 atm.

Thermodynamic analysis data for the decomposition of 1 mol of MgCO₃ in the presence of 1 mol of water at 20 atm is shown in Figure 56. Decomposition initiates around 400°C and favorable products are magnesium oxide and CO₂. Rehydroxylation of MgO to form Mg(OH)₂ appears to be unfavorable in the presence of CO₂. Decomposition of MgCO₃ at lower pressures occurs at lower temperatures. These analyses indicate that the MgCO₃ can be decomposed at relatively lower temperatures as compared to the other alkali/alkaline earth sorbents previously investigated at NETL.
After the regeneration, rehydroxylation of MgO is necessary to obtain Mg(OH)$_2$.
Thermodynamic analysis was conducted with 1 mol of MgO and 1 mol of H$_2$O. The resulting products at 20 atm are shown in Figure 57; complete conversion of MgO to Mg(OH)$_2$ is possible up to 300°C at 20 atm. When compared to a lower pressure, increasing pressure increases the temperature window for the rehydroxylation process. The thermodynamic analyses showed that the Mg(OH)$_2$ sorbent system is highly favorable for CO$_2$ capture within a wide temperature/pressure range (up to 300°C at 1 atm; up to 400°C at 30 atm); MgCO$_3$ decomposes to release CO$_2$ at temperatures as low as 400°C up to 20 atm; and MgO rehydroxylation to form Mg(OH)$_2$ is possible at temperatures up to 300°C at 20 atm. Because the thermodynamic analysis showed favorable results, Mg(OH)$_2$ was tested in two flow reactors to determine the experimental conditions for CO$_2$ capture and regeneration.
Sorbents were prepared by combining solid magnesium hydroxide and a promoter, sodium orthosilicate, in a mixer (Siriwardane and Stevens, 2009). Water was added to the mixture to pelletize the sorbent, yielding particles on the order of 2–3 mm. The pellets were dried in air at 100°C for 1 h. The resulting sorbent pellets exhibited low surface area, on the order of 2.4–3.0 m²/g as analyzed by BET. A sorbent, whose fabrication was varied somewhat, was studied later in the bench-scale reactor system (Fisher et al., 2012).

### 3.6.1 Laboratory-Scale Fixed Bed Study

A 10-cycle flow reactor test was conducted with 3 g of Mg(OH)₂ sorbent in a laboratory-scale reactor. The sorption was conducted at 200–250°C and 150 psig with a gas mixture containing 28% CO₂ in moist He at a gas hourly space velocity (GHSV) of 250 h⁻¹. Regeneration was conducted at 375°C and at both 1 atm and 150 psig (11.2 atm) with He and moisture. After the regeneration, the sorbent was cooled in the presence of moisture to ambient temperature prior to the next cycle. The laboratory-scale reactor was limited to an operating pressure of 150 psig. The water content in the feed to the laboratory-scale reactor was also limited as it was delivered via a bubbler that was maintained at room temperature, yielding an upper bound on the H₂O concentration of approximately 2.6%. A mass spectrometer analyzed the exit gas stream.

The data from the first six cycles of the 10-cycle laboratory-scale flow reactor test with 28% CO₂ in He at 200°C, 100–150 psi, and 250 h⁻¹ GHSV are shown in Table 22 (Siriwardane et al., 2007a; Siriwardane and Stevens, 2009). Regeneration during these six cycles was performed at 1...
The efficiency of the CO₂ removal was greater than 99% during these six cycles. The breakthrough times also increased with increasing the number of cycles, indicating that the sorbent’s capture capacity increased with cycle number. The CO₂ capture capacities calculated from the breakthrough curves listed in Table 22 show nearly a 3-fold increase in capacity between the first cycle and the ninth cycle. During regeneration at 375°C, both MgCO₃ and unreacted Mg(OH)₂ are converted to MgO. The MgO is converted to Mg(OH)₂ through a reaction with water vapor during the cooling process. The extent of hydroxylation was not controlled during the multicycle tests. The CO₂ sorption capacity during the subsequent cycles depends on the degree of rehydroxylation; the increased capacities are likely due to a greater extent of rehydroxylation. The rehydroxylation process is critical for retaining reactivity during cyclic operation and is thermodynamically more favorable at lower temperatures. Results from the CO₂ sorption data for cycles 7–10 are also shown in Table 22. The regenerations for these cycles were conducted at 150 psig and 375°C. The CO₂ removal efficiencies for these cycles remained greater than 99%, and the capture capacities were higher than those for the first six cycles where the regeneration was conducted at 1 atm. The CO₂ capture capacities were in the range of 3–4 mol/kg for the sorbent.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>CO₂ Sorption</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>P (psig)</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>9</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>150</td>
</tr>
</tbody>
</table>

### 3.6.2 Bench-Scale Fixed Bed Study

This sorbent was fabricated similar to the procedure previously described for the laboratory-scale testing. In the bench-scale flow reactor, the dried sorbent pellets were placed into a vertical tubular reactor with a 0.5 in diameter to form a 6-in bed (approximately 18 g of sorbent). The sorbent bed was heated in nitrogen to 200°C and then exposed to the inlet gas consisting of 28% CO₂, 15% H₂O, and 57% N₂ in a down-flow, packed bed configuration with a GHSV of 500 h⁻¹. The gas roughly simulates some of the components found in an IGCC power generation facility.
The capture was completed when the CO₂ outlet concentration matched the inlet concentration, which was monitored via a mass spectrometer (MS). After the completion of the capture, the sorbent was regenerated by flowing 15% H₂O with 85% N₂ at 500 h⁻¹ GHSV through the reactor at 400°C until CO₂ was no longer present in the effluent, as determined by a CO₂ profile. Subsequent to regeneration, the reactor was cooled to 200°C and 30% H₂O in N₂ was introduced for 2 h to hydroxylate the MgO to Mg(OH)₂. Following hydroxylation, the CO₂ capture cycle was repeated (Fisher et al., 2012).

The results of an earlier six-cycle test with the bench-scale flow reactor with feed containing 28% CO₂, 10% H₂O, 28% Ar, and 34% N₂ are shown in Table 23 (Siriwardane and Stevens, 2009). The first four cycles were conducted at 150 psig and the last two at 280 psig to determine the effect of pressure. The CO₂ capture capacity improves during cycling due to better rehydroxylation due to morphology changes. The formation of Mg(OH)₂ is critical to obtain higher CO₂ capture capacity of the sorbent. During all testing conditions, the sorbent was able to remove the CO₂ down to ppm levels, yielding a removal efficiency of approximately 99%. Increasing the pressure from 150 to 280 psig resulted in a favorable increase in the sorbent’s CO₂ capture capacity. Capture capacities on the order of 3 mol CO₂/kg of sorbent were realized at 280 psig and at 200°C. Table 24 shows the results of a four-cycle test where regeneration was conducted at 280 psig. The temperature during the high-pressure regeneration was raised from 375 to 400°C to ensure complete regeneration.

Table 23: Sorption capacities over Mg(OH)₂ during bench-scale flow reactor testing with feed composition of 28% CO₂, 10% H₂O and GHSV = 250 h⁻¹. Regeneration was at 20 psig.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>CO₂ Sorption</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>P (psig)</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>280</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>280</td>
</tr>
</tbody>
</table>
Table 24: Sorption capacities over Mg(OH)$_2$ during bench-scale flow reactor testing with feed composition of 28% CO$_2$, 10% H$_2$O and GHSV = 250 h$^{-1}$. Regeneration was at 280 psig.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>CO$_2$ Sorption</th>
<th></th>
<th>Regeneration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (°C)</td>
<td>$P$ (psig)</td>
<td>capacity (mol/kg)</td>
<td>$T$ (°C)</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>280</td>
<td>n/a</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>280</td>
<td>4.5</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>280</td>
<td>4.4</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>280</td>
<td>4.5</td>
<td>400</td>
</tr>
</tbody>
</table>

The experimental system was then modified to allow the H$_2$O concentration to be raised from 25% to 40% during the hydroxylation step (Fisher et al., 2012). This higher concentration of water allowed for enhanced hydroxylation, which resulted in an improved capture capacity. Figures 58 and 59 show the MS profile during capture and regeneration after the enhanced hydroxylation with 40% H$_2$O. Hydroxylation with 40% H$_2$O followed by CO$_2$ capture conducted over fresh sorbent resulted in 4.5 mol of CO$_2$/kg of sorbent, as shown in Figure 58. Prior to capture, the CO$_2$ concentration is shown to be at 32 vol % (dry basis) while the feed gas and injected water bypasses the reactor housing the sorbent bed. Capture was initiated by switching the reactor online (i.e., redirecting the feed gas and injected water into the reactor/sorbent bed). After capture was initiated, the CO$_2$ concentration in the reactor effluent decreased to ppm levels for more than 25 min, after which the CO$_2$ concentration profile increased sharply or broke through, indicating saturation of the sorbent by CO$_2$. The total amount of CO$_2$ capture was 4.5 mol of CO$_2$/kg of sorbent. The subsequent regeneration of the sorbent at 400°C and 280 psig led to desorption of 4.6 mol of CO$_2$/kg of sorbent (see Figure 25), which suggested that the sorbent is fully regenerable under the conditions investigated. Further, Table 24 shows that the sorbent is regenerable under the temperature and pressure indicated for the regenerator in an IGCC capture scheme. The rehydroxylation step of the process is critical to maintain the CO$_2$ capture capacity during cyclic process. A CO$_2$ capture test with MgO resulted in a low capacity of 0.25 mol CO$_2$/kg during a bench-scale flow reactor test at 200°C, despite the fact that the conversion of MgO to MgCO$_3$ reaction is predicted to be highly favorable thermodynamically. This result suggests that the kinetics of CO$_2$ capture with MgO is much slower than that with Mg(OH)$_2$. Either the presence of Mg(OH)$_2$ or having steam with MgO is necessary for the CO$_2$ capture process.
3.6.3 Preliminary Systems Analysis

On the basis of the experimental data that was previously presented, a multi-reactor process for CO₂ capture from moderate temperatures and high pressures within an IGCC power generation scheme was developed (Fisher et al., 2012). The process utilizes three reactors consisting of an absorber, a regenerator, and a polisher. The absorber and polisher units are maintained at 200°C while the regenerator is maintained at 385°C. The reactors can be configured as moving beds, circulating fluidized beds, or transport reactors. In the preliminary systems analysis, the power plant configuration used was from a DOE report that modeled an IGCC power plant utilizing a GE gasifier with the Selexol capture process after the water gas shift (WGS) reactor. The reactors for the magnesium-based sorbent capture process in this work were modeled after the three process steps (i.e., capture, regeneration, and hydroxylation), where each reactor operates at similar pressures and temperatures as described in the above experimental conditions. The flow rates of gases and sorbent for CO₂ capture were based on a 100 kg/h fuel gas flow, which allows scaling the results to any IGCC plant, given the fuel gas flow from the WGS reactor to the
capture unit. The unit was then scaled to the gas flows of the DOE report, where the GE gasifier and utility costs were estimated.

It is envisioned that in an IGCC application, the sorbent capture process is split, in that part of the CO₂ in the fuel gas is removed before the WGS reactor and the remainder removed afterwards. By staging the removal, the WGS system can be enhanced by the initial capture step by lowering the CO₂ content and increasing the moisture content before the shift reaction. Figure 60 shows a block diagram of the proposed system with a CO₂ capture reactor before and after the WGS reactor. Capture of 90% of the total amount of CO₂ produced in the plant is given.

Figure 60: Proposed CO₂ capture process.

In Figure 60, the fuel gas from the gasifier after impurity removal is introduced to the absorber. The composition of this stream is based on the DOE report. The stream is assumed to enter the absorber at 200°C, which is reported in the DOE report as the temperature of the fuel gas entering the water-gas shift reactor. The sorbent flow rate is scaled to accommodate the incoming CO₂ assuming a capture capacity of 4 mol CO₂/kg sorbent. Due to the exothermic nature of CO₂ absorption, cooling H₂O is employed to maintain the sorbent bed at nearly isothermal conditions. CO₂-free gas is removed from the top of the absorber and directed into the WGS reactor. The outlet gas stream from the WGS reactor is introduced to the second stage CO₂ capture unit and the effluent from the second CO₂ capture unit (i.e., H₂ and H₂O) is later recycled into the rehydroxylation unit, eliminating the requirement for additional steam for the hydroxylation of the sorbent. It is important to note that capturing a mole of CO₂ with the sorbent releases a mole of H₂O from the sorbent as shown in reaction 1, yielding a stream with an
The regenerator, shown in Figure 15, decomposes MgCO$_3$ to MgO and CO$_2$ at 385°C and 280 psig. Heating the sorbent from 200 to 335°C is accomplished through solid–gas heat exchange with a closed-loop steam cycle, where heat is provided by the sorbent leaving the regenerator (streams 11 and 12). The heat duty of heating the sorbent to 385°C, as well as overcoming the desorption energy, is accomplished through heat exchange with steam from an auxiliary steam generator. The auxiliary steam generator produces steam via coal combustion that heats the steam, which is then fed to the heat exchangers in the regeneration reactor. The steam is fed to the regenerator from the auxiliary steam generator and operates on a closed-loop cycle to minimize the duty. Steam produced (stream 9) by heat exchange with the post-regeneration gases of CO$_2$ and H$_2$O (stream 7) is also directly injected into the sorbent, which dilutes the desorbing CO$_2$ and shifts the decomposition equilibrium to increase the potential for sorbent regeneration. The direct steam injection is also expected to hydroxylate about 50% of the MgCO$_3$ entering the regenerator to produce Mg(OH)$_2$, while the remaining MgCO$_3$ is decomposed to MgO. The CO$_2$ and steam leaving the regenerator is then cooled, condensing the steam and purifying the CO$_2$. The purified CO$_2$ (99.4 mol % or 99.8 wt %, with a balance of H$_2$O) is then available at 50°C and 280 psig (stream 18) for sequestration.

The sorbent leaves the regenerator at 385°C, nearly devoid of MgCO$_3$ and largely rehydroxylated (stream 4 with 48.3 active mol % Mg(OH)$_2$). The sorbent is cooled to 200°C prior to entering the rehydroxylation unit by heat exchange with cooling water (stream 11), which is then used to preheat the sorbent entering the regenerator (stream 12). The cooled sorbent is then fed to the rehydroxylation unit near 200°C and 280 psig, where it reacts with H$_2$O from the recycled H$_2$/H$_2$O stream from the absorber unit (stream 2) to further convert the sorbent’s MgO content to Mg(OH)$_2$. The recycling of the H$_2$/H$_2$O through the rehydroxylator eliminates the need for additional steam from the power island to convert the MgO to Mg(OH)$_2$. The rehydroxylator unit is maintained isothermally at 200°C during the exothermic hydroxylation reaction through heat exchange with 25°C cooling water (stream 15). The sorbent leaves the rehydroxylator nearly fully converted to active Mg(OH)$_2$ via stream 6, which feeds back to the absorber to complete the cycle. The gaseous effluent of the rehydroxylator (stream 8 with 41.9 mol % H$_2$ and 58.1 mol % H$_2$O) is directed to the power island for power generation.

For the preliminary systems analysis, material and energy balances were performed using the DOE IGCC report as the basis (Fisher et al., 2012). The following assumptions were also employed to make the calculations possible:

1. CO$_2$ capture capacity of sorbent at 200°C, 280 psig is 4 mol CO$_2$/kg sorbent
2. heat of carbonation equals 19.6 kJ/mol CO$_2$ at 200°C
3. feed composition of 31.5 mol % CO$_2$, 44.7 mol % H$_2$, and 23.8 mol % H$_2$O
4. adiabatic reactor system
5. perfect mixing of gas/solids for heat transfer
6. power generation breakdown of gas turbine to steam turbine is 3:2
7. the WGS reactor operates at 100% conversion
8. sorbent does not absorb water during CO$_2$ sorption
9. isobaric thermal swing for CO$_2$/H$_2$O separation

10. sorbent utilization is 31%; remainder of active phase is inert and has no effect on equilibrium calculations

Details of the analysis can be obtained elsewhere (Fisher et al., 2012). Some of the key findings and advantages are summarized.

- As compared to Selexol that requires a low temperature of operation (~40°C), the warm gas capture eliminates the need to cool and then reheat the fuel gas before the gas-fired turbine in an IGCC scheme. The IGCC plant thermal efficiency with CO$_2$ separation by the proposed process was determined to be 33.0%, which compares favorably to the DOE report value of 32.6% for the same IGCC plant employing the Selexol process for CO$_2$ removal.

- An additional increase in efficiency occurs from reduced cost of compression from the capture process to sequestration pipeline pressure since purified CO$_2$ is at higher pressure from the magnesium-based sorbent process than that of the Selexol process.

- Steam within the fuel gas remains in the fuel gas as compared to the Selexol process, where steam needs to be removed beforehand. The steam within the warm fuel gas after the sorbent process will be used in the gas turbine to produce power.

- Removal of the CO$_2$ prior to the WGS reactor using the Mg(OH)$_2$-based sorbent would increase the H$_2$O content in the WGS inlet and reduce the requirement for additional steam. Another effect of CO$_2$ removal before the WGS reactor is the promotion of the thermodynamic and kinetics of the WGS reaction by reducing the product CO$_2$ concentration.

- No additional water feed is required for the rehydroxylation reaction within the rehydroxylation unit since the H$_2$O consumed in the rehydroxylation reaction is generated during the capture reaction within the absorber.

Of the alkali/alkaline earth-based sorbents tested to date, the magnesium-based sorbent is the most applicable to a power generation scenario. Its incorporation into a pre-combustion (i.e., IGCC) scenario has potential benefits. A key asset of this CO$_2$ capture process is that when capture technologies for other components within the fuel gas (e.g., ammonia, hydrogen sulfide, mercury, etc.) are conducted at warm gas cleanup temperatures, the thermal efficiency of the IGCC power generation system improves as compared to low temperature pollutant removal (Pennline et al., 2008). Further detailed system analysis studies will further elucidate the above advantages of this capture process.
4. AMINE-ENRICHED SORBENTS FOR POST-COMBUSTION APPLICATION

4.1 INTRODUCTION

Amine-enriched sorbents were originally prescribed for post-combustion application to replace monoethanolamine (MEA) scrubbing. Aqueous solutions of amine compounds are used in industrial wet scrubbing for CO₂ removal, and the use of amine compounds as a dry, regenerable sorbent was initially pursued at NETL (Soong et al., 2001). Amine compounds were deposited onto a fly ash enriched in carbon. Adsorption studies, followed by a temperature-programmed desorption (TPD) technique, were conducted under ambient pressure and at temperatures between 30 and 120°C. It was concluded that the amine-enriched samples chemically absorb CO₂ and H₂O upon contact with a gaseous stream, thereby forming the amine complexes. However, it was possible that a combination of both adsorption and absorption processes was occurring. (White et al., 2003). From some of the initial experimental studies (proposed mechanisms, temperature of operation, and other process parameters) and DOE programmatic goals, it was concluded that use of these types of sorbents would be most applicable in post-combustion capture schemes.

The key objective was to develop sorbent-based post-combustion CO₂ capture systems for both existing plants and advanced power generating facilities that lower the energy penalty and costs associated with capturing CO₂ from large point sources. In the Existing Plants, Emissions and Capture Program, the overall programmatic goal for the carbon sequestration scenario (of which carbon capture is the key step) was to develop fossil fuel conversion systems that achieve 90% CO₂ capture with 99% storage permanence at less than a 35% increase in the cost of energy services for post- and oxy-combustion capture at new and existing pulverized coal-fired power plants (DOE/NETL Capture Program, 2011). As will be seen, sorbent-based capture techniques with amine-enriched sorbents have the potential to meet this programmatic goal.

During the earlier stages of conducting research on CO₂ capture with amine-based solid sorbents, a preliminary systems analysis study was initiated to determine the merit of using this type of solid sorbent (Tarka et al., 2006). The main advantage of using solid versus liquid scrubbing (i.e., aqueous monoethanolamine or MEA) was borne out in the lower anticipated heat duty of regeneration. Several factors contribute to this, including lower heat capacity of the solid; higher amine loading on the solid as well as higher CO₂ loading on the solid; considerably negligible water in the solid versus the liquid MEA solvent (and therefore less evaporative loss); and less swing in temperature to regenerate the solid. A comparison between MEA scrubbing and amine-enriched sorbents illustrated the potential energy benefits of the sorbent system, including an overall heat duty of 783 Btu/lb CO₂ versus 1,934 Btu/lb CO₂ for MEA, due primarily to lower sensible heat and evaporative considerations. (It should be noted that advances in MEA scrubbing technologies have also lowered the MEA heat duty to lower than 1,500 Btu/lb CO₂.) Additionally, a sensitivity study related to cost of electricity and gauging the ranges of various parameters, such as sorbent cost, heat duty, sorbent replacement rate, and working capacity, was conducted for a stationary bed design in a coal-fired combustion system. Results revealed that the amine-enriched sorbent systems could reach the goal of the program at that time.

As the sorbents proceeded through additional development and continued to show promise, NETL sought industrial participation to help advance the technology out of the laboratory and towards commercialization, especially with an eye towards reactor process engineering and design. Mid-Atlantic Technology, Research and Innovation Center (MATRIC) was
commissioned by the in-house research effort at NETL to perform a systems study for conceptualized reactor configurations for a sorbent-based CO\(_2\) capture process (Fisher et al., 2006a; Hoffman et al., 2008a). Spreadsheet calculations for energy and mass balances were performed. The primary metric of performance was to compare the regeneration heat duty for the sorbent/reactor configuration versus a conventional wet scrubbing process using MEA. In order to meet DOE program goals, the study recommended certain targets and that the sorbent process should have a regeneration heat duty that is at least 30–50 percent less than the MEA heat duty, corresponding to the sorbent process having a heat duty generally between 500 and 1000 Btu/lb CO\(_2\). Specific success criteria or performance targets for the sorbent were established based on assumed sorbent properties, leading to the identification of critical process parameters and information that are required for further development evaluation, including: isotherms (\(\Delta\) (delta) loadings or working capacity of the sorbent) covering rich loading (absorption) and lean loading (regeneration); heat of reaction (\(\Delta H_r\)) for CO\(_2\) absorption; heat capacity (\(C_p\)) for sorbent; role of H\(_2\)O in the process; role of trace components (SO\(_2\) and NO\(_x\)); and reaction kinetics.

A later systems analysis (Matuszewski et al., 2009) was conducted within NETL using as a basis the reactor designs that MATRIC had developed. Increases in the cost of energy services, although somewhat more than the program target of 35%, were still substantially lower than that of MEA scrubbing.

As a result of the MATRIC study, the amine-enriched sorbent work evolved as collaboration between the areas of sorbent development and reactor design. Although the infancy of amine-enriched sorbents began much earlier, a concerted effort began in fiscal year 2007 with a continuation of two routes of sorbent investigation: immobilized amines on supports and encapsulated amine clay-based sorbents. The first type of sorbent initially used various amine-based compounds that were deposited onto a substrate. Candidate compounds included tetraethylenepentamine, pentaethylenehexamine, polyethylenimine, and others, and the supports included polymethylmethacrylate, polystyrene, and silicas. After screening studies, one of the choice materials was polyethylenimine (PEI) on silica. PEI can be linear or branched and can contain primary, secondary, and tertiary amines. Typical loadings of PEI on silica range from 40-50% by weight. The silica has a high surface area (upwards of 300-m\(^2\)/g) and could be obtained from Fuji Silysia or PQ Inc. In a typical fabrication, the PEI is dissolved in an organic solvent and combined with the support in a certain ratio. The slurry is placed in a rotary evaporator resulting in the immobilization of the amine onto the support. The patented fabrication technique produced samples for the laboratory scale testing but was also easily adapted to produce large (+600-lb) loads for subsequent larger scale testing with ADA-ES, as discussed later in this section. In general, fabrication methods should be easily scalable to keep sorbent costs at a minimum. More recent work involves stabilization of the sorbent by using silane compounds to perform a cross-linking function.

The second type of sorbent involves the encapsulation of an amine and/or polar liquid material within a clay substrate, for example bentonite. The clay matrix is inexpensive and readily available and has a low heat capacity. Fabrication of the sorbent starts with mixing the clay with a binder and desiccant homogeneously. The amine in an aqueous solution of ether is mixed with the clay until a solid consistency is obtained, and this is then dried. The amine and/or ether that are encapsulated within the clay substrate consist of about 50 weight percent of the sorbent. The patented scheme for sorbent fabrication contains various amines and ethers in a bentonite matrix.
Sorbents had been sized for various applications, and the fabrication technique was easily adapted for production of large loads of material by Sud Chemie.

In order for potential sorbent/reactor technology candidates to be experimentally evaluated at larger scale, it is prudent to perform engineering and economic analyses (i.e., system studies) upfront. The level of effort required depends on the maturity of the process to date. Amine-enriched solid sorbents were developed at laboratory/bench-scale by the NETL in-house researchers for their potential application in CO₂ removal processes. In support of these activities, reactor designs utilizing solid sorbents for flue gas applications continued to be developed, such as the collaboration that had occurred with MATRIC. Possible reactor configurations included non-stationary sorbent reactors, such as fluidized bed or moving bed, isothermal fixed bed, and fixed bed reactor with inter-staged cooling. System analyses of conceptual systems have traditionally been conducted by groups other than the in-house research effort at NETL and required coordination among the various investigations.

Once an understanding of the sorbent process is obtained, further reactor design and process development activities can occur. Down-selecting to a particular reactor design can occur once all the basic information is obtained in the sorbent studies. For example, if moisture adsorption, separate from moisture that reacts with CO₂ and amine, plays a major role with a particular sorbent, then this could direct designers to reactors where sorbent is transported between the adsorption and regeneration steps. Once a determination of a transport type system is made, then engineering research can proceed to determine information that is pertinent to the sorbent system within a specific transport design, for example, magnitude of internal heat transfer surfaces, heat transfer coefficients, etc.

Various types of experimental facilities have been used at both the Pittsburgh and Morgantown research campuses: thermogravimetric analyzers, laboratory- and bench-scale packed bed reactors, and calorimeters. The laboratory-scale packed bed reactor units currently use a mass spectrometer to determine inlet and exit gas compositions to and from the reactor. With respect to the mass spectrometer, the capability of the instrument was extended to facilitate measurement of H₂O in the process gas. The goal allowed breakthrough curves for both CO₂ and H₂O to be simultaneously measured. There is a desire to obtain consistent results between the types of units and the campuses. Additionally, as a form of an outside cross-check, external collaborators related to the work, such as ADA-ES (Sjostrom and Krutka, 2010) and Tennessee Valley Authority (Stephens and van Pelt, 2008) have validated the NETL in-house results. Good material balances with the laboratory- and bench-scale units were always strived for.

For the amine-enriched sorbents, a temperature swing is the choice method of regeneration. With respect to the encapsulated amine clay-based sorbent, regeneration can occur at elevated temperature under a sweep of CO₂. Although this is the preferred method of regeneration, the sorbent working capacity is on the low side. In contrast to this sorbent, the immobilized amine sorbent cannot be regenerated under an atmosphere of CO₂ without having a significant impact on the delta loading measured for CO₂. A recycle stream of the CO₂ regenerator off-gas (after moisture is removed) has always been considered an option for a sweep gas to be used during regeneration (MATRIC assumed this type of regeneration). However, the higher partial pressure of CO₂ in the regenerator impacts the level of sorbent regeneration achieved, and therefore the CO₂ delta loading or working capacity. For some of the preliminary research with an immobilized amine sorbent, if inert sweep gas was used during regeneration, ΔCO₂ is ~2.5 moles/kg. If CO₂ sweep gas was used during regeneration (simulated as 90%CO₂/He), ΔCO₂ is
much smaller, perhaps ~0.2 moles/kg. The preliminary results point to the need to use an inert sweep gas during regeneration. The obvious choice is steam, since it can be separated (condensed) from the CO₂ in the off-gas. However, a whole host of questions arose since little work with sorbents exposed to direct steam regeneration had been conducted. Therefore, with this type of sorbent, studies were conducted using direct steam regeneration and the implications for this type of temperature swing were determined.

For both types of amine-enriched sorbents, kinetic studies have been conducted. The kinetic studies were performed on representative sorbents from each of the two families to obtain a model that would represent each. Although further variations in the sorbents could impact each sorbent, it was felt that the kinetic expression would not significantly deviate from a representative sample. Results were obtained from thermogravimetric analyzers and a volumetric isotherm system. Results from the kinetic study will be fed into a computational modeling effort. If information from a systems analysis promotes a particular technology, then a computational model would be the next step in the evolution of the technology. For example, if in the sorbent work, a cross-flow moving bed is the projected best design, then a mathematical model that incorporates kinetic information, hydrodynamics, etc. can be commissioned. This model could then be used in scale-up determinations and in more realistic cost/system studies.

A brief summary of the experimental sorbent development work to date follows. For the immobilized amine sorbent, PEI on a mesoporous silica is the likely candidate of choice. Due to the sorbent’s reactivity with CO₂ even at elevated temperatures, regeneration under an atmosphere of CO₂ is unlikely, leading to the use of steam as a sweep during the regeneration step. The working capacity of the sorbent at typical flue gas conditions is 3–4 mole CO₂/kg sorbent. These results have been verified by testing through a memorandum-of-understanding with TVA and through a CRADA with ADA-ES. Accelerated exposure testing of the sorbent with high concentrations of SO₂ (1,000-ppm) and NOₓ (750-ppm) poisoned the immobilized amine sorbent revealing that for every mole of SO₂ or NO₂ that is absorbed by the sorbent, the capacity of the sorbent for CO₂ absorption decreases by a mole. It can be inferred that these type of sorbents behave similar to MEA with respect to SO₂/NOₓ and that scrubbing in the form of selective catalytic reduction/flue gas desulfurization would be needed upstream of CO₂ sorbent reactors. Moisture will adsorb on the sorbent and isotherms at absorption conditions (~15% H₂O) and regeneration conditions under near pure steam surroundings have been obtained. For the encapsulated amine clay-based sorbent, a composition of various amines and ethers encapsulated in a bentonite substrate is the sorbent of choice. The sorbent can be regenerated in the presence of CO₂ in the temperature range of 80–100°C, and the sorbent working capacity is near 1.7 mol CO₂/kg sorbent. Results have been confirmed on the small units and testing within a bench-scale fluid bed reactor system.

More recently, greater research efforts entail reactor development where the overall goal is to characterize the performance of sorbents used during post-combustion CO₂ capture in various promising reactors suitable for processing flue gas under near atmospheric conditions. The data generated are being used to validate simulated computer models and where necessary, generate constitutive laws consistent with theory and experimental results. Bench-scale facilities have been fabricated (C2U facility) and initially operated adiabatically with sorbents in a dry synthetic flue gas. Test data results are cataloged for model validation. Operations with an immobilized amine sorbent have included batch isolated absorption and regeneration, as well as fully integrated performance between the absorption and regeneration steps. Measurements include
reactor pressure and temperatures profiles, exit CO₂ levels, and gas and solid flows. Measurement, analytical, and diagnostic tools have been applied to evaluate process performance parameters that are critical for designing and scaling these process reactors. A fully integrated warm unit, the C2U facility, capable of conducting CO₂ capture and solid sorbent regeneration continuously was designed, constructed, and operated (Shadle, 2010). Literature and performance parameters for MEA, supported sorbents, and selected novel concepts will be used to compare various process concepts against the benchmark and further identify process targets needed to optimize economic performance. More importantly, the information obtained will be used to validate computational fluid dynamic simulations assembled within the Carbon Capture Simulation Initiative (CCSI) (Miller, 2011).

4.2 EARLY STUDIES WITH AMINE-ENRICHED SORBENTS

4.2.1 Initial Immobilized Amine Sorbent Studies

With the advent of the Carbon Sequestration Program, the in-house research effort at NETL with amine-enriched sorbents became a key activity. The initial rationale for using these type of sorbents evolved from wet scrubbing with amines. Amine-based, wet scrubbing systems have been proposed as capture techniques for CO₂ removal from flue gas streams, but are energy intensive due, in part, to the large amount of water needed in these systems. Excessive water is required because of the mechanism and due to the corrosiveness of the sole amine, such as monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA). The proposed reaction sequences in aqueous systems using primary and secondary alkanolamines reacting with dissolved CO₂ are shown in Figure 61 (Gray et al., 2004b). The majority of the CO₂ captured will result in the formation of bicarbonate in these liquid amine capture systems. In aqueous media, there is a requirement of 2 mol of amine/mol of CO₂ for the formation of stable bicarbonate compounds resulting in the capture of CO₂. Solid-amine CO₂ sorbents should have similar reactions with gaseous CO₂, water vapor, and the amine site on its surface, and thus certain parameters were initially investigated.

![Figure 61: Proposed reaction sequence for the capture of CO₂ by liquid amine-based systems.](image)

For the immobilized amine sorbent, initial studies revolved around the development and understanding of key variables. The type of amine—primary, secondary, or tertiary amine—is important with respect to the removal of CO₂ from the flue gas. How the amine is attached to the
Sorbent Research for the Capture of Carbon Dioxide

Substrate is also critical, as well as the availability of the amine to the carbon dioxide molecule. This has a direct relation to the type of substrate involved and its surface area and ability to bond (attach) the amine. Additionally, sorbent fabrication technique can have an impact on the sorbent performance. In all, these key parameters were initially investigated with the immobilized amine sorbents and the results directed the later work with this type of sorbent.

**Carbon-based Substrate**

The initial venture with amine-enriched sorbents involved combining a secondary amine with a carbon-based support. The objective in developing the novel amine enriched sorbents for the capture of CO₂ from flue gas streams was to prepare the sorbent by the chemical treatment of a high surface oxide material (for example, activated carbon with density of 2.3 g/cm³ has a surface area of 400 m²/g and a contact area of 9.2 x 10⁸ m²/m³) with various amine compounds. The implanting of amine groups on the high surface area material may increase the needed contact area between CO₂ and amine by several magnitudes. Furthermore, mass and heat-transfer problems can be reduced significantly by the novel concept of applying gas-amine enriched solid reactions for CO₂ capture versus that of gas-liquid reactions. Therefore, only a small amount of sorbent is needed for capturing the same amount of CO₂ versus that of the typical aqueous amine process. Thus, a significant improvement in the efficiency of the process can be realized due to increased contact area and less energy consumption for regenerating the adsorbents. In addition, the high surface area material can provide the physical/chemical adsorption function of CO₂ that might enhance the CO₂ capture process (Soong et al., 2001).

The proposed mechanism of incorporating the amine onto the substrate can be seen in Figure 6.2 and involves two major steps. The first step involves an initial treatment of an oxidized solid substrate with aqueous metal hydroxide. This treatment facilitates the formation of metal salts on the surface of the substrate. Metal salts include metal carboxylates and metal alkoxides and are formed via the interaction of the metal (from the metal hydroxide) with the carboxyl acid and alcoholic sites. These carboxylates and alkoxides react in turn with a substituted amine salt that, for example, includes hydrogen halide. Thus the second step is the treatment of the prepared solid substrate with the aqueous solution of a halogenated amine salt. Any type of amine can be used. The treated substrate is then dried by subjecting the product to a temperature sufficiently high and for a time to evaporate the solvent-carrier of the salt (Gray et al., 2003).
For the initial study with amine-enriched sorbents (Soong et al., 2001), fly ash and fly ash-derived carbons were used as the substrate material. A fly ash containing 9.5 wt% of unburned carbon was collected from the bag house from an experimental combustor on-site at NETL. The fly-ash sample examined resulted from the combustion of a Pittsburgh-seam coal from the Black Creek mine. Carbon concentrates, derived from the fly ash, were obtained and had about 52% carbon content. The amine, 3-chloropropylamine-hydrochloride (CPAHLCL), and the potassium hydroxide were reagent grade chemicals purchased from Aldrich Chemical Company. The quantity of ten grams of fly ash carbon concentrate was treated with 500 ml of $1\times10^{-3}$ molar 3-CPAHLCL salt solution with and without $1\times10^{-2}$ molar potassium hydroxide for 1 h at 25°C. The treated amine-enriched fly ash carbon concentrate was filtered and dried in an oven for 1 h at 105°C. The final amine-enriched fly ash concentrations were then tested as $\text{CO}_2$ capture sorbents in the DRIFTS/TPD reactor system. Additionally, the amount of nitrogen on the surface of the amine-enriched fly ash carbon sorbent was determined by XPS (N1s peak) analysis.
In order to understand the reaction of CO$_2$ on these amine-enriched solids and assess their relative CO$_2$ uptake capabilities, adsorption studies followed by a temperature programmed desorption (TPD) technique were conducted under ambient pressure and at temperatures between 30 and 120°C. Figure 63 illustrates a schematic of the experimental system. All gas flows to the system were regulated with Brooks 5850 mass flow controllers. The 4-port valve allowed for ease of switching between He and 10% CO$_2$/He flows to the reactor system; moisture was added to either flow stream via a water saturator maintained at ambient temperature (partial pressure of H$_2$O was 23.4 mmHg). A sample charge of 100 mg was used in each experiment; approximately 15 mg was placed into a Spectra Tech diffuse reflectance infrared Fourier transform infrared spectroscopy (DRIFTS) reactor while the remaining sample was charged to a tubular reactor connected to the effluent of the DRIFTS. Separate temperature control systems existed on each reactor. The sample in the DRIFTS reactor was examined in situ via a Nicolet Magna 560 infrared spectrometer (IR), allowing observation of CO$_2$ adsorbate formation/desorption on the sample surface. The gaseous effluent from the DRIFTS-tubular reactor was continuously analyzed by a Balzers QMG 112 mass spectrometer (MS), allowing determination of the CO$_2$ concentration in the effluent stream. Capture capacities of the different amine-enriched samples were calculated by MS analysis of the CO$_2$ (m/e = 44) desorption profile.

Each sample was first exposed to He at a flow rate of 30 ml/min for 3 hours, prior to any further experiment, to clean the sample surface (confirmed by observing stable background signals of both IR and MS). For the CO$_2$ absorption study, He flow was then replaced with 10% CO$_2$ in He at ambient conditions. The moisture content plays an important role in the CO$_2$ adsorption process; formation of CO$_2$-amine complexes takes place only in its presence. Therefore, after the exposure to 10% CO$_2$ in He, the flow was redirected through an H$_2$O saturator; the CO$_2$/H$_2$O/He
flow over the surface of the sample was maintained for 30 minutes. The CO$_2$/H$_2$O/He stream was then replaced by H$_2$O/He flow to expunge the system of gaseous CO$_2$.

For the TPD study, the H$_2$O/He flow was finally replaced with pure He flow to monitor desorption of adsorbed CO$_2$. Both reactors were heated, simultaneously, from 30 to 120°C at a rate of 10°C/min and maintained at 120°C for an additional 20 min. CO$_2$ desorption amounts were calculated by separate calibration factors that were obtained during each experiment. The calibration factors were obtained by pulsing 1 cc volumes of the 10% CO$_2$/He (4.089 micromol CO$_2$) directly to the MS using a 6-port valve. The CO$_2$ pulse profile (m/e = 44) was integrated and a calibration factor was calculated, equating areas to moles of CO$_2$. Using this calibration factor, the integrated CO$_2$ desorption curve could be converted into moles of CO$_2$ eluted (Soong et al., 2001).

Sample regeneration was also assessed via reusing a sample following its adsorption/desorption techniques. Following the TPD, the sample was cooled to ambient temperature and its surface was again cleansed via He flow for 3 h. This was followed by conducting the adsorption and desorption techniques, described above, again.

From XPS analysis of the prepared samples, there was an increase in the nitrogen content when these fly ash carbon concentrates were reacted with 3-CPAHCL with and without the presence of potassium hydroxide. Based on these results shown in Table 1, it is apparent that these fly ash carbon concentrates are slightly reactive with the 3-CPAHCL under these conditions. Since Sample 95C resulted in the highest nitrogen content, the presence of potassium hydroxide was not required for the incorporation of amine onto the surfaces of these fly ash carbon concentrates. (Gray et al., 2004a).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Chemical Treatment</th>
<th>XPS N1s (%) on surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>59 Feed fly ash</td>
<td>None</td>
<td>Not detected</td>
</tr>
<tr>
<td>95 Carbon</td>
<td>None</td>
<td>0.81</td>
</tr>
<tr>
<td>95A Carbon</td>
<td>CPAHCL and KOH</td>
<td>1.11</td>
</tr>
<tr>
<td>95B Carbon</td>
<td>KOH only</td>
<td>0.83</td>
</tr>
<tr>
<td>95C Carbon</td>
<td>CPAHCL only</td>
<td>1.29</td>
</tr>
</tbody>
</table>

These sorbents have shown the ability to capture CO$_2$ from a gas stream in the presence of moisture. The amine treated fly ash carbon concentrates (95A, 95B, and 95C – refer to Table 25 above) were examined as CO$_2$ capture sorbents. These sorbents were placed in a 10% CO$_2$/H$_2$O/He gas stream and DRIFTS, TPD, and MS analyses were conducted to determine the CO$_2$ capture capacities. The adsorption/desorption of CO$_2$ for these sorbents were determined at 25°C (adsorption) and 120°C (desorption). According to the DRIFTS spectra, formation of the corresponding carbamate-amine product was indicated and the other peak revealed adsorption of CO$_2$. From the fixed bed reactor, desorption of CO$_2$ was observed as the temperature was increased to 120°C. The overall CO$_2$ capture capacities are summarized in Table 26. As shown, the adsorption of CO$_2$ in samples 59 and 95 increased with the amine chemical treatment. Without treatment, they did show some CO$_2$ capture capability, but treatment enhanced their
performance. The best sample was 95C, which had the CO₂ capture capacity of 174.5 micromol/g, and was regenerable for an additional test (140.6 micromol/g) (Gray et al., 2004a; Soong et al., 2001). It was reported that the initial tests with these type of sorbents in the presence of air (oxygen) were successful (Gray et al., 2001).

Table 26: TPD CO₂ desorption results of substrates and sorbents

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Chemical Treatment</th>
<th>CO₂ release μmol/g sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>59 Feed fly ash</td>
<td>None</td>
<td>24.4</td>
</tr>
<tr>
<td>95 Carbon</td>
<td>None</td>
<td>72.9</td>
</tr>
<tr>
<td>95A Carbon</td>
<td>CPAHCL and KOH</td>
<td>81.1</td>
</tr>
<tr>
<td>95B Carbon</td>
<td>KOH only</td>
<td>117.9</td>
</tr>
<tr>
<td>95C Carbon</td>
<td>CPAHCL only</td>
<td>174.6</td>
</tr>
<tr>
<td>95C Carbon (regenerated)</td>
<td>CPAHCL only</td>
<td>140.6</td>
</tr>
</tbody>
</table>

Results were very encouraging from this initial foray using amine-enriched sorbents for CO₂ capture. Although it was noted that improvements in utilization were needed, the first indications were that these type of sorbents were capable of carbon capture followed by regeneration. This work led to possibilities in sorbent improvement by investigating the chemical composition variables, such as type of amine and substrate, along with novel fabrication procedures.

**Silica-based Aminated Sorbents**

Although the initial testing with carbon-supported sorbents was successful, certain improvements were needed. One was the CO₂ capture capacity, which was on the low side with the carbon-based sorbents. Another was the consistency of the substrate. With carbons extracted from fly ash, there are numerous factors that can impact the resulting substrate: the type of coal, the combustion conditions, and the processing of the fly ash to produce the carbon. Also, the final use of the material in a commercial environment must be considered. The carbon extracted from fly ash is typically very small particles and would most likely need to be bound to form larger particles that could be used in actual reactor (i.e., packed bed, moving-bed, and fluid-bed) systems. In addition, safety in a post-combustion atmosphere is always realized but the combination of an amine with a carbon utilized in an oxidizing atmosphere could lead to a potential combustibility issue. For the above reasoning, the emphasis of the sorbent development shifted to a silica-based substrate. This type of support is readily available on a commercial scale and is used as the support for numerous commercial sorbent and catalytic processes. The beginning of investigations with various amines also commenced during this time frame.

In the initial study with silica supports, the objective was to investigate the CO₂ adsorption/desorption process on mesoporous SBA-15 silica grafted with (aminopropyl)triethoxysilane (APTS) (Chang et al., 2003). The NH₂-functional group in APTS could provide CO₂ adsorption sites, and silane offers the linkage to bind APTS to the SBA-15 surface. Additionally, SBA-15 possesses a high surface area for grafting APTS, a large uniform
pore size to facilitate CO$_2$ diffusion inside of the pore, and a wall thickness of 35-65 Å that provides a stable structure under hydrothermal conditions.

SBA-15 was prepared by using TEOS (tetraethyl orthosilicate) as a silica precursor, Pluronic P123 (PEO20PPO70PEO20, poly-(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) as a template, TMB (1,2,3-trimethylbenzene) as an expander, and HCl to control pH. The specific steps for preparation of SBA-15 consist of (1) dissolving 4.0 g of Pluronic P123 in 30 g of water and 120 ml (2.0 M) of HCl solution at room temperature, (2) mixing the resultant solution with 30 g of TMB at 308 K for 2 h, (3) adding 8.5 g of TEOS into the resultant homogeneous solution and stirring it at 308 K for 22 h, (4) aging the solution without stirring at 393 K for 24 h, and (5) calcining the resultant solid particles from filtering the aging solution in flowing air at 3 K/min to 773 K and holding it at 773 K for 6 h.

The surface area of the untreated SBA-15 (200–230 m$^2$/g) and sorbent was determined by N$_2$ BET measurement at 77 K; the pore size was determined to be 21 nm by small-angle X-ray scattering analysis.

SBA-15 grafted with gamma-(aminopropyl)triethoxysilane (APTS) was prepared by impregnating an APTS/toluene solution into SBA-15. The impregnated sample was heated at 423 K for 20 h in a vacuum oven to obtain APTS-SBA-15. APTS-SBA-15 denotes the SBA-15 grafted with APTS. X-ray photoelectron spectra (XPS) of SBA-15 and APTS-SBA-15 were determined by a PHI5600ci instrument with monochromatic Al K-alpha X-rays.

The adsorption/desorption studies were conducted in an experimental apparatus as shown in Figure 63, which includes a flow control manifold, a H$_2$O saturator, a high temperature/pressure diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell with a Fourier transform infrared spectrometer, a fixed bed reactor, and a mass spectrometer (MS). [NOTE: Description and schematics of reactor systems may appear to be repetitive. However, subtle differences in sample sizes, flow rates, and operational procedures, as well as modifications/improvements to the system, make the repetition valuable in further understanding the experimental results.] The flow control manifold consists of (a) a 4-port valve for switching the flow from He to He/CO$_2$, (b) a 6-port valve for the injection of a known amount of CO$_2$ for calibration, and (c) a 4-port valve for bringing water vapor into the inlet flow via a saturator. Each adsorption study employed 20 mg of APTS-SBA-15 for the DRIFTS cell and 180 mg for the fixed bed. Sorbent (200 mg) was exposed to a 30 ml/min He flow at 298 K for 1 h to obtain a stable MS baseline for CO$_2$ and IR background spectra. The valve was then switched to allow He to flow through the H$_2$O saturator for adding moisture (23.4 mmHg partial pressure of water vapor) into the inlet He flow. Adsorption of CO$_2$ on APTS-SBA-15 was initiated by a step switch from the He/H$_2$O stream to the CO$_2$/He/H$_2$O stream. The flow rate of both streams was kept at 30 ml/min to obtain a step change in CO$_2$ concentration. The CO$_2$ stream entering the IR cell contains 4% of CO$_2$ and 23.4 mmHg partial pressure of water vapor balanced with helium. Adsorbed CO$_2$ was removed by temperature programmed desorption (TPD) in a flow of He or He/H$_2$O at 30 ml/min at a heating rate of 10 K/min from 298 to 393 K and holding at 393 K for 1 h. He/H$_2$O flow contains a partial pressure of 23.4 mmHg of water vapor. The effluent composition of the DRIFTS/ixed bed reactor was determined by MS; infrared spectra of the adsorbed species during TPD were collected by DRIFTS. Calibration of CO$_2$ (m/e = 44 intensity) was carried out by injecting 1 ml of 4% CO$_2$ into 30 ml/min He stream. The CO$_2$ MS calibration factor was obtained by dividing the area under the CO$_2$ MS curve by the number of moles of CO$_2$ injected.
Figure 64: Transmission infrared spectra of SBA-15, fresh APTS-SBA-15, and regenerated APTS-SBA-15.

The transmission infrared spectra of SBA-15, fresh and regenerated APTS-SBA-15 are shown in Figure 64. The regenerated APTS-SBA-15 underwent 3 cycles of CO$_2$ adsorption/desorption. The decrease in the OH intensity as well as the presence of the N-H bands and the C-H bands suggests that APTS had been grafted on the surface of SBA-15. The grafting reaction depleted the majority of the available OH on the SBA-15 surface. Fresh and regenerated APTS-SBA-15 show nearly identical IR intensity for the N-H and C-H bands, indicating that the grafted APTS stays intact during CO$_2$ adsorption/desorption cycles. Further IR studies were conducted by flowing CO$_2$ over APTS-SBA-15. IR spectra indicate that bidentate bicarbonate, bidentate carbonate, monodentate bicarbonate, and monodentate carbonate are produced. A minor amount of carbamic acid could be present (Chang et al., 2003).

The XPS intensity ratios listed in Table 27 show that the N/Si ratio remained at the same level after repeated adsorption/TPD of CO$_2$ in either He or H$_2$O/He environment. The XPS results further confirmed that grafted APTS stayed intact on the SBA-15 surface during CO$_2$ adsorption/desorption cycles. No change in surface area was observed during the cycling.
Table 27: XPS and BET results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Intensity Ratio</th>
<th>BET Surface Area (m²/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C/Si</td>
<td>N/Si</td>
</tr>
<tr>
<td>Untreated SBA-15</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Fresh sample (APTS-SBA-15)</td>
<td>1.5</td>
<td>0.34</td>
</tr>
<tr>
<td>He TPD regenerated sample</td>
<td>1.35</td>
<td>0.32</td>
</tr>
<tr>
<td>H₂O/He TPD Regenerated Sample</td>
<td>1.32</td>
<td>0.33</td>
</tr>
</tbody>
</table>

CO₂ MS intensity profiles are shown in Figure 65. The CO₂ MS intensity profile reflects the relative CO₂ concentration versus time at the effluent of the fixed bed reactor during CO₂ adsorption. The sharp decrease in CO₂ MS intensity profile in Figure 65 and the growth of IR bands for adsorbed CO₂ species reflect the rapid CO₂ adsorption on the APTS-SBA-15. The CO₂ MS intensity was returned to the initial level upon saturation of the adsorption sites with CO₂. The area of the resulting “well” in the CO₂ MS profile corresponds to the amount of CO₂ adsorbed. The fresh APTS-SBA-15 adsorbed about 30% less CO₂ than the regenerated one and may be due to partial saturation of APTS-SBA-15 with ambient CO₂ prior to the CO₂ adsorption study. Regenerated APTS-SBA-15 by TPD in He/H₂O flow exhibited a higher CO₂ adsorption/desorption capacity than those regenerated by TPD in only He (average 381 versus 289 micromole/g). The enhanced CO₂ adsorption capacity on the sorbent regenerated by TPD in He/H₂O can be understood by the fact that H₂O is needed to react with CO₂ to produce carbonate and bicarbonate (Chang et al., 2003).

Figure 65: CO₂ MS intensity profiles during CO₂ adsorption.
The sorbent was also compared with a commercially available immobilized amine sorbent (labeled IAS for brevity) that can be used in aircraft, submarine, and spacecraft technologies (Gray et al., 2004b). The experimental technique used was similar to that described above. The chemical CO$_2$ capture capacities were determined by the combination of TPD and MS analyses. The adsorption of CO$_2$ was achieved in the presence of moisture at 25°C, and the total desorption of CO$_2$ was achieved over the temperature range 30–60°C. The composition of the experimental gas stream used in these test runs was 10% CO$_2$/He saturated with water at 25°C.

Initially, the performance of the prepared amine-enriched silicon sorbent (APTS-SBA-15) was compared to the IAS. Each sorbent was placed in a 10% CO$_2$/H$_2$O/He stream and TPD and MS analyses were conducted to determine the performance of these CO$_2$ capture sorbents. The adsorption/desorption of CO$_2$ for these sorbents were determined over the temperature range 25-60°C. According to the TPD/MS analysis, all of the sorbents were successful in the capture of CO$_2$ from the moist experimental gas streams. The comparisons of the CO$_2$ capture performances and XPS results for these sorbents are summarized in Table 28. Work with titania-supported sorbent prepared in a similar manner was conducted. Nitrogen surface content as determined by XPS was much lower than the results from the other sorbents reported in Table 28. Additionally, the captured CO$_2$ was also lower (1057.2 micromol/g sorbent) (Gray et al., 2003a).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>μmol/g CO$_2$ captured</th>
<th>XPS % nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-fresh</td>
<td>2011.4</td>
<td>7.1</td>
</tr>
<tr>
<td>SBA-15-1st regeneration</td>
<td>1908.5</td>
<td>NA</td>
</tr>
<tr>
<td>SBA-15-2nd regeneration</td>
<td>1748.3</td>
<td>NA</td>
</tr>
<tr>
<td>IAS-fresh</td>
<td>1603.9</td>
<td>17.7</td>
</tr>
<tr>
<td>IAS-1st regeneration</td>
<td>1922.6</td>
<td>NA</td>
</tr>
<tr>
<td>IAS-2nd regeneration</td>
<td>1528.1</td>
<td>NA</td>
</tr>
</tbody>
</table>

As shown in Table 28, the APTS-SBA-15 had a lower % nitrogen value of 7.1 versus the IAS % nitrogen value of 17.7. Despite the differences in the nitrogen values, the sorbents had similar average CO$_2$ capture capacities. The APTS-SBA-15 and the IAS sorbent were regenerated at 60°C over two additional test runs and the average CO$_2$ capture capacity values were 1889 micromol/g and 1,820 micromol/g, respectively. The CO$_2$ capture capacity of these sorbents is dependent on several factors: a) basicity of the amine site for the formation of the carbamate ion; b) accessibility, distribution, and orientation of the amine sites; and c) surface area of the sorbents. Since the SBA-15 and IAS had similar basicities and surface areas of 227 versus 219 m$^2$/g, the potential major factors in affecting the performance of these sorbents are the accessibility, distribution, and orientation of the amine sites within the structure of these sorbents. The preparation of the IAS requires the evaporation and/or adsorption of the amines into the pores of the solid substrate, which may lead to multi-layering, uneven distribution, and limited access to all of the amine sites required for the capture of CO$_2$. However, the amine sites incorporated into the structure of the SBA-15 are chemically bonded or strongly absorbed to the
OH sites on the surface, which creates a more uniform distribution of the amine sites. Consequently, the majority of the amine sites on the SBA-15 are accessible for the capture of CO₂. Thus, the surface area, accessibility, distribution and orientation of the available amine sites all have the potential of playing an important role in the performance of these solid amine CO₂ capture sorbents (Gray et al., 2004b).

**Different Amines on Silica**

The APTS amine initially showed favorable results. However, variations in the sorbent fabrication process were conducted in order to improve the CO₂ capture capacity. Two trains of thought emerged at this juncture. The first was to again bond the amine to the support with a silane, but to use a diamine to increase the number of nitrogen-reactive sites. The adsorption capacity can be further increased if the surface density of amine functional groups per gram of sorbent is increased. A way to improve the surface density of amine functional groups is to graft a diamine containing two amine groups per molecule. The second was to use a secondary amine rather than primary. Better thermal efficiency in the regeneration process could be realized.

With respect to the diamine, the strategy to develop a high CO₂ adsorption capacity sorbent is to graft amine functional group(s)-containing species onto the high surface area supports, such as SBA-15, by the silanation approach. A high surface area support will allow grafting a larger number of active amine sites per gram of support. The nature of the grafted amine functional groups (primary or secondary amine) will determine the amount of CO₂ adsorbed and the energy required for regenerating the sorbent.

In the diamine study (Khatri et al., 2005), the objectives were to investigate the grafting of diamine on the high surface area mesoporous silica material, SBA-15, and to determine the CO₂ adsorption capacity of the diamine-grafted SBA-15. SBA-15 was prepared by using Pluronic 123 as a structure-directing agent, HCl solution for pH control, 1,3,5-trimethylbenzene as a pore expander, and tetraethyl orthosilicate as a silica precursor. The specific fabrication steps were similar to those described in the previous section. Amine-grafted SBA-15 was prepared by (i) heating 1 g of SBA-15 at 110°C in a vacuum for 6 h, (ii) impregnating 2.4 ml of [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane (i.e., diamine) in 4 ml of a toluene solution onto the pretreated SBA-15, and (iii) heating the impregnated SBA-15 at 150°C for 20 h in a vacuum oven.

The experimental system used in the study was a DRIFTS reactor that was described previously and shown in Figure 63. The DRIFTS reactor was filled with 30 mg of sorbent followed by a tubular reactor filled with 300 mg of sorbent, and a mass spectrometer. The tubular reactor allowed packing of a sufficient amount of sorbent for adsorbing CO₂, giving the change in the CO₂ effluent concentration for MS measurement. The surface-adsorbed species were monitored by the DRIFTS reactor (Spectra Tech) placed inside a Nicolet 560 FT-IR bench, and the effluent of the reactors was simultaneously analyzed with a Pfeiffer QMS 200 quadrupole mass spectrometer. A 10 vol% CO₂ in helium was present in the inlet gas. Procedures for experimentation can be found elsewhere (Khatri et al., 2005).
Table 29: CO₂ capture capacity of amine-enriched sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>CO₂ Capture Capacity (μmol/g of sorbent)</th>
<th>Adsorption/Desorption Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoamine-treated mesoporous silica (MCM-48)</td>
<td>1136</td>
<td>TGA and TPD</td>
</tr>
<tr>
<td>Amine-treated mesoporous silica (SBA-15)</td>
<td>400</td>
<td>MS and TPD</td>
</tr>
<tr>
<td>Polymer amine-based sorbent (HSC+)</td>
<td>909</td>
<td>TGA</td>
</tr>
<tr>
<td>Amine-treated silica gel</td>
<td>898</td>
<td>GC</td>
</tr>
<tr>
<td>Diamine-treated mesoporous silica (SBA-15)</td>
<td>768</td>
<td>MS and TPD</td>
</tr>
</tbody>
</table>

Figure 66 shows the MS intensity of CO₂ over a diamine-treated sorbent. The TPD study was carried out using a CO₂ partial pressure of 0.5 atm. The amount of CO₂ desorbed from the sorbent was 786.5 micromol/g, as calculated from the MS intensity profile of CO₂ during TPD. The amount of TPD-desorbed CO₂ was at the levels of the commercial polymer amine sorbent used for CO₂ capture in submarines and space shuttles and other amine-based sorbents reported in the literature, as shown in Table 29.

From the experimental study with this sorbent, insight is provided into the mechanism of diamine grafting on SBA-15 with in situ IR spectroscopy. The isolated surface hydroxyl groups are active moieties on the SBA-15 surface for reaction with methoxy groups of diamine-containing silanes. CO₂ adsorbs on the primary and secondary amine groups, forming carbonate, bicarbonate, and carbamic acid species. The major species formed by the adsorption of CO₂ on the surface are monodentate bicarbonate, bidentate bicarbonate, and bidentate carbonate. The bidentate bicarbonate species bind stronger to the diamine-grafted SBA-15 than bidentate carbonate. The amount of CO₂ desorbed from the carbonate and bicarbonate between 30 and 120°C is 2 times more than that of CO₂ adsorbed/desorbed during each cycle of the
concentration-swing adsorption/desorption. The CO₂ capture capacity of diamine-grafted SBA-15 is double that of mono-amine (APTS) grafted SBA-15 in a temperature-swing (25–120°C) process (Khatri et al., 2005). However, the overall CO₂ capture performance capacity was still relatively low, and new amines that could improve the capacity while reducing the regenerative heat duty were desired.

Secondary amines provide a way to improve sorbent utilization and overall regenerative heat duty as compared to primary amines. In another study (Gray et al., 2005), the results of a previous investigation (Gray et al., 2004b) were expanded to include a sorbent with a secondary amine. The one sorbent was a proprietary immobilized amine sorbent (IAS) that was commercially available and could be used in aircraft, submarine, and spacecraft technologies. The other sorbent was a bonded amine (APTS) on SBA-15 silica. The newer sorbent was a reformulated immobilized amine sorbent (R-IAS) with ethyleneamine.

The silica support, SBA-15, was prepared by using a previous procedure (Gray et al., 2004b). SBA-15 grafted with gamma-aminopropyltriethoxysilane (APTS) was prepared by impregnating an APTS/toluene solution into SBA-15 (see Gray et al., 2004b). The impregnated sample was heated at 423 K for 20 h in a vacuum oven to obtain APTS-SBA-15, denoted in this discussion as Aminated-SBA-15. The reformulated immobilized amine sorbent (R-IAS) was prepared by the method with ethyleneamine E-100 from Huntsmans. The secondary amine was prepared by reacting ethyleneamine E-100 with acrylonitrile and immobilized in a solid substrate. The exact composition of the reformulated secondary ethyleneamine-based sorbent was not presented due to its patentability at that time (Gray et al., 2005).

The chemical CO₂ capture capacities were determined by the combination of temperature programmed desorption (TPD) and mass spectrometry (MS) analyses. X-ray photoelectron spectroscopy (XPS) measurements determined the percent nitrogen on the surface of the aminated sorbent. These techniques for the experimental investigation are discussed previously.

Each sorbent was placed in a 10% CO₂/H₂O/90%He stream and TPD and MS analyses were conducted to determine their performance. The adsorption/desorption of CO₂ for these sorbents were determined over the temperature range of 25–60°C. Desorption curves were used to determine the amount of CO₂ adsorbed. An average value combining three consecutive runs is used. The reproducibility of the TPD/MS measurement is typical within 5%. According to the TPD/MS analysis, all of the sorbents were successful in the capture of CO₂ from the moist simulated flue gas streams.
The comparison of the CO₂ capture performances and XPS results for these sorbents are summarized in Table 30. The aminated SBA-15 had a lower nitrogen surface concentration value of 7.1% (atomic) versus the IAS nitrogen value of 17.7%. The aminated SBA-15 sorbent was prepared with a primary amine (propyl amine type) while the exact type of the amine used in the IAS was unknown. According to the patents, the preparation of the IAS requires the evaporation and/or adsorption of the amines into the pores of the solid substrate, which may lead to multilayering, uneven distribution and limited access to all of the amine sites required for the capture of CO₂. Because of the procedure used to prepare the aminated SBA-15 sorbent, the amine sites incorporated into the structure of the aminated SBA-15 are chemically bonded or strongly absorbed to the OH sites on the surface. This should result in a more uniform distribution of the amine sites compared to the IAS sorbent. Despite the differences in the nitrogen values, the sorbents had similar average CO₂ capture capacities. After regeneration at 60°C, the aminated-SBA-15 and the IAS sorbents were retested in two consecutive cycles. The average CO₂ capture capacity values over all three cycles were observed to be 1,889.4 micro-mol CO₂/g and 1820.8 micro-mol CO₂/g for the aminated SBA-15 and IAS sorbent, respectively. Noting that the amine nitrogen concentration, as determined by XPS, is greater for the IAS sorbent than for the SBA-15 sorbent in the near surface layer (~50 angstrom), it appears that the majority of the amine sites on the aminated SBA-15 are more accessible for the capture of CO₂ resulting in similar capture capacities. However, in comparison to the other sorbents, the performance of the R-IAS was significantly better than the other two sorbents when tested under similar conditions. With an increase in the secondary ethyleneamine loading in the R-IAS, which is indicated by the higher nitrogen value of 21.9%, the average CO₂ capacity was increased to 3,015.6 micromol CO₂/g. It is assumed that the higher CO₂ capture capacity of the R-IAS may be partially attributed to the increase loading of the secondary ethyleneamine. However, in all cases, there were decreases in the CO₂ capture capacities upon regeneration, which may indicate instability in the amines used in these sorbents or that desorption of the CO₂ was incomplete (Gray et al., 2005).

### Table 30: TPD/MS CO₂ adsorption and XPS data for the amine-enriched sorbents

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>μmol CO₂/g sorbent</th>
<th>XPS % nitrogen (N1s peak) surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>*SBA-15-fresh</td>
<td>2011.4</td>
<td>7.1</td>
</tr>
<tr>
<td>*SBA-15-1st regeneration</td>
<td>1908.5</td>
<td>NA</td>
</tr>
<tr>
<td>*SBA-15-2nd regeneration</td>
<td>1748.3</td>
<td>NA</td>
</tr>
<tr>
<td>IAS-fresh</td>
<td>1603.9</td>
<td>17.7</td>
</tr>
<tr>
<td>IAS-1st regeneration</td>
<td>1922.6</td>
<td>NA</td>
</tr>
<tr>
<td>IAS-2nd regeneration</td>
<td>1528.1</td>
<td>NA</td>
</tr>
<tr>
<td>R-IAS-fresh</td>
<td>4188.1</td>
<td>21.9</td>
</tr>
<tr>
<td>R-IAS-1st regeneration</td>
<td>2690.2</td>
<td>NA</td>
</tr>
<tr>
<td>R-IAS-2nd regeneration</td>
<td>2169.4</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA=not analyzed  
* Aminated-SBA-15
The initial success with the secondary amines directed pursuit of a patent pertaining to the fabrication of a sorbent (Gray et al., 2008). The method entails treating an amine to increase the number of secondary amine groups and impregnating the amine into a porous solid support. Ultimately this increases the CO\textsubscript{2} capture capacity and decreases the cost of utilizing amine-enriched solid sorbent in CO\textsubscript{2} capture systems. The protocol has two major steps: modification of an amine and then impregnation of the support substrate with the modified amine. In the first step, a nucleophilic primary amine attacks a reactant to add across a carbon-carbon double bond to create a secondary amine in a Michael addition reaction. In the second step, the now created amine is contacted with a support substrate having a suitable surface area for a time and at a temperature sufficient for the modified amine to impregnate the pores of the support structure. Optionally, the modified amine is contacted with the support substrate in the presence of a solvent that reduces surface tension. The amine is not chemically bonded to the surface of the substrate, but rather immobilized within its pore structure. The final product behaves like a solid sorbent.

Temperature dependent adsorption profile curves for a sorbent (139a) are shown in Figure 67. The sorbent was similar to the secondary amine enriched sorbent reported above and was fabricated using the novel technique. Ethyleneamine is reacted with acrylonitrile and deposited within a polymethylmethacrylate support. XPS nitrogen results indicated a 21.9 surface concentration that is identical to the previously described reformulated ethyleneamine deposited within SBA-15 (Gray et al., 2005). CO\textsubscript{2} capture capacity is reported for temperatures ranging from between 25 and 65°C. As shown in Figure 67, the sorbents capture CO\textsubscript{2} above ambient temperatures with increased CO\textsubscript{2} capture capacities, ranging from 3,411 to 6,615 micromol/g sorbent.
Figure 67: Adsorption breakthrough curves for sorbent 139a at various temperatures.

The success of these type of newer sorbents could improve the capture capacities, the regenerability, cost reduction, and stability of the sorbents. Although the sorbent development was on track for these sorbents, goals and targets were needed in order to realistically place the sorbents into a commercial CO₂ capture system. This, in turn, required a further study of these sorbents and led to the MATRIC report and subsequent establishment of targets that is discussed in Section 4.3.2.

4.2.2 Early Encapsulated Amine Clay-Based Sorbent Studies

Amine-enriched sorbent with a clay-based substrate was another type of sorbent that was developed during the initial sorbent research phase at NETL. The method for fabricating the sorbent involves treating substrates with an amine and/or an ether so that the amine and/or ether comprise at least 50 wt% of the sorbent. The sorbent acts by capturing compounds contained in gaseous fluids via chemisorption and/or physisorption between the layers of the substrate lattice where the polar amine/ether is located. The sorbents can be regenerated by heating to temperatures in excess of 35°C (Siriwardane, 2005).

The process for producing an encapsulated amine and/or ether-enriched clay-based sorbent comprises first, adding an amine to a substrate, mixing the amine and the substrate, and drying the product formed. The interaction between the amine and CO₂ is a chemical reaction which can form a carbamate. Bicarbonates could be formed at high CO₂ concentrations. A salient feature of the sorbent is that the absorption properties of the amine sorbent produced by the process are independent of the surface area. Amines could be primary, secondary, tertiary, aromatic or cyclic.
The sorbent is prepared utilizing substrates capable of providing reaction surfaces on other than the external surfaces of the substrate. These substrates are homogeneously and thoroughly mixed with inorganic and organic liquids/solids that are reactive with gases, such as CO$_2$. Preferable organic liquids and solids come from the group comprising of amines and ethers. The organic liquids and organic solids comprise at least 50 wt% of the sorbent.

In general, any substrate that can accommodate a plurality of reaction sites within its confines is suitable. For example, a solid that has a layered structure which can expand to allow polar molecules to reside within is suitable. Clays are excellent substrates for the sorbents since they have the ability to retain a large quantity of polar liquids, such as water and amines, between their unit layers, causing the clay lattice to expand to provide internal reaction cavities.

Various sorbents with an amine or ether have been tested. Competitive gas adsorption studies and temperature programmed desorption studies were conducted in a laboratory-scale fixed-bed reactor (Micromeritics model Autochem 2910 atmospheric flow reactor) at 14.7 psi and 25°C at a flow rate of 5-cc/min. The gas mixture had a typical composition of 15 vol % CO$_2$, 82 vol % N$_2$, and 3 vol % O$_2$, and was bubbled through water at 25°C to saturate the gaseous mixture with water vapor before the mixture was introduced to the sorbent. The outlet gas stream from the reactor was analyzed using a mass spectrometer (Pfeiffer Vacuum Thermostar).

An example of one of these types of sorbents is the combination of diethanolamine (DEA) with bentonite (Siriwardane, 2005). The sample was prepared by combining 20-g of bentonite, 8-g of calcium sulfate dihydrate, and 3-g of anhydrous calcium sulfate desiccant. These substances were combined in a mixer to produce a homogeneous blend. Twenty grams of DEA were mixed with 6.5-g of ethylene glycol monooctylether and 2-ml of water. Twenty ml of this liquid mixture was added slowly to the solid mixture while stirring to create a homogeneous combination having the same consistency throughout. Pellets eventually were formed and were dried in an oven for one hour at 60–80°C. The amount of diethanolamine bentonite (DEAB) placed in the reactor for flow studies was 1.16-g.
In Figure 68, the adsorption isotherms of pure CO$_2$ and pure N$_2$ over DEAB are plotted. The upper curve is for pure carbon dioxide and the lower curve for pure nitrogen. As the equilibrium pressure is increased, the moles of gas absorbed per kg of sorbent increases. As the equilibrium pressure becomes greater, near the end of the two curves, the slopes of the curves decrease due to oncoming saturation of the sorbent and lack of availability of active sites for absorption.
Figure 69: Sorption of CO₂ on DEAB as a function of time.

The reactor exit gas concentrations of CO₂, O₂, and N₂ over DEAB are plotted versus time in Figure 69. The CO₂ concentration decreased to ppmv levels while the N₂ concentration increased. The sorbent was exposed to the gas mixture at point A. After approximately 50 minutes, breakthrough occurred as evidenced by a rising CO₂ concentration at point BB. The oxygen concentration remains approximately the same, but there is a slight increase due to volumetric gas change related to CO₂ removal. When the curve begins to rise above the CO₂ concentration of zero, the sorbent has become saturated with CO₂.
Figure 70: Cumulative sorption of CO$_2$ on DEAB.

Figure 70 is a graph of the sorption of CO$_2$ over DEAB in moles of CO$_2$ absorbed per kg of sorbent as a function of time and was calculated from the previous figure. The absorption of the gas into the sorbent follows straight-line behavior, with the slope approaching zero as the sorbent approaches saturation with the gas. The total uptake of CO$_2$ at breakthrough was about 1.2 moles CO$_2$ per kg of sorbent.

Regeneration studies were carried out using nitrogen as a sweep gas to regenerate the sorbent. Either an inert gas sweep or a vacuum could be used for sorbent regeneration in conjunction with a temperature swing at less than 50°C. Results indicated that the temperature and time duration of regeneration were important parameters. CO$_2$ uptake capacity during subsequent sorption cycles for sorbents is higher when regeneration is performed at higher temperatures, such as 60 or 80°C. A longer regeneration time also results in a higher CO$_2$ uptake in subsequent sorption cycles (Siriwardane, 2005).

Results for a ten-cycle test with DEAB sorbent are shown in Figure 71. Regeneration was carried out at 38°C while the spent sorbent was purged with nitrogen. Consistent data and CO$_2$ absorption capacities were obtained and indicate that sufficient regeneration could be achieved at 38°C with this sorbent sample.
Figure 71: Absorption of CO₂ on DEAB sorbent after successive regenerations.

Figure 72: Effect of regeneration temperature on CO₂ absorption for DEAB sorbent.
Another multi-cycle test was carried out for DEAB sorbent (see Figure 72). Regeneration under a flow of nitrogen was carried out at 50°C for 1, 2, and 3 hours; at 60°C for 1 and 2 hours; and at 80°C for 1 hour. The curves in Figure 72 are labeled with the temperature at which regeneration was carried out and the time period for that regeneration. Very consistent CO₂ absorption/uptake was observed after a given regeneration temperature and heating time period. An example can be seen in the breakthrough curves that are very similar when the regeneration was conducted at 50°C for 1 hour. Again, the CO₂ uptake capacity was greater when the regeneration was performed at a higher temperature. At a given temperature, higher regeneration time also resulted in higher CO₂ uptake in the following sorption cycle.

Initial studies indicated that the liquid-impregnated solid sorbent can go through numerous absorption/regeneration cycles. As seen, sorbent regeneration tests were not only conducted at near ambient temperature with nitrogen, but also regeneration tests were conducted at 50, 60, and 80°C. Better CO₂ sorption capacities were observed when the sorbent was regenerated at these higher temperatures. The presence of water vapor did not affect sorbent performance. In a realistic carbon capture scenario, to obtain a concentrated gas stream of CO₂, regenerations have to occur either with a gas stream containing steam or in the presence of a mild vacuum. Since the presence of steam does not appear to affect sorbent performance, regeneration in the presence of steam would be a reasonable choice. The ability to regenerate the sorbent at lower temperatures and the resistance to steam were advantages of this type of sorbent (Siriwardane et al., 2004).

Like the previously discussed immobilized amine on support category of sorbent, the initial findings with the encapsulated amine clay-based category were very promising. However, goals and targets were needed in order to realistically place the sorbent into a commercial CO₂ capture system. This led to the establishment of targets that is discussed next.

4.3 TARGET ESTABLISHMENT FOR POST-COMBUSTION USAGE OF AMINE-ENRICHED SORBENTS WITH REACTOR DESIGN CONSIDERATIONS

The early stages of the amine-enriched sorbent research led to exciting results that appeared to be delineated into two different camps based on sorbent fabrication technique: immobilized amine sorbents and encapsulated amine clay-based sorbents. In any event, it was imperative that some type of systems analysis be conducted to determine the feasibility of the sorbent-based technology and to determine if the technology could approach the cost goals of the Carbon Sequestration Program at that time. Results from annual merit reviews of the NETL in-house carbon capture projects repeatedly screamed that systems analyses were needed for not only sorbent technologies, but all proposed carbon capture processes. During this time, the systems analyses that were conducted within the NETL organization could be conducted at one of three levels, with the rudimentary one just involving back-of-the-envelope mass and energy balances, and the most complex one entailing detailed ASPEN programming (Tarka et al., 2006a).

4.3.1 Initial Systems Analysis Conducted by NETL

During the earlier stages of conducting research on CO₂ capture with amine-enriched solid sorbents, a systems analysis study (level two) was initiated to determine the merit of using this type of solid sorbent (Tarka et al., 2006b). The main advantage of using solid versus liquid scrubbing (i.e., aqueous monoethanolamine or MEA) was borne out in the lower anticipated heat duty of regeneration. Several factors contributed to this, including lower heat capacity of the solid; higher amine loading on the solid as well as higher CO₂ loading on the solid; considerably
negligible water in the solid versus the liquid MEA solvent (and therefore less evaporative loss); and less swing in temperature to regenerate the solid. The effectiveness of a generic solid sorbent versus the liquid MEA solvent can be seen in Table 31, where the sorbent has a higher CO₂ carrying capacity per lb of sorbent (Tarka et al., 2006a).

Table 31: Comparison of CO₂ carrying capacity of solid sorbent and MEA solvent

<table>
<thead>
<tr>
<th></th>
<th>30% MEA</th>
<th>Amine Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (lb/ft³)</td>
<td>22</td>
<td>44</td>
</tr>
<tr>
<td>Working Capacity (lb CO₂/lb sorbent)</td>
<td>0.052</td>
<td>0.264</td>
</tr>
<tr>
<td>Mass sorbent per pound CO₂</td>
<td>19 lbs solution</td>
<td>3.8 lbs sorbent</td>
</tr>
<tr>
<td>Volume per Pound CO₂ (ft³/lb CO₂)</td>
<td>0.8</td>
<td>0.08</td>
</tr>
</tbody>
</table>

A comparison between MEA scrubbing and amine-enriched sorbents, as seen in Figure 73, illustrated the potential energy benefits of the sorbent system, including an overall heat duty of 620 Btu/lb CO₂ versus 1,934 Btu/lb CO₂ for MEA, due primarily to lower sensible heat of the solid versus the liquid (mostly aqueous) and evaporative considerations. (It should be noted that more recent advances in optimization of MEA scrubbing technology have also lowered the heat duty to lower than 1,500 Btu/lb CO₂.) Additionally, a sensitivity study related to cost of electricity and gauging the ranges of various parameters, such as sorbent cost, heat duty, sorbent replacement rate, and working capacity, was done for a stationary bed design in a coal-fired combustion system. Results revealed that the amine-enriched sorbent systems could reach the goal of the program at that time. Also noted was that in the absorption step with amine-enriched sorbents, heat would be emitted. In previous packed bed studies with zeolites and alkali/alkaline earth sorbents, the temperature rise within a bed could be significant and adiabatic bed calculations confirmed this temperature rise. Thus, with all types of sorbents, heat management would be a key in scale-up to practical reactor systems and would need to be addressed.
A summary of the analysis conducted in this first systems study (Tarka et al., 2006b) is given below. Although this study was rudimentary with respect to the sorbent, since the basis was on some of the initial sorbents developed to that date, the results are meaningful and would have implications and confirmations in studies that would follow.

The amine-enriched solid sorbent was evaluated within a pulverized-coal power plant with a net output of 400 MWe. The unit is designed to capture 90% of the CO₂ exhaust and the system cost includes compression required to raise the CO₂ pressure to 2,200 psig and transport it through 10 miles of pipeline and storage in a saline formation. Power plant data were based primarily on the DOE/EPRI interim report (EPRI, 2000). The performance of amine-enriched solid sorbents is compared to that of conventional amine wet scrubbing in terms of steam load, parasitic load, and cost of electricity (COE). The design criteria, similar to the MEA wet scrubbing system, for the CO₂ capture system was as follows:

- Flue gas flow rate of 1,200,000 acfm
- 90% CO₂ removal efficiency (30,000 moles CO₂ per hour)
- Regeneration energy less than 2,000 BTU/lb-CO₂
- Pressure drop of less than 6 psig
- Footprint of less than 10,000 ft²
- Maximum tower height of 100 ft
- Maximum absorber diameter of 30 ft

The amine-enriched solid sorbent was assumed to have certain physical and chemical properties. A silica substrate was chosen in the sorbent design:

- Shape: Spherical
- Density: 2.4–2.6 g/cm³

---

**Figure 73: Comparison of regenerative heats between amine-enriched sorbent and MEA.**

<table>
<thead>
<tr>
<th>Amine Enhanced Sorbents</th>
<th>30% MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heat Capacity (Btu/lb-°F)</strong></td>
<td>0.3</td>
</tr>
<tr>
<td><strong>ΔT Regeneration</strong></td>
<td>80°F</td>
</tr>
<tr>
<td><strong>Regeneration Energy (Btu/lb CO₂)</strong></td>
<td></td>
</tr>
<tr>
<td>Sensible</td>
<td>40</td>
</tr>
<tr>
<td>Reaction</td>
<td>+ 580°</td>
</tr>
<tr>
<td>Vaporization</td>
<td>+ 20°</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>620</td>
</tr>
</tbody>
</table>
• Diameter: 50–100 μm

Once enriched with amine groups, the sorbent has a total CO₂ transfer capacity of 6.4 moles CO₂ per kilogram of sorbent at 130°F, based on complete regeneration of the sorbent. The sorbent is regenerated at 210°F and requires 60 minutes for complete regeneration, at an estimated 620 BTU per pound of CO₂. CO₂ absorption kinetics is considered fast and the process would not be mass-transfer limited.

With respect to the design of the CO₂ capture system, a number of assumptions were made:

• Heat management: temperature can be controlled during absorption and direct use of steam is acceptable for regeneration
• Absorption kinetics are fast
• Economics: equipment costs are small compared to initial sorbent cost; cost of related ductwork and valves not considered; and sorbent needs to be replaced every 2 years
• Maximum pressure drop across the absorber is 6 psig

Three types of gas-solid systems were evaluated for post-combustion capture of CO₂ with the amine-enriched solid sorbent: a traditional fixed bed, a fluidized bed, and a novel fixed-bed system. Each system was evaluated based on its ability to meet the design criteria listed above, with particular attention being paid to the maximum allowable pressure drop of 6 psig and system footprint of 10,000 ft². All of the systems utilize temperature swing for sorbent regeneration.

**Fixed Bed**

The fixed bed absorption unit consists of two or more cylindrical vessels packed with sorbent. The gas to be scrubbed enters the first absorber and passes through the sorbent, as shown in Figure 74. While the first absorber is processing the gas flow, one or more additional absorbers are being regenerated. Prior to CO₂ breakthrough, flow is switched from the first absorber to a freshly regenerated one. The saturated absorber is then regenerated by cycling the vessel temperature. The number of absorber vessels required for the fixed bed gas scrubbing system is determined by the amount of time required to regenerate the sorbent and the length of time to breakthrough. A minimum of two vessels are required, which correlates to one vessel absorbing and one regenerating at any point in the process. The exact number of absorbers can be determined by dividing the regeneration time by the breakthrough time and adding one. In cases where the number of absorbers is greater than two, one vessel is utilized for absorption while the others are regenerated in a staggered fashion.

Primary design concerns for a fixed bed, temperature swing CO₂ capture system are: absorption and desorption kinetics, effective heat transfer for regeneration, and pressure drop. As assumed, the absorption kinetics are fast such that absorption rate is not an issue; however the desorption kinetics are slow requiring an assumed regeneration time of 60 minutes. This long regeneration time affects the number of absorbers required and the amount of sorbent required and has ramifications as to the overall system footprint.
Of the remaining concerns, effective heat transfer within the bed for regeneration was not included but could be a significant factor, as shown in the MATRIC work described in the next section. The bed pressure drop was considered and the small sorbent particle size (50–100 μm diameter) and the large flue gas flow rates result in potentially large pressure drop. The pressure drop can be somewhat mitigated by splitting the gas stream to be processed into parallel fixed bed systems, thus reducing the overall flow to any given reactor. Unfortunately, the results (Tarka et al., 2006b) show that none of the proposed configurations meet the 10,000 ft² or less footprint design constraint. The large footprint is a direct result of the large number of absorbers used in the system, which in turn is the result of a large regeneration time and small particle diameter. The large regeneration time requires a large amount of total sorbent to be in the system, which requires either small breakthrough times (many absorbers per stream) or small flow rates (many parallel streams) in order to meet the pressure drop design requirements. The small particle diameter makes the pressure drop design requirements more difficult to attain. As a result, a fixed bed system does not seem viable unless some stacking of capture units is possible or a very large area is available. In either case, reactor design will be critical to obtain an evenly distributed flow over such a short sorbent bed. Later studies by MATRIC will reveal that heat management is a difficult hurdle within fixed, packed beds (Fisher and Keller, 2006a).

**Fluidized Bed**

A fluidized bed CO₂ capture system consists of one or more absorption units, a solid-gas separator, and a series of regeneration vessels. The gas to be scrubbed enters at the bottom of the first absorber and the upward force of the gas lifts the sorbent pellets, resulting in sorbent being suspended by the gas flow. This fluidization of the sorbent occurs when the upward force exerted by the gas exceeds the weight of the sorbent, i.e. when the pressure drop of the gas is equal to the weight of the sorbent per unit of cross-sectional area. The flue gas velocity, pressure drop, and sorbent requirement for various flue gas flow rates (i.e. CO₂ capture rate) were calculated and assessed to determine both if fluidization was achieved and if the pressure drop was within the design constraints. These calculations assume the minimum amount of sorbent required for 90%
CO₂ capture, an absorber diameter of 30 feet, a 5 minute residence time for the sorbent, and are based on a total flue gas flow rate of 1,200,000 acfm. It is important to note that the total amount of sorbent required per absorber is dependent on the sorbent residence and regeneration time. As the residence time increases, the amount of sorbent in the absorber at any given time increases as well, increasing the bed height and pressure drop. One potential drawback to the fluidized bed design is a likely increase in sorbent attrition rate. This is a result of physical damage that may occur to the sorbent pellets during fluidization, either destroying the pellets or reducing their CO₂ capacity. The attrition rate may also be affected by sorbent residence time, as a longer residence time will result in a longer period of physical abuse (Tarka et al., 2006b). Further considerations with this type of reactor were not pursued in this initial study.

**Novel Fixed Bed**

A traditional fixed bed absorption unit operates utilizing axial flow, meaning that the flue gas enters the bottom of the absorber and flows up along the axis of the cylindrical absorption unit. In CO₂ capture operations, this results in large pressure drops even for thin beds of sorbent if the flue gas flow rate is high and the diameter of sorbent pellets is small. One method of minimizing bed thickness without sacrificing sorbent volume is the use of radial flow absorption. A typical radial flow absorption unit consists of a pipe which passes through a second, larger cylinder, as shown in Figure 75. Sorbent is packed in the annulus of the two pipes, both of which have perforated (or otherwise permeable) walls, and the flue gas flows radially through the sorbent. A similar concept is that of a flat screen design but with a moving-bed of sorbent rather than fixed (Pennline et al., 2002). Radial-flow absorption has the advantage that more sorbent volume can be added to the system without increasing the thickness of the sorbent bed—and therefore the pressure drop—merely by lengthening the reactor pipe.

Commercial radial-flow absorption systems exist for the treatment of gas flow rates up to 30,000 acfm and it is assumed that larger capacity units are possible. One such system, Calgon Carbon’s Phoenix™ technology, utilizes a solid sorbent for sulfur removal from up to 30,000 acfm of air. The design for this unit was used as a model for a radial-flow, fixed-bed absorber for the removal of CO₂ from flue gas. The Phoenix unit consists of a number of vertical compartments each of which contains three or more fixed-bed reactors. Air to be processed enters the top of the Phoenix unit, where it flows into the vertical compartments. The air then flows radially through the fixed bed reactors, where it collects in the innermost pipe and exits the absorption unit. The system is designed so that the air flow is divided equally among each of the fixed-bed reactors in a compartment. The compartmental design of the absorption unit allows a part of the unit to be isolated for sorbent regeneration. When the fixed-bed pipes in a compartment have approached breakthrough, the compartment is sealed, and is flooded with water (in the case of Calgon Carbon Corporation’s odor control system) for regeneration. After regeneration is complete, the water is pumped out, and the compartment is unsealed to receive airflow again. It is presumed that only one compartment is regenerated at a time and that airflow continues to all other compartments during this time. These compartments are also described as “banks.” The design requirements of the Phoenix™ system vary from that of an amine-enriched solid sorbent-based CO₂ absorption system in a number of ways, especially with respect to regeneration. The primary difference is the regeneration method, which is a temperature swing for the amine-enriched solid sorbent. There are a number of ways in which this can be addressed, but the two likely configuration modifications seem to be: (1) flooding of the bank with steam instead of water, or (2) passing steam through the innermost pipes of the fixed bed reactors. In either situation,
insulation between the compartments which is not necessary in the Phoenix system is likely to be required. The other design requirement differences are the processing capacity of the unit and the size of the sorbent pellets. The Phoenix™ system is designed to process up to 30,000 acfm of air, whereas the CO₂ absorption unit needs to process 1,200,000 acfm of flue gas, or 40 times the amount of gas. Furthermore, the diameter of the sorbent pellets used by Calgon Carbon for odor control is 3.7 mm as compared to 50–100 µm for the amine-enriched solid sorbent (Tarka et al., 2006b).

![Figure 75: Radial flow reactor concept.](image)

A spreadsheet model was created based on available product data of the Phoenix™ system. Best guess estimates of the fixed bed reactor pipe dimensions and sorbent bed thickness were made based on dimensional data, sorbent diameter, and reported pressure drops. These data were used to create a spreadsheet model for the design of a Phoenix-type system that could be used for CO₂ absorption and the smaller diameter amine-enriched solid sorbent. The model was designed to cover parallel absorption operation utilized in the Phoenix™ system (only one compartment being regenerated at a time) and expanded to also cover series operation, where one compartment is in absorption mode and the rest are being regenerated in a staggered manner.

Design parameters, such as flowrate per unit, number of absorption units, number of banks, cylinders per bank, and staggered regeneration techniques, have implications on the overall pressure drop and total plant footprint. The novel fixed bed design did have benefits over the other two proposed designs at that time (Tarka et al., 2006b).

Table 32 depicts the economic and performance details of a PC power plant with CO₂ capture utilizing either MEA wet-scrubbing or an amine-enriched solid sorbent in one of the previously described reactor designs. In all but one case, the solid sorbent systems have a reduced pressure drop compared to the wet-scrubbing system, which results in a reduced load for the induced draft (ID) fans. The ID fan load is further reduced by the reduced turbine heat rate—and therefore more efficient plant—which means that the flue gas flowrate is reduced. The solid sorbent systems also do not have a solvent circulation pump, which results in a further reduction in
overall plant load. These reduced parasitic loads drastically improves the performance of the plant and results in a smaller gross plant size to reach a net output of 400 MW. (Case 5 relates to 8-parallel flow absorption units and Case 11 relates to a series operation where only one bank of the absorber is actively absorbing at any given time while the rest of the banks are being regenerated in a staggered fashion.)

The reduced plant size, combined with reduced capital costs as compared to the MEA system, result in a 15–16% decrease in cost of electricity with CO$_2$ capture for the traditional fixed bed system and for the series-flow novel fixed bed reactor over the wet-scrubbing case. These plants are also more efficient with a 9–14% decrease in parasitic load over the MEA case. The fluidized bed and parallel-flow novel fixed bed reactor have an 8–9% decrease in cost of electricity with CO$_2$ capture over MEA and result in a 29% and 19% decrease in system parasitic load, respectively. This dramatic reduction in parasitic load is primarily due to a reduction in system pressure drop.

A sensitivity analysis was performed to determine the effects of changing various properties of the amine-enriched solid sorbent to determine how the overall performance of the system would change. One property was varied at a time to determine the effects of that property alone. The base case used for this analysis was Case 11, the series flow configuration of the novel fixed bed system. The properties that were varied, the baseline value and the “best” and “worst” case values of that property, can be seen in Figure 76. As shown, lower sorbent cost and regeneration energy each result in a 2.5 percentage point decrease (from 30% to 27%) in the COE increase due to CO$_2$ capture. Reducing the replacement rate was slightly more effective and resulted in a 3.2% improvement in capture economics, for a 26% increase in cost of electricity over the no-capture case. Increasing the sorbent capacity, however had the smallest effect on economics and only resulted in a 0.8% improvement over the base case. (However, the next section will emphasize the extreme importance of working capacity.) Combining all of these “best case” scenarios resulted in a 5.89 ¢/kWh cost of electricity, or a 21% increase in COE over the no capture case. Further investigation determined that in the “combined best cases” scenario, capital costs are essentially negligible and either a further reduction in regeneration energy or an increase in CO$_2$ outlet pressure was necessary in order to achieve the program goal (at that time) of 20% increase in cost of electricity. (Note that the program goal for post-combustion
sequestration technologies had been originally a 10% increase in COE, 20% at the time of this study, and more recently 35% (Klara, 2004; DOE/NELT Capture Program, 2011).

To summarize, the amine-enriched solid sorbent being developed at NETL at that time was technically/economically analyzed for use in three different reactor types of CO₂ capture systems: a traditional fixed bed, a fluidized bed, and a novel, radial-flow fixed bed. Each system was evaluated for approximate system cost, pressure drop, and footprint size and then optimized to meet the provided design criteria. It was found that the traditional fixed bed system had the largest allowable pressure drop, but did not meet the 10,000 ft² footprint design constraint. This is primarily due to slow desorption kinetics, which, combined with a small sorbent particle diameter (and therefore pressure drop concerns), results in a large number of very wide absorber vessels that contain very thin beds of sorbent. Unless the desorption kinetics can be improved, the sorbent particle diameter drastically increased, or reactor vessels created that can be stacked eight to ten units high, the fixed bed system is not a viable option for this sorbent. The fluidized bed was found to have the smallest sorbent requirement of the three systems and appeared to meet the proposed design constraints. A concern was raised, however, that the attrition rate of the solid sorbent will drastically increase under fluidized bed conditions. Based on the assumption that the attrition rate had been increased from requiring replacement every two years to requiring replacement every 6 months, the economics of the fluidized bed are not as attractive as that of the novel, radial-flow fixed bed system. This fluidized bed system could, however, be considered...
if the sorbent cost was reduced below $10 per kilogram or attrition effects could be quantified as minimal, and should therefore was not discounted as a possible process configuration. The novel, radial-flow, fixed bed reactor was found to meet all of the design criteria, and, when operated in “series” mode (Case 11), it had the best economic performance of all the options at a 30% increase in cost of electricity over the “no capture” case. A sensitivity analysis determined that a combined “Best Case” scenario of a reduced sorbent cost, attrition rate, and regeneration energy approached the DOE program goal at that time with a COE of 5.89 ¢/kWh (a 21% increase in COE).

This system analysis was one of the first pertaining to amine-enriched sorbents. From it, the parameters that would impact the sorbent reactor performance were established. However, the analysis did not go deep enough with respect to heat management and overall reactor design. It was realized that a more detailed investigative analysis was needed, and this led to the MATRIC study.

### 4.3.2 The MATRIC Study

As the sorbents proceeded through additional development and continued to exhibit promise, NETL sought industrial participation to help advance the technology out of the laboratory and towards commercialization, especially with an eye towards reactor process engineering and design. Mid-Atlantic Technology, Research & Innovation Center (MATRIC), a small engineering firm located in Charleston, WV, was commissioned by the in-house research effort of NETL to perform a systems study for conceptualized reactor configurations for a sorbent-based CO₂ capture process (Fisher et al., 2006a; Hoffman et al., 2008a). Spreadsheet calculations for energy and mass balances were performed to identify possible designs for a dry sorbent capture system applicable to the dry sorbents being investigated at NETL. Amine-enriched sorbents in a post-combustion application were the candidate materials of choice. The dry sorbent concept requires a reactor for capturing the CO₂ from the flue gas, and then regenerating the sorbent to release the CO₂. The released CO₂ is then compressed for sequestration, with the smallest possible amount of energy desired for regeneration and compression. Objectives for this work included:

- Identify candidate process design concepts for the dry sorbents
- Determine experimental data requirements to carry out a conceptual process design for the dry sorbents
- Review the available experimental data and identify any data gaps; recommend additional experimental tests that may be required based on the review
- Prepare a concept design
- Prepare an assessment of the dry sorbent concepts and recommend a development program

Up to this time, certain proclivities with respect to post-combustion sorbent application were restated.

- Temperature swing absorption (TSA) appears to be the mode of operation with these types of sorbents. The fact that there is no substantial pressure drop other than small losses through the equipment connected with the process is favorable as compared to the
substantial pressure drops in both pressure-swing adsorption and membrane-based processes. In the pressure swing case, either the stack gas would have to be compressed to several atmospheres or, more likely, the sorbed stream would have to be removed from the sorbent under a vacuum of perhaps 0.1 atmosphere absolute to get the CO₂ purity desired. Similarly with a membrane process, either feed compression or CO₂ product removal under an even higher vacuum would be necessary. In either case, a substantial energy-use penalty accrues. Additionally, instead of requiring energy from a turbine as needed in the pressure-swing-absorption and membrane-based processes, it may be possible to use condensing steam from a low-pressure steam turbine outlet to supply the energy to desorb the CO₂, resulting in a much lower energy penalty. Electricity produced to run the compressors would minimally be used in TSA applications.

- Heat management is important. It was discovered early on (see Sections 2 and 3) that the large amount of heat that had to be removed during sorption had major implications for the design of the reactor systems, and in fact this was the primary problem to be dealt with in the process design effort. Heat would need to be extracted from the sorbent during the absorption step and a massive amount of heat would need to be added during the regeneration step. From past experimental work with the amine-enriched sorbents and other post-combustion sorbents at NETL, the adiabatic temperature rise in a fixed, packed bed could be substantial, and heat would need to be removed so that the absorption temperature could remain near the optimum temperature rather than increase to near the regeneration temperature (less capacity) or even near the decomposition temperature of the sorbent.

- For sorbent systems, countercurrent flow of the sorbent with the feed gas would be more viable than co-current flow, since countercurrent flow increases the driving force for CO₂ removal. This certainly depends on the equilibrium loadings of the sorbent, with a larger CO₂ reactor gas exit – carbonated sorbent differential concentration occurring in the countercurrent mode of operation.

- A major contributor to the system cost is the volume of gas which must be handled. Since the flue gas is at near atmospheric pressure, equipment to handle it will be large, and pressure drop will be a significant issue. Compression of this stream, to recover pressure drop through process equipment, will be energy intensive and will degrade the economics, so minimizing the pressure drop of the flue gas in equipment is of high importance. The power requirement to compress the flue gas stream to raise the CO₂ partial pressure to enhance sorption is excessive, as the amount of gas is very large.

- The low partial pressure of CO₂ available in the process is a challenge. Figure 77 shows a conceptual CO₂ removal process using a solid sorbent cycled between conditions of absorption and regeneration in a non-stationary sorbent arrangement. For 90% recovery of CO₂, the CO₂ partial pressure in the exit flue gas needs to be reduced to 0.24 psia, so the sorbent needs to be able to take up CO₂ (equilibrium loading) at this pressure. The performance capabilities of the sorbent, as defined by isotherm data (CO₂ pressure versus sorbent loading at temperature), will be needed to determine the best operating points, and to differentiate between the process alternatives (Hoffman et al., 2008a).
As mentioned above, the heat of sorption must be accounted for in the design of the system. The cost advantage that the solid sorbent system has over the current aqueous MEA system for this operation is the small amount of sensible heating (20% to 50% of heat of sorption) that is required in relation to the heat of sorption. To take advantage of this lower sensible heating requirement in the operating cost (heating energy) of the process, the sorption zone temperature must be controlled, by removing the heat of sorption within the sorption zone. The MEA solution system for this operation has a high operating cost due to the heat of sorption plus the sensible and latent heating of the solution (200%+ of the heat of sorption) which must be added to desorb the CO$_2$ each cycle (Fisher et al., 2006a). Note that current in-roads to minimize sensible heating in the MEA process have been made. For example, the optimization of cross-flow heat exchange is one energy-saving technique.

An objective of the MATRIC study was to develop a workable process for using a solid sorbent to capture and recover CO$_2$ from a flue gas stream in a more cost-effective operation than currently existing technology. The reference technology for comparison was a 30% MEA solution, cycled to recover 90% of the CO$_2$ emitted from a 500 MW coal-fired power plant. The process system will be required to recover 750,000 lb/hr of CO$_2$ from a flue gas stream of 866,000 ACFM. The initial concentration of CO$_2$ is 14%, and the ending concentration is 1.6
volume % of the reduced flue gas stream, after the CO₂ is removed. The conditions of the process stream present some significant challenges that affect the relative value of alternative processes.

During the material/energy balance analysis, the gross capacity of the power plant was kept constant, and this makes comparison of ancillary systems more direct. The analysis is based on the same power plant and therefore no economy of scale differences in the power plant itself. This means that the coal-firing rate for the power plant remained constant for any case, and the actual usable power output changed depending on the parasitic power load, heat use for sorbent regeneration, and power requirements for system drives. Gas treating (sulfur, NOₓ, and water removal/adjustments) requirements for the various sorbents and systems were not addressed by this analysis, since it was assumed that the amine-enriched sorbents would need similar gas pretreatment as the MEA solution. Additionally, for comparative purposes, compression of the captured CO₂ and facilities to deliver it to the sequestration end use were not included, since the facilities for this operation, and the cost of running them, will be identical between the cases, as the recovered CO₂ is the same flowrate and comes from the sorbent regeneration step in the same condition (pressure and temperature) for all cases (Fisher et al., 2006a).

Four process concepts for solid sorbents were examined for comparison with the MEA solution system. The descriptions of these cases were:

- Isothermal structured fixed bed
- Isothermal moving bed absorber/moving bed regenerator
- Isothermal fluid bed absorber, staged as necessary with moving bed regenerator
- Adiabatic fixed particle bed absorber, staged with heat removal between stages

For the process development, the process design and equipment estimates (see Figure 77) are based on the following assumptions for the sorbent and system:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas supply pressure</td>
<td>17 psia</td>
</tr>
<tr>
<td>Flue gas CO₂ inlet concentration</td>
<td>14% (2.4 psia partial pressure)</td>
</tr>
<tr>
<td>CO₂ capture</td>
<td>90%</td>
</tr>
<tr>
<td>Resulting CO₂ outlet concentration</td>
<td>1.6% (0.24 psia of 14.7 psia)</td>
</tr>
<tr>
<td>Heat of sorption</td>
<td>580 Btu/lb CO₂, constant</td>
</tr>
<tr>
<td>Sorbent CO₂ loading, maximum</td>
<td>6 gmol/kg, in equilibrium with 2.4 psia CO₂</td>
</tr>
<tr>
<td>Sorbent CO₂ loading, regenerated</td>
<td>0.25 gmol/kg</td>
</tr>
<tr>
<td>Diffusion path limit, sorbent thickness</td>
<td>1.5 mm (radius, for cylinder or sphere)</td>
</tr>
<tr>
<td>Gas/sorbent contact time for equilibrium</td>
<td>&lt; 0.5 seconds</td>
</tr>
<tr>
<td>Specific heat of sorbent</td>
<td>0.3 Btu/lb°F</td>
</tr>
<tr>
<td>Sorption temperature</td>
<td>140°F</td>
</tr>
<tr>
<td>Regeneration temperature</td>
<td>220°F</td>
</tr>
</tbody>
</table>
Time required for regeneration is based on time required to supply sufficient heat to raise the temperature of the sorbent to regeneration temperature and desorb the CO$_2$. Once temperature is reached, no additional time is required. A summary of what each of the four concepts would approach in a commercial plant design follows (Fisher et al., 2006a).

**Moving-Bed Concept**

**Design Basis:**
- Flu gas superficial velocity: 2 ft/sec
- Sorber bed dimensions: 30 ft diameter, 25 ft tall
- Sorber bed internals: 30,000 sq ft heat exchange tubes area
- Number of parallel systems: 12
- Regenerator vessels: 25 ft diameter, 25 ft tall
- Regenerator internals: 110,000 sq ft heat exchange surface area
- Number of regenerators: 6
- Sorbent conveyors: bucket elevators, from sorption to regeneration

Heating and cooling supplied inside beds of sorbent, through heat exchange surface area

Sorbent fed to process vessels by gravity through hoppers

The moving bed concept absorber will be designed to operate isothermally, with countercurrent flow, to obtain the CO$_2$ capture requirements and sorbent loading. Figure 78 shows a representation of an absorber and regenerator combination; both are moving beds. There will be multiple parallel systems, to get enough flow cross sectional area to accommodate the flue gas flow for the system. Lean sorbent is added to the top of the absorber to keep the bed full, as rich sorbent is removed from the bottom. The exiting flue gas will cool the regenerated sorbent to operating temperature, so that it will be ready to take up CO$_2$ as it enters the active sorption zone. The bed volume is made up of heat exchange surface (tubes) separated by minimum distance to still allow continuous plug flow of sorbent particles down the bed, while the flue gas flows upward. The pressure drop through this system will require some compression of the flue gas to operate.

The moving bed regenerator will receive sorbent fully saturated with CO$_2$, heat it to drive the CO$_2$ off for recovery, and thus refresh the sorbent for re-use. Enough heat needs to be added for both sensible heating of the sorbent and CO$_2$, and to supply the heat of sorption. This is accomplished by direct contact of the sorbent particles with heat exchange surface (heated by steam) as they move down the regenerator bed volume. As sorbent flows out the bottom of the bed, the particles flow down to fill in the void. If possible, the regenerator would be placed above the absorber so the regenerated sorbent could gravity flow to the absorber, to avoid handling hot sorbent particles. Evolved CO$_2$ will flow through the bed and help transfer heat as it flows to compression/recovery.
Use of a fluidized bed for CO₂ adsorption will require multiple parallel systems to handle the gas volume. Each system will likely be several stages (at least 4, countercurrent in sorbent and flue gas) to achieve the CO₂ capture and sorbent loading requirements to make the system viable. The
thermodynamics of the system will not affect the number of stages, as the heat of sorption will be removed internal to the fluid bed. Figure 79 shows the sequential fluidized beds, but the system may be simplified by putting beds in one vessel. The pressure drop through this system will likely require some compression of the flue gas to make up for the system pressure drop. Staged operation decreases the equilibrium loading capability of the sorbent by some amount. For purposes of comparison, the maximum loading for this system is assumed to be limited to 90\% of sorbent maximum.

The regenerator is assumed to be a moving bed regenerator and will receive sorbent fully saturated with CO\(_2\), heat it to drive the CO\(_2\) off for recovery, and to refresh the sorbent for re-use. Enough heat needs to be added for both sensible heating of the sorbent and CO\(_2\), and to supply the heat of sorption. This is accomplished by direct contact of the sorbent particles with heat exchange surface (heated by steam) as they move down the regenerator bed volume. As sorbent is removed at the bottom of the bed, the particles flow down to fill the void. Evolved CO\(_2\) will flow through the bed and help transfer heat.

![Figure 79: Fluid bed conceptual schematic.](image)

In a related study sponsored by the in-house effort at NETL, preliminary commercial designs were conducted for a fluidized bed as a CO\(_2\) adsorber and a moving bed as a CO\(_2\) regenerator (Yang and Hoffman, 2009). The designs were hampered by the lack of design information, such as particle characteristics of solid sorbents to be employed for CO\(_2\) adsorption, intrinsic kinetics for CO\(_2\) adsorption and regeneration, and mass transfer and diffusion effects. A reverse engineering methodology was adapted on the basis of a commercial 500 MWe supercritical pulverized coal power plant whereby the boundaries required for a particular reactor design and configuration could be set. Due to the unavailable pertinent information related to the sorbent at the time of the study, employing the proposed moving bed for regeneration was not promising
because of poor heat transfer, evolution of CO2 during regeneration, and high pressure drop when small particles are used. If regeneration kinetics is slow, the bed height can be quite high and the reactor can be quite costly. In its place, a so-called assisted self-fluidization bed with embedded heat transfer surface was proposed. In this novel design, the majority of the fluidization gas is provided by the evolving CO2 gas during sorbent regeneration, and to assure the solids are properly fluidized, the fluidization is partially assisted by recycled CO2. Success with this design would only occur with a sorbent that can be regenerated under CO2 pressure in a temperature swing application.

Theoretically, there is no reason why the fluidized bed cannot be successfully designed and operated both as an adsorber and a regenerator under proper adsorption and regeneration kinetics. Staging may not be necessary employing the fluidized bed technology because of the capability to control reaction temperature at the optimum operating temperature through embedded heat transfer surface in the fluidized beds. Even if the staging is necessary, as was found in the MATRIC study, the implementation of staging in fluidized beds at ambient pressure and moderate temperature is relatively easy and with minimum cost penalty.

**Isothermal Structured Bed Concept**

Design Basis:

- Flue gas superficial velocity: 8 ft/sec
- Sorber bed dimensions: 60 ft x 50 ft cross section, 12 ft high + headspace
- Number of parallel systems: 1
- Number of beds needed for cycle: total of 4 beds
- Sorbent conveyors: none, fixed beds.

Heating and cooling supplied inside beds of sorbent, through heat exchangers

The isothermal structured bed concept absorber operates isothermally, since the bed is composed of sorbent bonded to heat exchange surface. The bed is composed of a stack of plate heat exchangers, with the gas flow vertical, and the heat exchange fluid flow horizontal for a cross flow arrangement. Figures 80 and 81 represent the sorbent bed arrangement. The heat of sorption will be fully removed from the sorbent and flue gas, as the area used to support the thin sorbent layer is much greater than the heat transfer requirements. In operation, the loading of the sorbent is continuous and will follow the material equilibrium isotherms. Changeover between sorption and regeneration for each bed will be rapid since heating and cooling are supplied internal to the bed in the heat exchanger.

Since the sorbent remains fixed in place, the sorption cycle is achieved by switching the flue gas sequentially through the sorption heat exchanger beds, by use of ductwork and valves/dampers. The beds will be operated as one in primary sorption, one in secondary, and one in regeneration. When a bed becomes fully loaded, it is taken off-line and the secondary bed becomes primary. As each bed is finished regenerating, cooling water is routed through it, and then it is put in service in secondary position. The heat exchanger will be designed for the allowable or desired pressure drop.
As each bed is fully saturated, ductwork valves are used to divert flue gas flow from it and connect it to the CO₂ product compressor suction. Heat for regeneration of this concept design is provided by supplying steam at the appropriate pressure to the bed heat exchanger, which heats the bed quickly. The evolved CO₂ flows to the suction of the CO₂ product compressor.

Although this concept is desirable, one major uncertainty is whether the sorbent could indeed adhere to the outer surface of this “heat exchanger.” At a later date, a proposal was actually submitted for outside funding based on this concept. NETL was to collaborate with an outside organization (Catacel Inc.) that was experienced in placing catalysts/substrates onto heat exchange surfaces. The proposal was not funded and thus key questions with this technology remained unanswered, making it a high risk technology compared to the other concepts (NETL/Catacel, 2009).

![Diagram of heat exchanger](image)

Figure 80: Each heat exchanger within the bed.
Figure 81: Each bed of the structural sorbent system.

Fixed Packed Bed Concept

Design Basis:

- Flue gas superficial velocity: 1.5 ft/sec
- Sorber bed dimensions: 30 ft diameter x 4 ft tall (or horizontal equivalent area)
- Number of parallel systems: 20
- Number of beds needed, sorption: 10 per parallel system
- Number of beds in regeneration: 2 per parallel system
- Total number of beds: 240
- Number of interchangers: 240
- Sorbent conveyors: none, fixed beds.

Heating and cooling supplied to gas stream between beds in interchangers

The fixed particle bed concept absorber can only operate adiabatically, since the bed will contain no heat removal internals. The heat of sorption will need to be removed in order to fully load the sorbent, following the loading-isotherm characteristics of the material. The process design accomplishes this step in intercoolers (external heat exchangers) between absorber beds. There will be multiple stages of sorption to achieve the needed loading on the sorbent. There will be multiple parallel systems, to get enough flow cross sectional area to accommodate the flue gas flow.

Since the adsorbent remains fixed in place, the sorption cycle is achieved by switching the flue gas sequentially, by use of a complex piping (ductwork) and valving system, through the sorption beds in each of the parallel trains. The richest gas finishes loading the nearly saturated bed, and then is routed sequentially through progressively less loaded beds to fully deplete the
flue gas of CO$_2$. Figure 82 represents one train. When the first bed becomes fully loaded, it is taken off-line and the next bed becomes first. As each bed is ready for service, it is put online, at the last bed position, and is cooled with depleted flue gas. The resulting pressure drop through this system, due to the equipment and material that the flue gas must pass through, will require compression of the flue gas to operate.

Heat must be brought to the particle bed to regenerate it, so regeneration of this type of system is typically done by passing a heated gas stream through the saturated bed to heat and strip absorbate (CO$_2$) from the sorbent. Since a purified product is needed from this process, the only fluids which will perform this task are either CO$_2$, or a condensable vapor medium, such as steam. If the sorbent is compatible with steam condensate, then steam is the easiest medium to use to regenerate the bed; otherwise the only sure material that can be used is recycled CO$_2$.

As each bed is fully saturated, valves are used to divert flue gas flow from it, and connect it to the CO$_2$ product compressor suction. Heated regenerating fluid, as described above, flows through the bed until it is heated fully, and the CO$_2$ is driven off, to the product system. Once the sorbent in the bed is fully lean, the bed must be cooled so that it can adsorb CO$_2$. This is accomplished by putting it into service at the last bed position, and allowing the CO$_2$-lean flue gas to cool the bed, while rising in temperature. Of the four process concepts investigated, the fixed, packed bed one has the most disadvantages.

For the fixed bed system, operation will be sequential. As the first bed is saturated with CO$_2$, it is switched to regeneration, and the second becomes first. As a bed is regenerated, it is switched to cooldown mode and cooled in preparation for service. Once a bed is ready for service, it is put into the final bed position, and the sorption cycle begins. The number of stages of operation needed will be defined by the equilibrium isotherms for the sorbent.

System pressure drop will be a minimum of 5 psi per sorption stage, at near atmospheric operation.

The regeneration gas is assumed to be CO$_2$ product, though direct steam regeneration will be quicker and less costly if condensing steam will not affect the sorbent. Valving requirements in the gas stream to be able to switch flows to sequence beds are 10 gas stream valves per bed. For sorbent regeneration (product CO$_2$ recovery), there will need to be an additional 2 valves per bed. Compression for regeneration is not shown but will be required.

Figure 82: Fixed bed concept.

From the material and energy balances, the justification for a dry sorbent-based CO$_2$ removal process, as contrasted to the traditional monoethanolamine (MEA)-based scrubbing, lies in the potential for substantial energy reductions (and therefore cost reductions) in the former over the
latter. Such energy reductions would come primarily from the potential for substantially higher CO\textsubscript{2} delta loadings (the difference in the loading at the end of the sorption cycle and the residual loading at the end of the desorption cycle, also referred to as working capacity) for dry sorbent-based processes. The dominating economic importance of the sorbent delta loadings for all three of the favored dry sorbent-based processes is evident and can be seen in Figure 83. (Note that the fixed bed concept was dropped because of major deficiencies in its inherent design.) The regeneration heat shown in Figure 83 is the total external heat applied to regenerate the sorbent, including both the heat of sorption, and the sensible heating of the materials and equipment which cycle in temperature in a given system. It does not, however, include any other utilities for pumping, compression, cooling, or conveying materials in the process system. It is important to note that the moving-bed and fluidized-bed processes have not been analyzed as thoroughly as the isothermal structured bed, and the curves shown for the former two may eventually be somewhat higher. However, from Figure 83, a crude recommendation with respect to regeneration energy would be that the material flow systems (i.e., moving and fluidized) would be more advantageous than the stationary sorbent system, most likely due to the penalties in heating and cooling the stationary reactor mass between the absorption and regeneration steps.

![Figure 83: Graph of regenerative heat duty versus sorbent working capacity.](image)

Figure 83 shows that the energy requirements for the dry sorbent-based processes increase monotonically as the delta loadings decrease. Note that this trend is not followed by the aqueous MEA-based process, and this fact limits this process to relatively low delta loadings. The reason
for the increased energy usage with decreasing delta loading stems from the fact that the lower this value, the greater the amount of sorbent that must be heated and cooled for each unit mass of CO₂ recovered. The sensible heat requirement associated with this additional mass that must be cycled in temperature adds to the energy requirement. It can be concluded that, economically, it is extremely important to develop sorbents with the maximum possible delta loadings. The total heat of sorption in the process is determined by the amount of CO₂ handled, and the limiting factor for the absorber design is the heat transfer area required. Another advantage of a high delta loading is the fact that the (primarily electrical) energy usage associated with physically moving the sorbent between the two zones will also decrease as the delta loading increases. The amount of this drop, which will certainly be smaller than the heating loads discussed above, was not estimated in this exercise and is not included in the curves in the figure (Hoffman et al., 2008a).

Using the spreadsheet calculations of MATRIC, a sensitivity study was conducted to determine the impact of certain parameters on the regenerative heat duty for the various reactor systems (Hoffman, 2008b). The parameters used in the original analysis and the step change for the individual parameter can be seen below. Only one parameter was changed from the baseline condition at a time. The results for the moving-bed concept can be seen in Figure 84.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent Heat Capacity, Btu/lb °F</td>
<td>0.3</td>
<td>0.49</td>
</tr>
<tr>
<td>Heat of Absorption CO₂, Btu/lb CO₂</td>
<td>580</td>
<td>420</td>
</tr>
<tr>
<td>Heat of Absorption H₂O, Btu/lb H₂O</td>
<td>0</td>
<td>999</td>
</tr>
</tbody>
</table>
Figure 84: Sensitivity study for moving-bed concept.
From the sensitivity analysis, the heat capacity for the sorbent has the least impact, since almost doubling it did not significantly alter the overall heat duty for the sorbent. As expected, the heat of reaction had the most impact. Decreasing the heat of reaction of CO\(_2\) by near 25% played a major role in reducing the overall heat duty. In the original analysis by MATRIC, impact of water adsorption followed by desorption during regeneration was not considered. In the analysis in Figure 84, the water loading on the sorbent was assumed to be equimolar with that of the CO\(_2\). The heat of adsorption was assumed to be similar to the heat of condensation of water at the temperature of regeneration (although this is probably an overestimation of the heat of adsorption). As seen in Figure 84, the impact for the water was very significant, and would need to be quantified in future sorbent studies (Fisher et al., 2006b). Results from this exercise stressed the importance of certain sorbent parameters as related to the regeneration heat duty.

In a related exercise that occurred during this time frame, a general energy balance was conducted around a CO\(_2\) sorbent system (Richards, 2006a). The energy necessary to be added during the regeneration step to reverse the CO\(_2\) absorption reaction is found in equation 1. The energy balance assumes that state 1 is the system after CO\(_2\) absorption, and state 2 is the system after CO\(_2\) regeneration. The energy balance also assumes a change in temperature occurs between states 1 and 2 (i.e., temperature swing or thermal regeneration is employed). The subscripts represent the equipment (e), the sorbent (s), and the CO\(_2\) (c), and with the indices 1 and 2 added to reference the states. The variable m is the mass, C is the specific heat, \(C_p\) is the constant pressure specific heat for the gaseous CO\(_2\). Q is the heat input, and \(Q_r\) is the heat of reaction (represented as a positive number) for breaking the chemical bond between the active species and the CO\(_2\). B is a constant of proportionality for dimensional units, and L is the CO\(_2\) loading capacity expressed in gmole CO\(_2\)/kg. The equation shows that for fixed swing in temperature, regeneration energy can be reduced by increased loading L or decreased specific heat C or by finding a sorbent with a lower heat of reaction. The energy balance also assumes that the only gas adsorption reaction occurring is CO\(_2\) – adsorption of moisture was not considered here. A plot of the regenerative heat duty versus loading using Equation 1 can be seen in Figure 85 and is very similar to the curves produced by using the MATRIC spreadsheets (see Figure 84).

\[
\frac{Q}{m_c} = \frac{m_e}{m_c} \cdot C_e \cdot \Delta T + \frac{B}{L} \cdot C_s \cdot \Delta T + \frac{C_{p_c}}{C_s} \cdot T_2 - C_s \cdot T_1 + \frac{Q_r}{m_c} \quad (1)
\]

- Sensible heating of the “equipment” that supports the process
- Heating the active species and sorbent
- Delta enthalpy between gaseous CO\(_2\) and base sorbent
- Heat of reaction
Figure 85: Plot of heat duty (regeneration energy) versus sorbent loading using Equation 1.

If there are additional separate reactions taking place, i.e., adsorption/desorption of H$_2$O, then additional analogous terms need to be included in Equation 1. This can be seen in the equation below:

\[
\frac{Q}{m_c} = \frac{m_e}{m_c} \cdot C_e \cdot \Delta T + \frac{B}{L} \cdot C_s \cdot \Delta T + \frac{C_p \cdot T \cdot (2 - C_s \cdot T)}{m_c} + \frac{Q^c}{m_c} + \frac{m_w}{m_c} \left( C_{p,w} \cdot T - C_s \cdot T \right) + \frac{Q^w}{m_c}
\]

The above energy balance equation highlights the need for several sorbent parameters to be determined in value for a particular sorbent. They include the heat of adsorption of the gas (CO$_2$ reaction), the specific heat (heat capacity) of the sorbent, and the CO$_2$ working capacity of the sorbent. Another but very important consideration is the role of moisture, whether as a participant (reactant) in the CO$_2$ reaction or as a competitor in adsorption/desorption.
4.3.3 Targets

From the design work of MATRIC and additional computations at NETL, the formulation of an ideal but realistic sorbent emerged. One of the primary metrics of performance was the regeneration heat duty for the sorbent. In order to meet DOE program goals, the studies recommended certain targets and that the sorbent process should have a regeneration heat duty that is at least 30–50 percent less than the MEA heat duty, corresponding to the sorbent process having an overall regeneration heat duty generally between 500 and 1,000 Btu/lb CO₂. Specific success criteria or performance targets for the sorbent were established based on assumed sorbent properties, leading to the identification of critical process parameters and information that are required for further development evaluation, including: isotherms (Δ loadings or working capacity of sorbent) between rich loading (absorption) and lean loading (regeneration); heat of reaction (ΔHᵣ) for CO₂ absorption; heat capacity (Cₚ) for sorbent; role of H₂O in the process; role of trace components (SO₂ and NOₓ); and reaction kinetics.

The working capacity as related to the loadings on the sorbent is one of the most important parameters in an actual sorbent reactor system (Richards, 2006b). If the regenerator heats the sorbent with indirect heat (for example, a heat exchanger), then the sorbent must release CO₂ in an environment with essentially atmospheric pressure CO₂ present. Achieving a high regeneration therefore requires a high regeneration temperature, and this is why a clear knowledge of the isotherms for the sorbent is required. As shown conceptually in Figure 86, the equilibrium loading depends on the CO₂ partial pressure and temperature.

![Figure 86: Schematic of isotherms for sorbent.](image-url)
Isotherms for the absorber and regenerator temperatures are show schematically in Figure 86. The absorption process occurs at point A, and the regeneration occurs at point B. The delta-loading or working capacity is the difference in equilibrium loading between the points A and B. Obviously, the shape of the isotherms and the absorber and regenerator design conditions (temperature, regenerator CO\textsubscript{2} partial pressure) will determine how much delta-loading could be achieved in practice. This is why knowledge of the isotherms is essential for designing a useful sorbent system.

To reiterate from the MATRIC study, the results emphasized obtaining the following sorbent information:

- Isotherms (Δ loadings) between rich loading (absorption) and lean loading (regeneration). This would establish the temperature envelope for the cycling of the sorbent.

- Δ\text{H}_r for absorption

- C\text{p} for sorbent

- Role of H\textsubscript{2}O in process

- Role of trace components (SO\textsubscript{2} and NO\textsubscript{x})

- Kinetics

The sorbent information used in the MATRIC calculations was used as a baseline. (See the process design and equipment estimates on page 194 of the previous section.) Certainly deviations from these numbers could have implications. Tradeoffs on these numbers and the magnitude that these numbers have on the regeneration heat duty could be minimal or quite significant. In addition to properties listed above, other sorbent characteristics would have implications on the overall process as well as the regeneration heat duty. The sorbent must demonstrate stability and retain the CO\textsubscript{2} capture capacity during multi-cycling between the absorption and regeneration steps. Additionally, the sorbent must be durable within the operating parameters of the selected reactor design, for example having negligible physical and chemical attrition. The path forward for post-combustion carbon dioxide capture sorbent development and reactor design was established in the MATRIC study, and these benchmarks would be used in future amine-enriched sorbent work at NETL.

4.4 BASIC IMMOBILIZED AMINE SORBENTS (BIAS)

As a result of the MATRIC study, the amine-enriched sorbent work evolved as a collaboration between the areas of sorbent development and reactor design. A concerted effort began in FY2007 with a continuation of two routes of sorbent investigation: immobilized amines on supports and encapsulated amine clay-based sorbents. The first type of sorbent initially used various amine-based compounds that were deposited onto a substrate. Candidate compounds included tetraethylenepentamine, pentaethylenehexamine, polyethyleneimine, and others, and the supports included polymethylmethacrylate, polystyrene, and silicas. After screening studies, one of the choice materials was polyethyleneimine (PEI) on silica. PEI can be linear or branched and can contain primary, secondary, and tertiary amines. Typical loadings of PEI on the silica range from 40–50% by weight. The silica has a high surface area (upwards of 300-m\textsuperscript{2}/g) and could be obtained from Fuji Silysia or PQ Inc. More recent work involved stabilization of the sorbent by using silane compounds to perform a cross-linking function. The patented fabrication technique produced samples for laboratory-scale testing but was also easily adapted to produce large...
(+600-lb) loads for subsequent larger-scale testing with ADA-ES, as will be discussed in a later section.

Not only were various amines and supports investigated, but clarification in the evolution of different classes of immobilized amines became pronounced. As can be seen in Figure 87, three different pathways for sorbent materials are defined as derived by researchers at Georgia Tech and NETL (Li et al., 2010a; Li et al., 2010b). Thus three classes of supported amine sorbents exist. Class 1 adsorbents are based on porous supports impregnated with monomeric or polymeric amines. The amine species are thus physically loaded onto or into the support. Class 2 adsorbents are based on amines that are covalently linked to a solid support. This has most often been achieved by binding amines to oxides via the use of silane chemistry or via preparation of polymeric supports with amine-containing side chains. Class 3 adsorbents are based on porous supports upon which aminopolymers are polymerized in situ, starting from an amine-containing monomer. Representative examples of each of these adsorbent classes can be seen in Figure 88 (Li et al., 2010a).

**Pathways to Solid Amine Sorbents**

![Pathways diagram](image)

Figure 87: This illustrates three potential pathways to making solid amine sorbents. Immobilization/impregnation, the typical technique NETL utilizes for making BIAS sorbents, is the simplest followed by synthesis and polymerization that are increasingly more complex.
4.4.1 More Recent Sorbent Development

As mentioned, the development of the sorbents revolved around various amines deposited on various substrates. Some of the research dealt with incorporating primary and/or secondary and/or tertiary amine functionality into these supports. Additionally, the method of attachment of the amine to the support was of interest. The success of using these sorbents was based on the targets developed within the MATRIC study.

TEPA-Derived Sorbents

One sorbent study (Fauth et al., 2007) investigated the interaction of CO\(_2\) with linear tetraethylenepentamine, TEPA, acrylonitrile-modified, tetraethylenepentamine (TEPAN), and a single formulation consisting of TEPAN and N, N’-bis(2-hydroxyethyl)ethylene diamine (BED). These three substances were individually impregnated within the pores of a high surface area, polymethylmethacrylate support. Organic ethyleneamines, TEPA, and TEPAN display considerably lower vapor pressures relative to alkanolamines, thus making them less susceptible to loss from devolatilization within the target operational temperature range of 25–100°C. Furthermore, the chemical interaction between TEPA, or TEPAN, and CO\(_2\) is deemed to benefit from the presence of moisture, which within a power generation setting will typically exist. CO\(_2\) uptake profiles for these immobilized amine sorbent (IAS) materials were determined using thermogravimetric analysis (TGA) under a dry 10% CO\(_2\) gas mixture at 25°C. Cyclic experiments utilizing a packed-bed flow system with a gas mixture simulating a flue gas...
environment (9% CO₂, 3.5% O₂, nitrogen balance with water vapor) with trace contaminants were also performed. The goal of the work was to determine CO₂ adsorption properties for the IAS materials along with investigating the effects of trace gas constituents (moisture, O₂, NO/NOₓ, and SO₂) present in flue gas on the IAS performance over a series of temperature swing cycles.

Tetraethylenepentamine (TEPA), an organic amine consisting of both primary and secondary amino groups supported on a highly porous substrate (polymethylmethacrylate or PMMA) was used in the synthesis of the initial IAS. The support before amine impregnation provided sufficient surface area (~500 m²/g), and pore volume (1.2 ml/g) to adequately retain the amine within the pores of the support. In a second IAS synthesis, modification of TEPA was carried out by reaction with acrylonitrile prior to immobilization within the pores of the polymeric support. For this reaction, TEPA was added to a 500 ml round bottom flask followed by slow addition of acrylonitrile while stirring. To help minimize the exothermic reaction, an ice bath was utilized. The TEPA/acrylonitrile solution was slowly heated to 50°C and stirred for one hour. The reaction product formed a Michael adduct, TEPAN, that altered the original structure, as can be seen in Figure 89. Acrylonitrile reacts largely with primary amine functionalities in forming secondary amines upon completion of reaction. In the last IAS synthesis, equal mass percentages of TEPAN and N, N’-bis(2-hydroxyethyl)ethylenediamine (BED) together with the PMMA support were utilized.

![Figure 89: TEPAN, Michael adduct produced by reaction of TEPA with acrylonitrile.](image)

To immobilize the amines within the pores of the polymeric support, a solvent evaporation method was used. Initially, PMMA beads were uniformly dispersed in methanol within a rotary evaporator flask. The amines (solubilized in methanol) were then added to the beads, followed by the solution rotated at ambient temperature for 5–10 minutes producing a homogeneous slurry. Subsequent removal of the solvent was conducted by heating the rotary evaporator flask in a heated water bath. The procedure produced an IAS material with a high percentage of its theoretical pore volume filled with liquid amine(s). TGA weight loss curves were used to help estimate organic amine loading (wt% concentration) for each IAS. The onset of thermal
decomposition for the PMMA support starts at approximately 252°C. Based on these weight loss curves, amine loadings for TEPA/PMMA, TEPAN/PMMA, and TEPAN+BED/PMMA were estimated at 38.6 wt%, 35.2 wt%, and 35.4 wt%, respectively.

Testing of the sorbents was conducted in a thermogravimetric analyzer, a laboratory-scale packed bed system, or a bench-scale packed bed system. Unless noted, all the testing was conducted in the units described below or almost identical systems. The carbon dioxide capture capacities of the immobilized amine sorbents were determined utilizing a Thermo Cahn Thermax 300 instrument. For a typical test, a 50 mg sample was placed in the microbalance quartz sample bowl. The adsorption cycle was conducted within the temperature range (typically 40–60°C) using 10–100% CO₂ with balance nitrogen and occasionally in the presence of water vapor. CO₂ adsorption was followed by a desorption cycle at 105°C under nitrogen gas flow only. The weight gain and loss were recorded throughout the entire test. From the recorded weight data with time, CO₂ capacities were calculated. The gas flow rate for these analyses was maintained at 200 ml/min. A picture of the TGA is shown in Figure 90.

![Figure 90: Photograph of the TGA system.](image)

In the laboratory-scale packed bed studies, CO₂ capture capacities are determined by monitoring the CO₂ concentration in a simulated flue gas using an Ominostar mass spectrometer manufactured by Pfeiffer Vacuum. A near one gram sample of the sorbent is charged into a tubular fixed-bed reactor. Typical procedure is similar to the following. The reactor is purged with helium flowing at 200 ml/min allowing the system to come to an equilibrium state at 25°C. After approximately 30 minutes, the reactor and the saturator heaters are turned on and the temperatures are gradually raised to 40°C for the saturator and 45°C for the reactor at atmospheric pressure. With the reactor off-line, the main gas inlet line was flowed with either 10% CO₂ in helium or 10% CO₂ and 7% water vapor in helium for an hour, and the mass spectrometer was calibrated at this time. Upon reaching steady state conditions in the main gas inlet lines, the reactor was brought on-line and the sample was exposed to the CO₂/water/helium simulated flue gas stream at the dry flow rate of 100 ml/min. The adsorption of CO₂ was recorded until the CO₂ exit concentration reached the initial inlet feed concentration of 10%, completing the adsorption stage of the test. The reactor was then switched off-line and the system was purged with helium to remove residual CO₂. The reactor was then switched back on-line with helium for 30 minutes leaving the reactor temperature at 45°C and allowing the helium
to desorb the CO₂ (based on swing in partial pressure) for one hour. The reactor temperature was then increased to 105°C to start the desorption stage based on temperature swing. After approximately one hour, the reactor was cooled back down to 25°C, completing the adsorption/regeneration cycle test for the sorbent. The CO₂ breakthrough curve was generated using an Excel spreadsheet and the area under the adsorption and desorption portions of the curve was calculated by a linear integration method. A schematic of the system is shown in Figure 91.

![Figure 91: Schematic of laboratory-scale packed bed reactor.](image)

In the bench-scale packed bed reactor, the effects of trace flue gas contaminants on IAS performance were determined, and CO₂ adsorption, desorption, and thermal regeneration measurements were conducted utilizing a fixed-bed flow system. For these tests, about 90 cc of the IAS was placed onto a fritted disc located in the center of a 450 mm long quartz tube and at the center of a 400 mm split-tube furnace. In this vertical reactor, bed temperature was measured and controlled using a dual type K thermocouple located ~2 mm above the frit. Secondary temperature controls for heater tapes along the gas inlet path regulated the temperatures of several gas mixing chambers and a water humidification chamber. Gas compositions were established by blending respective gases from cylinders using thermal mass flow controllers; moisture content was produced by using a variable flow dispensing pump. The system was configured with a series of gas analyzers for continuous monitoring of CO₂ (infrared), O₂ (paramagnetic), NO/NO₅ (chemiluminescent), and SO₂ (infrared). Prior to entering the analyzer section, process gas was passed through a Perma Pure™ drying tube removing moisture from the gas stream. Data acquisition was obtained utilizing a data logger. A schematic of the system is seen in Figure 92.
With the TEPA and TEPA-derived sorbents (Fauth et al., 2007), TGA results with respect to CO₂ absorption capacity are seen in Table 33. The highest capacity obtained was achieved by the TEPA/PMMA sample; both TEPAN/PMMA and TEPAN+BED/PMMA produced lower CO₂ capture capacities compared to the unaltered TEPA/PMMA sample. These results were somewhat surprising in that the TEPAN/PMMA sample was specifically tailored with an increased abundance of secondary amines. It was speculated that a plausible cause for the lower sorption capacity for these samples stemmed from poor dispersion of the active amine sites, which influences the final adsorption of CO₂. In rapidly heating the IAS materials (10°C/min) to 100°C in N₂, the TEPA/PMMA sample showed some evidence of incomplete desorption; whereas both TEPAN/PMMA and TEPAN+BED/PMMA exhibited complete desorption of CO₂ during experimentation. Bench-scale packed bed tests with the TEPAN+BED sorbent as related to trace contaminants in flue gas (i.e., SO₂ and NO) will be discussed later in Section 4.4.3. Because of the low CO₂ capacity of the TEPA-derived sorbents at low temperature, the research effort with this sorbent was discontinued.

Table 33: CO₂ capture properties for TEPA-based sorbents at 25°C

<table>
<thead>
<tr>
<th>Sorbent ID:</th>
<th>Time of Exposure, min</th>
<th>CO₂ absorbed, mass %</th>
<th>CO₂ adsorbed, mmol/g of sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEPA</td>
<td>60</td>
<td>14.0</td>
<td>3.2</td>
</tr>
<tr>
<td>TEPAN</td>
<td>60</td>
<td>7.5</td>
<td>1.7</td>
</tr>
<tr>
<td>TEPAN_BED</td>
<td>60</td>
<td>9.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>
**DBU-Containing Sorbents**

Another IAS sorbent that was investigated during this era utilized an immobilized tertiary amine to capture CO₂ from a simulated flue gas stream (Gray et al., 2008). The tertiary amine immobilized in the solid substrate was 1, 8 Diazabicyclo-[5.4.0]-undec-7-ene (DBU). An advantage of this amine is that it has the potential to capture carbon dioxide at a R-NH₂: CO₂ molar ratio of 1. This is a unique feature compared to primary and secondary amines that capture CO₂ at a 2:1 molar ratio. Since DBU-based sorbents have the capability of capturing CO₂ at a 1:1 molar ratio, they create the potential for making a more cost effective sorbent.

The solid amine sorbents were prepared by immobilizing DBU from the Sigma–Aldrich Company onto Diaion HP-2MG polymethylmethacrylate (PMMA) beads from Mitsubishi Chemical. Beads with 10, 5, and 2.5 weight ratios (bead:DBU) were tested as CO₂ capture sorbents. The amine was dissolved in methanol and combined with the polymeric beads. This bead slurry was then placed in a rotating evaporator and the methanol was removed resulting in the physical absorption (immobilization) of the amine into these polymeric beads. Testing was conducted in the laboratory-scale packed bed reactor and in the TGA, both previously described. Additionally, X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI 5600ci instrument using monochromatic Al Ka X-rays. The levels (atomic %) of chemically attached nitrogen in the form of strongly adsorbed amines were determined for each of the CO₂ capture sorbents.

Table 34 represents some of the results from the laboratory-scale packed bed reactor and XPS study. It must be remembered that DBU-1, DBU-2, and DBU-3 represents the bead/DBU sorbent weight ratio of 10, 5, and 2.5, respectively. As shown, the performance of these sorbents in capturing CO₂ improved with an increase in DBU loading. XPS analysis verifies the increase in nitrogen with increased DBU loading. An average CO₂ capture capacity of 3.02 mol CO₂/kg sorbent was achieved at the adsorption temperature of 25°C for the DBU-3 sorbent. Following CO₂ adsorption, the saturated CO₂ sorbent was heated to 87°C to desorb the CO₂, thus completing one cycle of testing for the sorbent. Upon the completion of four test cycles, each with adsorption at 25°C, two additional cycles were performed with adsorption at 45 and 65°C to determine the sorbent’s performance at these higher temperatures. The sorbent’s performance at higher capture temperatures can be seen in Table 35. The CO₂ capacity decreases from 3.43 to 2.34 with the increase in capture temperature from 25–65°C. A decrease in adsorption capacity is expected at the higher temperatures given that desorption of the CO₂ was achieved at 87°C. Furthermore, the DBU appears to be stable over the temperature range used for adsorption and desorption, as illustrated by the XPS data in Table 34, that show the results before and after cyclic testing (Gray et al., 2008a).
Table 34: Performance of DBU-based sorbent at 25°C in a 10 vol% CO₂/2% H₂O/88% helium atmosphere

<table>
<thead>
<tr>
<th>Sorbent/bead</th>
<th>Average CO₂ capacity (mol CO₂/kg sorbent)</th>
<th>XPS N atomic % {before} [after]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diaion-PMMA bead</td>
<td>0.0</td>
<td>Not detected</td>
</tr>
<tr>
<td>DBU-1</td>
<td>2.08</td>
<td>{0.49} [0.51]</td>
</tr>
<tr>
<td>DBU-2</td>
<td>2.41</td>
<td>{0.92} [1.00]</td>
</tr>
<tr>
<td>DBU-3</td>
<td>3.02</td>
<td>{1.03} [1.26]</td>
</tr>
</tbody>
</table>

* Average over four adsorption/desorption test cycles

Table 35: Performance of DBU-3 at 25–65°C in a 10 vol% CO₂/2% H₂O/88% He atmosphere

<table>
<thead>
<tr>
<th>Capture Temperature K</th>
<th>Test Cycle Number</th>
<th>CO₂ Capacity (mol CO₂/kg sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1</td>
<td>3.43</td>
</tr>
<tr>
<td>318</td>
<td>4</td>
<td>2.47</td>
</tr>
<tr>
<td>338</td>
<td>6</td>
<td>2.34</td>
</tr>
</tbody>
</table>

To summarize, these DBU-based sorbents did exhibit acceptable stability over the adsorption/desorption temperature range of 25–87°C based on XPS and TGA analyses. The best performing sorbent (DBU-3) was prepared at a 2.5 weight ratio (bead/DBU) and had an average CO₂ capture capacity of 3.02 mol CO₂/kg sorbent at 25°C. However, the capacity was reduced to 2.34 at the capture temperature of 65°C. The sorbent’s performance at higher capture temperatures is critical, since the flue gas stream entering a capture system in an actual power plant will be in the range of 40–60°C, as identified in the previous MATRIC study. Since the working capacity of this sorbent at the elevated temperature was less than that of the target 3-mol/kg sorbent identified in the MATRIC study, further testing of this sorbent was not warranted.

**Hyperbranched Aminosilicas (HAS)**

A vast majority of the amine-enriched sorbent research at NETL has involved the Class 1 type of sorbent, as defined in the introduction of Section 4.4. However, through a collaboration with researchers at Georgia Tech, research of hyperbranched aminosilicas (HAS) has been conducted. These HAS sorbents are Class 3 adsorbents and are prepared through polymerization of an amine-containing reactive species, such as aziridine, from the surface silanols or other reactive functional groups of the support, creating covalently bound aminopolymers in the pore space. The HAS adsorbents consist of organic polymers chemically tethered to the walls of the silica support, typically being prepared by in situ polymerization (Hicks et al., 2008). Although the location of the polymer in the pore space cannot always be precisely identified, it was suggested that at low polymer loadings, most of the pore surface was functionalized with small molecular weight polymers, perhaps preferentially at or near the pore openings (Drese et al., 2009).
However, at higher amine loadings, polymerization was suggested to propagate axially into the pore space and, in some cases, the polymerization blocked the pores, again perhaps preferentially at or near the pore openings. In the previous study using SBA-15 as the mesoporous silica, a set of HAS adsorbents was synthesized with a range of organic loadings by adjusting the aziridine to silica weight ratio used in the synthesis. Characterization of the adsorbents revealed that below a critical radius of about 5-nm, the aziridine polymerization progressed to a point so as to severely hinder mass transfer, resulting in reduced amine efficiencies (mol CO$_2$/mol N) over the course of the adsorption experiment. Analysis of the HAS aminopolymer formed in these slower adsorbing materials showed that the molecular weight remained nearly constant at these higher loadings, supporting the hypothesis that polymerization propagated until the pore was blocked (Drese et al., 2009). This can be seen in the results of Figure 93.

![Figure 93: Single-component CO$_2$ adsorption isotherm for a highly-loaded HAS adsorbent at 35 and 75°C.](image)

Single-component isotherms for a highly loaded adsorbent (Figure 93) were measured at 35 and 75°C using pressure–volume–temperature techniques. The results indicate a higher dry capacity at 75°C than at 35°C. Fundamentally, thermodynamics suggests that capacity should decrease with increasing temperature. Hence, this observation is probably associated with severely hindered diffusion at the 35°C adsorption condition. This result again fits with the hypothesis that nearly complete pore blockage occurs at or near the pore mouths of the HAS adsorbent, effectively blocking off access to amines already in the pores. It should also be noted that in a temperature swing process in a capture system for flue gas, these sorbents would not be that applicable since the sorbent capacity at the elevated temperature (regeneration) is greater than that at the lower temperature (absorption).
With the previous findings in mind, more recent investigations (Drese et al., 2012) hypothesized that polymerizing aziridine on silicas with larger pores than SBA-15 could result in adsorbents with larger amine loadings and thus faster kinetics and/or higher adsorption capacities. Proper control over the degree of polymerization in these materials could yield a regime of material compositions with amine loadings higher than those found in the above-mentioned HAS materials, but with adequate porosity to maintain unhindered mass transfer. Adsorbents with these characteristics would likely possess superior CO₂ capacities and kinetics. The synthesis and characterization of these HAS adsorbents were prepared using several different large pore mesoporous silicas (pore diameters >10 nm) as the solid supports. This strategy was applied to the HAS synthesis to minimize pore blocking from polymerization and potentially improve adsorption performance in CO₂ capture experiments using simulated flue gas. However, it was shown that the use of larger pore, high porosity supports did not positively affect the adsorption performance of these pore-expanded hyperbranched aminosilica (PEHAS) CO₂ adsorbents, yielding the opposite results than initially hypothesized. A comparison of these types of sorbents can be seen in Figure 94 that shows the amounts of CO₂ adsorbed by HAS and PEHAS adsorbents with different amine loadings after 13.5 min of adsorption. This time was selected because it was the shortest near total uptake time for any of the adsorbents. At equal adsorption times, the HAS adsorbents with high amine loadings still adsorbed substantially more CO₂ than the PEHAS adsorbents with lower amine loadings. Therefore, while HAS adsorbents with high amine loadings have slower relative kinetics, their absolute kinetics are still superior. Also, the HAS adsorbents with moderate amine loadings (3–5 mmol N/g) outperform the PEHAS adsorbents. In summary, because of their limited amine loadings, PEHAS materials adsorbed lower absolute quantities of CO₂ than the original HAS adsorbents, even with short adsorption times. These results indicate that adsorbents prepared from aziridine polymerization on/in pore-expanded silicas requires further exploration to increase the degree of polymerization, and that a mechanism of polymerization termination unrelated to the effect of support pore diameter is important. Research is continuing to increase amine loadings and adsorption capacities so that these sorbents could even be considered in a flue gas CO₂ capture scenario.
Figure 94: Amounts of CO$_2$ adsorbed by HAS and PEHAS adsorbents with different amine loadings at 13.5 min. SBA-15 HAS materials were previously reported by Drese et al. (2009).

**PEI-Containing Sorbents**

By far, most of the recent basic immobilized amine sorbent (BIAS) research has involved polyethylenimine (PEI) incorporated into a support. PEI is a linear or branched amine compound that can have various molecular weights and various ratios of primary, secondary, and tertiary amines. Initial results were obtained through the use of a TGA (Fauth et al., 2008). Commercially available amine polymer polyethylenimine (M$_w$800) (CAS# 25987-06-8) was purchased from Sigma-Aldrich, USA. PEI (see Figure 95) was impregnated within the interior pores of three distinctive supports, each possessing sufficient surface area and pore volume to adequately retain the highly branched liquid amine. Spherical, macroporous, methacrylate-type Diaion® HP2MG (PMMA) and styrene-type Sepabeads® SP700 (PS) adsorbent resins were obtained from Mitsubishi Chemicals America, Incorporated; granular silica support Cariact® G10 was procured from Fuji Silyvia Chemical, Ltd., Japan. Typically, 15.0 g of support was dispersed in methanol (100 ml) within a rotary evaporator flask, wetting initially the polymeric (or inorganic) support by mechanically rolling the mixture for 15 min. The dissolved amine polymer (6.0 g) was then added to the slurry and dynamically rotated within a pre-heated water bath (75°C) for an additional 45 min. Removal of the solvent was undertaken upon heating the rotary evaporator flask under reduced pressure. Analyses of the produced materials substantiated that a high percentage of the theoretical pore volumes was filled with liquid amine.
Figure 95: Chemical structure of a highly branched polyethylenimine compound having two carbons per nitrogen with a ratio of 1:2:1 between primary, secondary, and tertiary amine groups.

A ThermoCahn TherMax 300™ TGA was used to monitor adsorption and desorption of CO₂ from PEI-based adsorbents utilizing dry N₂ as the carrier gas. Samples (50 mg) were initially heated in dry N₂ (200cc/min) to 105°C (5°C/min) and held for 1 h, purging any pre-adsorbed CO₂ and H₂O. The samples were then cooled to 40°C under dry N₂ prior to introduction of adsorbate gas mixture of 10 vol%CO₂/N₂ or 20%CO₂/N₂ or 50%CO₂/N₂ (200 cc/min) for 90 minutes. CO₂ adsorption capacities were calculated from the TGA weight record and the dry mass of the adsorbents. Weight gain (and loss) measurements in pure CO₂, N₂, and air were also performed employing a slow heating rate of 0.25°C/min. These experiments aided in defining preliminary temperature ranges for both adsorption and desorption of CO₂.

Trends with the PEI/PMMA sorbent and the PEI/PS sorbent were similar to the results with the PEI/silica sorbent (Fauth et al., 2008). However, the PEI/silica sorbent was more stable at elevated temperatures. In Figure 96, TGA profiles can be seen for PEI supported Cariact® G10 silica sample produced by similar experiments utilizing dry, individual pure gases of CO₂, N₂, and air at different temperatures. By using a very slow ramp rate in temperature, near equilibrium results in the TGA were obtained at each temperature. A substantial gain in weight equivalent to about 15% was monitored during the initial adsorption stage of the experiment. However, unlike PEI on other supports, the CO₂ adsorption capacity remained relatively constant up to approximately 80°C. Beyond this temperature, the near-equilibrium performance of the sample declined gradually to its lowest possible value at 160°C. Unexpectedly at this point, an additional weight gain was observed during the latter stages of the experiment in CO₂, indicating the potential of undesirable secondary reaction(s) with CO₂ and PEI. Finally, for the PEI supported Cariact® G10 material, one significant weight loss event in the range of 140°C to 200°C in dry pure air was also observed, again indicating where probable thermal/oxidative degradation of the amine polymer appears to occur. However, for the PEI supported Cariact® G10 sample, the onset temperature at which degradation of the amine polymer starts was approximately 140°C, some 35°C higher than the PEI supported on PMMA. Thus, the temperature at which the oxidative degradation of the PEI initiates appeared to be influenced by the nature of the support.
From this initial investigation, several conclusions were drawn pertaining to PEI/silica sorbent. The first was that the silica support would be more stable than supports of a polymer nature, like the polystyrene or polymethylmethacrylate. The second was that, using the MATRIC targets discussed previously, this sorbent could be used in the absorption/regeneration temperature zone of 40–105°C without any apparent deterioration of the activity of the sorbent. The third was that the capacity of the sorbent was relatively high at near 3.5 mole CO₂/kg sorbent. This was a criterion from the MATRIC report. However, although the interest is to obtain a high capacity during absorption, it is the working capacity that is critical. In an ideal case, regeneration would occur under a pure stream of CO₂. If the CO₂ capture curve is observed in Figure 96, it can be seen that at the regeneration temperature of 105°C, as specified in the MATRIC report, this particular sorbent has a relatively large CO₂ capacity. Not only this, but at the absorption temperature of 40–60°C, the capacity is not too different from the regeneration condition. Additionally, at 40–60°C in an actual power plant scenario, the CO₂ concentration in the flue gas would actually be lower (15%) and the loading capacity would actually be lower and closer to the CO₂ loading at the regeneration condition. This reveals that with this PEI-based sorbent, regeneration cannot occur under an atmosphere of pure CO₂, but must be conducted in another manner. For this sorbent, regeneration must occur using an inert, but separable sweep gas, such as steam as the regenerant. In this manner, the CO₂ working capacity as defined in the MATRIC targets can be approached.
The research with PEI was further advanced by continued testing not only in the TGA but also in the laboratory-scale packed bed reactor (Gray et al., 2009a; Gray et al., 2009b). The sorbents tested were fabricated similar to the previous study (Fauth et al., 2008). Polystyrene, polymethylmethacrylate, and silica were again the substrates of choice. A total of 40% PEI by weight was immobilized into each of these substrates, and then these CO₂-capture sorbents were tested by both a packed-bed reactor and gravimetric methods. The TGA was discussed previously and can be seen in Figure 90. In the modified laboratory-scale packed bed reactor, as can be seen in Figure 91, the chemical CO₂ capture capacities were determined by monitoring the CO₂ concentration in a simulated flue gas using an Ominostar mass spectrometer manufactured by Pfeiffer Vacuum. A 1 g sample of the sorbent was charged into a tubular fixed-bed reactor, and the reactor was purged with helium flowing at 200 ml/min, allowing the system to come to an equilibrium state at 25°C. After approximately 30 min, the reactor and the saturator heaters were turned on and the temperatures were gradually raised to 40°C for the saturator and 45°C for the reactor at atmospheric pressure. With the reactor off-line, the main gas inlet line was flowed with either 10% CO₂ in helium or 10% CO₂ and 7% water vapor in helium for 1 h, and the mass spectrometer was calibrated at this time. Upon reaching steady-state conditions in the main gas inlet lines, the reactor was brought online and the sample was exposed to the CO₂/water/helium simulated flue gas stream at the dry flow rate of 100 ml/min. The adsorption of CO₂ was recorded until the reactor exit CO₂ concentration reached the initial inlet feed concentration of 10%, completing the adsorption stage of the test with a gas residence time ranging 1–2 s. The reactor was then switched off-line, and the system was purged with helium to remove the residual CO₂. The reactor was then switched back online with helium for 30 min, leaving the reactor temperature at 45°C and allowing the helium to desorb the CO₂ (on the basis of the swing in partial pressure) for 1 h. The reactor temperature was then increased to 105°C to start the desorption stage based on temperature swing. After approximately 1.0 h, the reactor was cooled to 25°C, completing an adsorption/regeneration cycle test for the sorbent. The CO₂ breakthrough curve was generated using an Excel spreadsheet, and the area under the adsorption and desorption portions of the curve was calculated by a linear integration method. A graphic illustration of the stages of the CO₂ breakthrough curve for a test run in the laboratory-scale packed bed reactor is shown in Figure 97.
Figure 97: Graphic illustration of breakthrough curve of the adsorption and regeneration of CO$_2$ with PEI/silica sorbent.

From the loading results in Table 36, the TGA results were higher due to the pure conditions under which they were obtained. The laboratory-scale packed bed results were obtained at lower partial pressure of CO$_2$ (10% concentration) that approaches what would be found in an actual power plant flue gas. This loading was lower than the 3 mol CO$_2$/kg sorbent target but still was encouraging since the fabrication of the sorbents was not refined at that time.

Table 36: Capture loading capacities at 40$^\circ$C for PEI sorbents. aTGA measured at 100% CO$_2$. bLab reactor at 10% CO$_2$ in helium.

<table>
<thead>
<tr>
<th>Sorbent (40% PEI wt basis)</th>
<th>TGA$^a$ (mol of CO$_2$/kg of sorbent)</th>
<th>Lab reactor$^b$ (mol of CO$_2$/kg of sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macronet</td>
<td>na</td>
<td>1.04</td>
</tr>
<tr>
<td>CARiACT</td>
<td>3.1</td>
<td>2.55</td>
</tr>
<tr>
<td>Diaion</td>
<td>2.50</td>
<td>2.40</td>
</tr>
</tbody>
</table>
As mentioned in the discussion above, a critical parameter for the regeneration of these sorbents is the type of sweep gas required for the desorption of CO$_2$ at temperatures less than 120°C. Ideally, CO$_2$ sweep gas would be best in an actual capture process, resulting in a pure CO$_2$ gas stream, which can then be pressurized, transported, and sequestered. However, the CO$_2$ delta loading (the difference between the capture and regeneration sorbent loading capacities) are targeted as a minimum of 3.0 mol of CO$_2$/kg of sorbent. Figure 98 shows TGA results where the composition of the regeneration gas ranged from 10 to 80% CO$_2$; the higher CO$_2$ concentration approaches the ideal regeneration condition where pure CO$_2$ would be the sweep gas (Gray et al., 2009b). The absorption condition was constant at a concentration of 10% CO$_2$ and an absorption temperature of 60°C. According to the TGA analysis shown in Figure 98, under dry CO$_2$ conditions, the delta loading decreased with the increase of CO$_2$ content up to 80%, which simulates a high concentration of CO$_2$ during regeneration under a sweep of CO$_2$. Again as concluded previously, the potential of using CO$_2$ as a sweep gas is significantly reduced because the delta loading was only 0.3 mol of CO$_2$/kg of sorbent at the higher CO$_2$ gas concentration. Consequently, in a commercial application of this sorbent, the use of steam will have to be considered as a regenerant and CO$_2$ can be recovered by condensing the steam and collecting the CO$_2$ for compression. The use of direct steam for regeneration may complicate the design of the reactor process and could increase the overall cost. Initial results indicate that water management will be a critical parameter in process design with the PEI-containing sorbent.

![Figure 98: Absorption and regeneration TGA curves for CARiACT sorbent. Absorption CO$_2$ loading capacity averaged 2.64 mol of CO$_2$/kg of sorbent; delta loadings shown after regeneration at 120°C at various CO$_2$ concentrations.](image-url)
Since these PEI-containing sorbents gave some of the best capture performance from the amine-enriched sorbents studied to date, an investigation into the thermodynamic properties of these materials was warranted (Hoffman, 2012). Heat capacities and heats of reaction were of prime interest. Experiments were conducted in various instruments by several participants in an attempt to garner information on these various sorbent materials. The overall goal was to measure loading capacity, heat capacity, and heats of reaction for various materials as they were exposed to CO$_2$ and H$_2$O, both individually and in simultaneous combination. Considerable experimental difficulties, particularly with moisture-containing gas mixtures, were encountered throughout the testing program. Over time it became apparent that the nature of these tests is indeed difficult to perform and interpretation of results are challenging.

The experimental participants included Setaram Instrumentation, Inc. (experiments conducted in Caluire, France), Pennsylvania State University, and NETL (experiments conducted in facilities both in Pittsburgh and Morgantown). The instrumentation included differential scanning calorimeters (DSC) and thermogravimetric analyzers (TGA) as well as laboratory-scale packed-bed reactors. Mass spectrometers (MS) were utilized on some of the research units to conduct gas analysis of the reactor effluent. In the case of Setaram, the instrumentation consisted of SENSYS TGA-DSC coupled with their mass spectrometer and their WETSYS humidity controller. In the case of Penn State, the instrumentation consisted of a tubular breakthrough reactor interfaced with a Setaram Sensys Evo differential scanning calorimeter without thermogravimetric option. A volumetric adsorption apparatus (Micromeritics ASAP 2020) interfaced with the DSC was also available at Penn State to measure heats of reaction as a function of equilibrium CO$_2$ pressure. NETL-Pittsburgh instrumentation included a Perkin-Elmer Pyris Diamond DSC, a Thermo Cahn Thermax 300 TGA, previously described, and a lab-scale packed bed reactor equipped with an Omnistar MS manufactured by Pfeiffer Vacuum, also previously described.

Materials of interest included the substrate materials as well as the substrates with amine incorporated. Polyethylenimine (PEI) was the one amine compound physically immobilized onto the supports, with the resulting sorbent composed of approximately 40–50 wt% PEI. Performance was also standardized for comparison using a commercially available physical zeolitic sorbent, molecular sieve 13X. As mentioned in Section 2, the zeolitic material had been extensively studied at NETL for CO$_2$ capture and a high degree of experimental familiarity and experience exists using this material. Brief descriptions of the sample materials with abbreviations are listed below.

13X: Molecular sieve zeolite 13X composed of sodium aluminosilicate, obtained from Zeochem
PMMA: Substrate composed of polymethylmethacrylate.
Q-15: Cariact Q-15 substrate composed of silica.
G-10: Cariact G-10 substrate composed of silica.
184a: NETL sorbent composed of PEI immobilized onto PMMA.
195a: NETL sorbent composed of PEI immobilized onto Q-15.
196c: NETL sorbent composed of PEI immobilized onto G-10.
A typical DSC experiment would entail loading a pre-weighed sample into the instrument. The sample was then dried under inert purge and ramped up in temperature and held isothermal for a period of time to condition the sample and activate or regenerate the material near 105°C. The material was then cooled back down and stabilized at the temperature of interest, either near ambient temperature if initiating a heat capacity determination or typically between 40–60°C if for an absorption determination. At this point, a second heating cycle could be conducted under inert purge for determination of heat capacity during temperature ramping. An empty reference pan, having no sample, would be analyzed under identical heating procedure so that the baseline heat signal could be subtracted, yielding a heat flux attributable to sample only. The sample would then be cooled back down to the absorption temperature and stabilized under inert purge.

Feed gas composition would then be switched from inert purge to CO₂/H₂O mixture with balance inert gas, initiating gas absorption and the resulting exothermic heat of reaction. After allowing sufficient time for the absorption to achieve steady state (90 min), the absorption would be terminated by switching to inert purge gas. In some instances, the desorption and regeneration was conducted stage-wise, with isothermal desorption under inert purge for a period of time, followed by temperature ramp (thermal regeneration) to the regeneration temperature (typically 105°C) and held for a period of time. In other instances, the desorption and regeneration was conducted in one step, switching gas composition to inert purge and beginning temperature ramping immediately. After completion of the regeneration step, the sample would be cooled back down under inert purge, completing the cycle.

![Figure 99: Typical heat capacity results from NETL laboratory.](image-url)
Heat capacity as a function of temperature was determined for the various materials. Typical results are shown in Figure 99 for NETL-conducted measurements. The temperature range of 40–105°C is the range that the sorbent would see in an absorption/regeneration cycle, although Penn State ramped the materials to much higher temperature ranges (above the regeneration temperature) to examine amine decomposition and other possible effects on the sorbent. Generally, similar trends are noted among the heat capacity measurements from the different organizations. Values for comparison are extracted for a mid-range temperature near 70°C, unless otherwise noted. The silica substrates (G-10 and Q-15) have values near 0.21–0.22 Btu/lb°F. The PMMA substrate has higher heat capacity, near 0.30–0.33 Btu/lb°F, although Penn State’s value was somewhat lower (0.23 Btu/lb°F). The molecular sieve 13X lies intermediate in value (0.22–0.28 Btu/lb°F) between the silica and PMMA substrates. Incorporation of the amine, at roughly 40–50 wt%, clearly raises the overall heat capacity of the sorbent, regardless of the type support. In fact, the heat capacity nearly doubles with the physical immobilization of the amine versus the individual substrate. There was more variability in the 184a sample (PMMA-based sorbent), with values of 0.46–0.49 Btu/lb°F and Penn State reporting higher value at 0.63 Btu/lb°F. However, much better agreement was obtained for the silica-based sorbents (196c and 193d), with values of 0.39–0.41 Btu/lb°F. Since sample 196c has received considerable experimental evaluation as a baseline immobilized amine sorbent at NETL, it is noteworthy that the amine/silica sorbent has a heat capacity of 0.4 Btu/lb°F, which exceeds the MATRIC study value of 0.3 Btu/lb°F by a factor of one-third, and this will have implications in the heat duty requirement (Hoffman, 2012).

With respect to measured heats of reaction, it was generally observed that the substrate supports do not absorb CO₂, and therefore calorimeter results are not available for these materials. The supports do exhibit some affinity towards H₂O, but the associated heat flux curve is broad and flat for H₂O. However, the effect of the support to absorb H₂O is minimal in comparison to amine-impregnated sorbents, suggesting that the presence of the amine is largely responsible for H₂O uptake. The sorbents do absorb CO₂, and the heat flux curve is very sharp and narrow, unlike the H₂O heat flux curve. When both CO₂ and H₂O are simultaneously present in the feed gas, there can be a slight enhancement in the measured overall gross heat, but the results cannot be put on a per-mole of specific gas basis since the TGA loading cannot distinguish weight gain between the components in a binary gas mixture. This was the motivation of conducting experiments with single component adsorption gas in an attempt to interpret the binary gas experiments.

Setaram conducted measurements with samples 196c and 195a (silica-based) and found that the CO₂ heat of reaction is similar for both samples ranging between 800–830 Btu/lb CO₂. The effect of moisture added in the feed gas serves to raise both the absolute weight gain during absorption as well as the absolute exothermic heat. Both observations are consistent with the presence of moisture slightly enhancing CO₂ sorption. Since MS gas analysis was not permissible during the moist CO₂ tests, it is not possible to partition the loading or heats among CO₂ and H₂O individually. Calculation of CO₂ heats of reaction for moist CO₂ tests yields values near 815 Btu/lb CO₂, consistent with the range of values determined for the dry CO₂ tests. Penn State measurements with sample 196c determined a heat of reaction of 825 Btu/lb CO₂. This value is very consistent with the Setaram values near 800 Btu/lb CO₂ and lends confidence to these overall results.
The determination of heat of adsorption/reaction for water with the immobilized amine was not as conclusive. Measureable exothermic heats for sorbent 196c were recorded for the H$_2$O and combined CO$_2$/H$_2$O feed gas cases. The H$_2$O case has a calculated heat of reaction of 808 Btu/lb H$_2$O. Thus samples 196c and 184a (797 Btu/lb H$_2$O) are very consistent with moisture heat of reactions near 800 Btu/lb H$_2$O, again suggesting that moisture absorption on the amine-based sorbent represents a strong bond of attraction. For sample 196c, Penn State measured a heat of reaction of 242 Btu/lb H$_2$O. This value is much lower than the Setaram values near 800 Btu/lb H$_2$O. The reasons for the discrepancy are unknown. However, it is intuitively felt that the moisture is weakly bonded to the sorbent, as evidenced by the fact that in a simulated regeneration with a switch to inert gas flow, temperature swing is not required to desorb the moisture from the sorbent, whereas temperature swing is required for total CO$_2$ desorption. Also bear in mind that the latent heat of water vaporization is near 1,000 Btu/lb, so the fact that the water absorption for the sorbent is nearly a quarter of the latent heat is consistent with the moisture being weakly bonded and is more representative of physical adsorption rather than chemical absorption. Water adsorption heat of reaction is not well defined at this point, but is probably closer to the lower 242 Btu/lb H$_2$O value (Hoffman, 2012).

The results of these thermodynamic measurements have implications with respect to the overall regeneration heat duty. It is envisioned that this PEI-containing sorbent can be used in a process that is shown in Figure 100. In this case, the sorbent would be used in a continuous flow system where it is cycled between the absorber and regenerator, very similar to a continuous flow MEA wet scrubbing system. The CO$_2$ capture sorbent is downstream of a coal-fired power plant where the flue gas prior to the capture step has been cleaned of SO$_2$ in an upstream flue gas desulfurization (FGD) unit, either a wet scrubber or dry scrubber. Nitric oxides would have been removed prior to the capture unit by selective catalytic reduction (SCR). In any event, the inlet SO$_2$ and NOx are held to a minimum, similar to MEA wet scrubbing restrictions. The stream coming into the absorber may contain upwards of 15% H$_2$O at 14.7 psia, at 60°C, and with 10–15% CO$_2$. When introduced into the absorber, the CO$_2$ reacts with the sorbent. The decarbonated flue gas then exits from the absorber to the stack. The spent sorbent containing the reacted CO$_2$ and adsorbed H$_2$O flows from the absorber and through a heat exchanger before entering the regenerator. The heat exchanger can be a solid-solid heat exchanger where the sorbent from the absorber is heated by the sorbent exiting the regenerator. The sorbent then enters the regenerator where it is directly contacted with a steam regenerant. Low pressure steam from before the low pressure steam cycle can be used. The temperature of the steam can be as low as 105°C, slightly superheated at ambient pressure, or greater. The steam must be at the correct temperature so that moisture will not condense on the sorbent within the regenerator, and the steam must indirectly and/or directly provide the heat of regeneration for the spent sorbent.

With sorbent absorption of CO$_2$, a temperature swing/quasi pressure swing to regenerate the sorbent is proposed in this scheme; steam is used as the regenerant. In this thermal swing regeneration, the gas stream exiting the regenerator will be enriched with CO$_2$ and moisture. A cooler on the regenerator exit stream will condense the moisture from the stream and produce a pure stream of CO$_2$ for sequestration or utilization purposes. The solid stream leaving the regenerator will have been exposed to moist steam and precaution will be needed to prevent condensation of moisture onto the sorbent. A conditioner/dryer of minimal size is in order. Immediately after the regeneration, the sorbent will be exposed to a small flow of ambient air in
the conditioner. This will shift the water loading of the sorbent to a low number to prevent condensation downstream during the cooling process. Ambient air is used similar to a pressure swing step where the sorbent is exposed to a small stream of air to drive off some of the moisture and partially cool the sorbent. The sorbent would then flow to the heat exchanger where it is cooled to the temperature of absorption and then sent to the absorber.

Disregarding any issues with moisture adsorption onto the sorbent for now, a heat balance can be conducted around the regenerator and cross flow heat exchanger to obtain an estimate of the heat duty. The equation for the heat duty from the MATRIC study is used:

\[
\text{Regenerative heat duty} = \text{Sensible heat to heat sorbent to regeneration temperature} + \text{Sensible heat to heat CO}_2 \text{ to regeneration temperature} + \text{Heat of reaction for CO}_2
\]

For the exercise, the 500-MWe plant that is described in the MATRIC final report is used as a basis for the flow streams (Fisher et al., 2006a). Since this is a continuous flow system, the one term in the MATRIC equation that pertains to heating and cooling of the reactor is nil since the process proposed is a continuous flow system. The results of a sensitivity study can be seen in Table 37. From the MATRIC study and using their target sorbent properties, a heat duty of 779 Btu/lb CO$_2$ is calculated. The impact on heat duty can be obtained from the measurements conducted with the PEI-based sorbents. The larger heat capacity and heat of reaction will
increase the overall heat duty. The steam sweep regeneration will increase the working capacity of the sorbent and thus decrease the heat duty. The crossflow heat exchanger temperature is analogous with MEA scrubbing in that the sorbent/solvent exiting the regenerator is cooled by the sorbent/solvent exiting the absorber and eventually entering the regenerator. Solid-solid heat exchangers are available and can be used in this application (Zeigler, 2010). Thus heat can be recovered and the heat duty improved using this application. From the measured thermodynamic properties of the sorbents and what was felt reasonable in the operation of the continuous flow system, an overall heat duty of 857 Btu/lb CO₂ was calculated. This was within the range of 30–50% regenerative heat savings for this sorbent (roughly 500–1,000 Btu/lb CO₂) in the MATRIC study and thus provided some justification for continuation of this sorbent development effort.

| Table 37: Sensitivity analysis for immobilized amine sorbent |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                 | MATRIC Baseline | Heat Capacity   | Heat of Reaction | Working Capacity | Temperature Difference | Accumulative Effect |
| Heat capacity, Btu/lb·°F         | 0.3             | 0.4             | --              | --              | --              | 0.4             |
| Heat of reaction, Btu/lb CO₂     | 580             | --              | 800             | --              | --              | 800             |
| Working capacity, mol CO₂/kg sorbent | 3               | --              | --              | 3.5             | --              | 3.5             |
| Crossflow exchanger temperature difference, °F | 80 | -- | -- | -- | 20 | 20 |
| Heat Duty, Btu/lb CO₂            | 779             | 840             | 998             | 754             | 630             | 857             |

In later NETL studies to improve the stability of the PEI-containing sorbent, mixtures of aminosilanes with PEI were deposited on a silica substrate. The previous laboratory-scale packed-bed flow system investigations at NETL, utilizing a porous silica substrate impregnated with different weight percentages of PEI, revealed both a significant uptake of water (as will be explained in the next section) and a loss of PEI resulting in sorbent degradation during multiple CO₂ adsorption-desorption cycles under simulated regeneration streams containing 90 vol % water vapor in helium at 105°C and 1.01 bar of pressure. For these reasons, a single-step material synthesis was devised, entailing hydrophobic aminosilane modification of the silica support coupled with immobilization of PEI with the expectation in enhancing the sorbent CO₂ adsorption performance, potentially improving the thermal and hydrolytic stability, and advancing the equilibrium and kinetic behavior. The immobilization and covalent attachment of PEI with 3-aminopropyl triethoxysilane or 3-aminopropyl trimethoxysilane as a chemical linker onto the silica support was anticipated to provide improved CO₂ sorption performance over many cycles of thermal swing adsorption/regeneration cycles.
One of the first screening investigations at NETL with the aminosilanes involved the addition of 3-aminopropyltriethoxysilane or 3-aminopropyltrimethoxysilane to PEI on a silica support (Gray et al., 2010). Tests were conducted on the laboratory-scale packed bed reactor described previously. For the testing of each sorbent, two cyclic tests were conducted where moisture was not present and the sorbent was exposed to CO$_2$ at 40°C and then regenerated under an inert stream at 105°C. Four additional tests were conducted where 8% moisture was added to the absorbing gas to further simulate flue gas, and the regeneration was carried out under a 90% H$_2$O/inert stream to simulate steam-sweep regeneration. This was then followed by two cyclic tests identical to the first two where moisture was not present and the sorbent was exposed to CO$_2$ at 40°C and then regenerated under an inert stream at 105°C. Results of the testing are seen in Table 38. The sorbent designated as 15E was PEI on silica; 15C was 3-aminopropyltriethoxysilane with PEI on silica; and 14C was 3-aminopropyltrimethoxysilane with PEI on silica.

### Table 38: Initial cyclic testing of aminosilane/PEI sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>PQ 2129 grams</th>
<th>PEI Mn 600 grams</th>
<th>Silane grams</th>
<th>Mol CO$_2$/kg sorbent</th>
<th>8th Cycle</th>
<th>Capacity % Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 E</td>
<td>10.0</td>
<td>10.0</td>
<td>0-</td>
<td>3.091</td>
<td>1.888</td>
<td>38.9</td>
</tr>
<tr>
<td>15C$^1$</td>
<td>10.0</td>
<td>5.0</td>
<td>5.0</td>
<td>2.697</td>
<td>2.270</td>
<td>15.8</td>
</tr>
<tr>
<td>14C$^2$</td>
<td>10.0</td>
<td>5.0</td>
<td>5.0</td>
<td>2.542</td>
<td>2.064</td>
<td>18.8</td>
</tr>
</tbody>
</table>

From the preliminary results, it appeared that the addition of the aminosilane enhanced the stability of the PEI sorbent under representative steam regeneration conditions. However, this was at the expense of the CO$_2$ performance of the sorbent. Although the capacity was decreased at the end of the cyclic testing in all cases as compared to the initial activity, the sorbents with the aminosilanes still had a capacity greater than 2-mol CO$_2$/kg sorbent.

With the above results in mind, a study of just the 3-aminopropyl triethoxysilane with PEI on silica was conducted (Fauth et al., 2012a). The study was conducted at NETL and at the laboratory of ADA-ES, a collaborator at that time. The rationale for the testing was similar to the previous tests. The materials to be developed and tested would be CO$_2$ capture sorbents comprised of a large-pore-volume silica matrix (with adequate surface area) immobilized with various weight ratios of 3-(aminopropyl)triethoxysilane (APTES) and polyethylenimine (PEI). The commercially porous silica matrix has rapid adsorption (due to relatively large pore diameters), excellent selectivity, and good mechanical stability. Furthermore, the abundant hydroxyl groups present within the porous silica surface can condense with the chemical linker APTES in forming Si–O–Si networks. This one-step approach in functionalizing porous silica surfaces using PEI and APTES together in anhydrous ethanol can provide, in a simplistic way, the insertion of spatially spaced site-isolated amines and silanol groups. By providing a sufficient number of silanol groups in forming covalently attached aminosilane layers coupled with PEI incorporation within the interior pores of the silica matrix, the formulated samples were examined with the expectation in enhancing the sorbent CO$_2$ adsorptive performance, improving thermal and hydrolytic stability, equilibrium, and kinetic behavior.
For this study, supported mixed-amine (PEI+APTES) materials were prepared by a wet impregnation technique. In a typical preparation, the required amounts of PEI and APTES were dissolved in methanol, the dissolution of which was aided by mechanically stirring within a round-bottom flask. A predetermined mass of the silica support was then added to the solution and placed onto a rotary evaporator producing a slurry containing the organic constituents and inorganic silica. The flask carrying the resulting slurry was continuously turned at a high rpm rate under various stages of reduced pressure. The slurry was agitated for an additional 40–60 min above 80°C until the solvent was drawn off. The flask containing the final product was then removed from the rotary evaporator for product characterization. The desired as-prepared, supported amine-functionalized materials theoretically had a 50 wt% organic loading with the PEI wt% on five samples as 0, 15, 25, 35, and 50. Testing at NETL was conducted using the TGA and laboratory-scale packed bed reactor that were described previously. Testing at ADA-ES used similar type of instrumentation (Fauth et al., 2012).

Thermal decomposition tests conducted in the TGA to 650°C led to the conclusion that the APTES by itself or with PEI did not decompose as much as PEI by itself. Using this information and TGA testing of the sorbents under pure CO₂ at 60°C, 1.01 bar led to Figure 101. Higher amounts of the chemical linker APTES, within the mixed-amine (PEI+APTES) sample revealed lower near-equilibrium CO₂ adsorption capacities, as compared to the PEI only sample. The high amine density of PEI was attributed for its higher CO₂ capacity, relative to the mixed-amine PEI+APTES samples, as shown in Figure 101. Note that the combined quantities of PEI and APTES, as labeled on the x-axis, are the estimated weight percentages of PEI and 3-aminopropyl groups that are contained in each sample. Lower loadings as a function of increasing chemical linker were also seen in the earlier tests. Speculation relating to the lower near-equilibrium CO₂ absorption capacities may stem from the formulation of the (PEI+APTES) samples.
From the stability aspect of using APTES with PEI, multiple cycling tests were conducted to help further evaluate its long-term stability and CO₂ capture reactivity. The 25% PEI/25% APTES/silica sorbent was tested by ADA-ES in a fixed-bed flow system, but for numerous absorption/regeneration cycles (i.e., >250 cycles). The testing conditions at ADA-ES were similar to those at NETL. The near-equilibrium CO₂ adsorption capacities obtained from the long-term cyclic testing are shown in Figure 102 (Fauth et al., 2012a). Similar to the evaluation at NETL, the fixed-bed tests completed by ADA-ES revealed an initial decrease in near equilibrium CO₂ adsorption capacity. However, beyond the initial 50 adsorption-desorption cycles of the total 250 completed, the near-equilibrium CO₂ uptake for the PEI+APTES sorbent seems to be constant. This result implies that this organic-mixture sorbent may be a potential candidate upon increasing its adsorption capacity. To determine if the initial loss in CO₂ capacity can be avoided would possibly entail modifications to the sorbent synthesis process involving different synthesis conditions and different aminosilane coupling agents (Fauth et al., 2012a).
Figure 102: Multiple adsorption–desorption testing of the (PEI-25-APTES-25)-silica in a simulated humidified flue gas stream containing 12% CO₂, 4% O₂, balance N₂, with 9 vol % water vapor. Adsorption temperature is 55°C at 1.01 bar. Desorption temperature is 100°C in nitrogen.

4.4.2 Impact of Moisture

From the target establishment in Section 4.3, a recommendation was to determine the role of moisture as related to the overall regenerative heat duty and to its influence in the sorbent process. For the basic immobilized amine sorbents to be used in a post-combustion application, the sorbent will initially be exposed to moisture in the absorption step. Within flue gas produced from combustion of coal, there is typically around 8 vol% of H₂O at near atmospheric ambient pressure. However, flue gas also contains sulfur dioxide that is a poison to these sorbents and thus must be eliminated. The flue gas would need to be sent to a wet lime/limestone scrubber for desulfurization before introduced to the CO₂ capture unit. The flue gas exiting the wet scrubber will be near saturation at temperatures in the vicinity of 55–60°C, and saturation of the flue gas at these conditions corresponds to the gas having approximately 15–17 mole percent moisture. The possibility exists for moisture—that moisture not entering into the chemical reaction with the CO₂—to adsorb on the sorbent. Supported amine CO₂ sorbents are most effectively regenerated in a temperature swing process, as energy is necessary to break the amine/CO₂ bonds. As seen with the BIAS sorbents, particularly those containing PEI, regeneration by using elevated temperature under a sweep of CO₂ is not feasible since the resulting working capacity of the sorbent is very low. A more reasonable approach is to regenerate under a sweep of steam. This steam sweep provides (1) a partial pressure driving force, as in the case of inert gas temperature swing that is customarily used in researcher’s regeneration schemes and (2) a thermal driving force for desorption. It is envisioned that the majority of heat required for regeneration/desorption would be provided by indirect use of steam. In the steam sweep case, the product stream, containing only CO₂ and water, can be easily purified by compression and condensation, removing the water as a liquid, to produce a highly concentrated CO₂ gas stream
suitable for sequestration. Furthermore, low-grade, low-cost steam near the ambient boiling temperature in a coal-fired power plant exists and would be used to remove CO$_2$ from the spent solid sorbent.

**Loading of Water on Sorbents**

To determine the impact of various moisture concentrations in the gas on sorbent performance in both the absorption and regeneration steps, testing was conducted on the laboratory-scale packed bed reactor using a standardized, excellent sorbent candidate. Sorbent was synthesized by impregnating polyethylenimine (PEI) onto silica (SiO$_2$) support. PEI (Mn-423) was supplied through Sigma-Aldrich USA. Reagent grade methanol was received from Sigma Aldrich USA. Both PEI and methanol were used as received in the preparation of the sorbent. The silica support was obtained from Fuji Silysia and is CARiACT G-10 high pore volume series (G-10 HPV, Lot # GH080702, particle size 75–500 μm, surface area 294 m$^2$/g, pore volume 1.77 ml/g, pore diameter 24.0 nm). In a typical synthesis, a homogeneous solution of PEI and methanol was added to SiO$_2$ to form a slurry. The slurry was then placed in a rotary evaporator set to 80°C and left to rotate for 1–2 hr. During rotation, methanol was removed with a vacuum pump and the resulting solid was refrigerated. The target PEI loading within the sample was 50 wt%. The final immobilized amine sample bears the designation 196c and consists of approximately 45 wt% PEI and 55 wt% G-10 silica. (As discussed previously in Section 4.4.1, thermodynamic properties were obtained with sample 196c.) For experimental consistency, a large homogenous batch of material was made and drawn from during the test campaign. As a follow-up effort to this study, this same material has been studied more recently to further evaluate the effect of steam regeneration on stability (Hammache et al., 2011).

Experiments were conducted in a laboratory-scale packed bed reactor, details of which have been described elsewhere but are summarized here. A flow diagram of the unit appears in Figure 91. The reactor used a clam-shell furnace in the earliest sorbent studies but was more recently replaced with a flexible insulated blanket heater obtained from HTS/Amptek Company (HeatingJackets.com, model A510-USDE0309-32 with type K T/C, 110W, 120 V). Simulated flue gas mixtures consisted of carbon dioxide in balance helium using certified calibrated cylinder gases obtained from Butler Gas. Feed gas flow rate was established using calibrated mass flow controllers (Brooks 5850e). The feed gas could be passed through a sparger vessel to humidify the stream if desired, or it could simply bypass the sparger for dry feed conditions. The sparger was heat traced and insulated and had a Type K thermocouple inserted into the liquid reservoir to measure the bath temperature. A bypass on the reactor allowed steady state feed conditions to be obtained before subjecting the sorbent sample to the feed gas flow for either the absorption or desorption/regeneration stages.

One gram of dry sample was pre-weighed and loaded into the test section. Glass wool plugs encapsulated the loaded sample within the reactor tube (3/8 in OD) to keep it stationary within the vertical tube. Gas flow passed vertically up through the bed. A Type K thermocouple (1/16 in diameter) was positioned immediately above the upper plug, representing the bed exit temperature. Gas composition was continuously measured downstream of the reactor using a Pfeiffer Omnistar® mass spectrometer (MS). Parent ions for helium, water, and carbon dioxide were scanned for identification and quantification. Carbon dioxide calibration was performed on a dry basis using the certified cylinder standard. Water calibration was performed using helium passed through the sparger and assuming equilibrium saturation for the measured sparger bath temperature and sparger pressure (approximated as the measured barometric pressure in the
laboratory since negligible back pressure exists in the unit). The back pressure was monitored downstream of the MS sampling location using a pressure transmitter and typically was 0.1–0.2 psig. Upon cooling the exit gas flow to ambient temperature, a condensate pot was used to collect excess moisture prior to venting the gas. All vessels and ductwork downstream of the sparger were heat traced and insulated to prevent condensation of elevated moisture in the gas stream.

Concentration versus time data acquired with the MS was exported into Excel spreadsheets. The breakthrough curves were integrated within the spreadsheets using discrete summation of the material balance equations to arrive at totalized gas amounts absorbed/desorbed from the sample. The material balance equations considered the effect of volume change across the reactor. The background carrier gas, helium, acts as a tracer since it does not absorb/desorb from the sample, and is used to account for change in total gas flow rate as a result of other components (CO₂, H₂O) absorbing or desorbing from the solid. Totalized gas amounts (reported in moles) were normalized by the weight of loaded sample, such that capacity is reported as moles of gas per kg of sample charged to the reactor.

After the sample was charged to the reactor, it was dried and activated under helium purge near 105°C. The sample was then cooled to the desired absorption temperature of interest, generally 60°C. The MS was calibrated for CO₂ using a standard gas blend of 10% CO₂/He. If the feed gas was to contain moisture, the MS was calibrated for H₂O using pure helium passed through a heated water bath. With the reactor off-line, a steady-state calibrated feed gas composition was established. The absorption stage would commence with manual valve switch to bring the reactor on-line. The absorption was typically held for 30–60 min, or longer as necessary, until the exit feed composition approached the inlet feed composition, signifying bed saturation. The reactor was then switched off-line, and the feed gas was switched to pure helium to purge residual CO₂ and H₂O from the system. Upon complete purge of residual gases, the reactor was switched on-line under pure helium flow to begin an isothermal desorption stage, typically for one hour. The desorption temperature was maintained the same as was used during the absorption stage, typically 60°C. The desorption stage represents an isothermal pressure swing desorption step. Upon completion of one hour desorption and while still under pure helium flow, the reactor temperature was ramped 2°C/min to 105°C and held for approximately 15 min at the upper temperature. This stage represents temperature swing regeneration. Upon completion of the sorbent regeneration, the reactor was switched off-line and cooled, signifying the completion of the cycle. Once cooled to the absorption temperature of interest for the next cycle, the reactor was briefly purged under pure helium and then switched off-line so as to establish the next absorption feed gas composition. Recalibration of the MS was conducted between cycles on an as-needed basis. (Note that the experimental “artifact” or “empty-volume” of the reactor was measured over multiple cycles for specific temperatures and gas compositions of interest used during sorbent evaluation. Although typically this was negligible, in certain instances corrections were made to the loadings (Hoffman et al., 2012a).

Before the moisture tests were conducted, the CO₂ capture performance of these sorbents was defined. From past tests with this sorbent in the TGA, an attempt was made to validate experimental results related to CO₂ capture and the parameters of temperature and CO₂ concentration. The baseline absorption loading for sample 196c is typically in the range of 3.2–3.3 mol CO₂/kg of sorbent at 60°C using dry 10%CO₂/He feed. The baseline adsorption loading at 45°C using dry 10%CO₂/He feed is slightly lower, near 3.0 mol CO₂/kg. Regeneration under
helium sweep gas was conducted stage-wise, with one hour isothermal desorption followed by temperature swing desorption to 105°C. The two-stage regeneration suggests both weakly bonded and strongly bonded CO₂ sites are present. Good material balances/recoveries were obtained for the baseline tests when comparing the absorption and total desorption/regeneration fragments. This can be seen in Figure 103 where both CO₂ and H₂O balances were conducted over the absorption and regeneration steps and compared. The distribution of the liberated CO₂ is greatly affected when comparing 45°C versus 60°C data. Roughly one third is liberated by quasi-pressure swing (desorption under helium) at 45°C and the remaining two-thirds is liberated by temperature swing. However, the distribution is reversed at 60°C with roughly two thirds liberated by pressure swing and the remaining one-third liberated by temperature swing. Hence, the active sites for weakly bonded versus strongly bonded CO₂ are strongly influenced by just a small change in temperature from 45°C to 60°C.

![Figure 103: Material balances for 196c for water and carbon dioxide comparing absorption and regeneration recoveries.]

The effect of raising the adsorption temperature from 60°C to 105°C under dry conditions using 10% CO₂/He shows that a significant amount of CO₂ will still absorb at this higher temperature, roughly 1.2 mol CO₂/kg sorbent, in the presence of 10% CO₂/He. The 105°C temperature represents the ceiling temperature attained during temperature swing regeneration. The working capacity of the sorbent is defined as the difference in loading between the rich loading (i.e., the absorption capacity under flue gas conditions) and the lean loading (i.e., the absorption capacity under regeneration conditions). The type of sweep gas employed during regeneration, whether
CO₂ recycle or inert gas sweep, will affect the lean loading attained during regeneration. Thus for the above example, the working capacity of the sorbent will be greatly reduced by about 40% when attempting to regenerate in a CO₂ partial pressure of 0.1 atm versus pure helium sweep regeneration. Attempting to regenerate under higher partial pressures of CO₂ will further reduce the working capacity for this particular sorbent (Hoffman, et al., 2012a).

The effect of high CO₂ partial pressure (0.9 atm) was examined at low temperature (45°C) for absorption conditions as well as high temperature (105°C) for regeneration conditions. Under 0.9 atm CO₂, the sorbent absorbs significant loadings (corrected) of CO₂, roughly 3.5–4 mol CO₂/kg of sorbent at 45°C and 2.9–3.0 mol CO₂/kg at 105°C. Hence, the CO₂ capacity is increased by roughly 0.5 mol CO₂/kg when comparing 0.1 atm CO₂ versus 0.9 atm CO₂ under same absorption temperatures. However, when comparing the loading at 60°C and 0.1 atm CO₂ (3.2–3.3 mol CO₂/kg) versus 105°C at 0.9 atm CO₂ (2.9–3.0 mol CO₂/kg), a very low working capacity of about 0.3 mol CO₂/kg is obtained. Therefore these results again confirm earlier results (see Section 4.4.1) that attempting to regenerate under high partial pressures of CO₂ yields unacceptably low CO₂ working capacity for this particular sorbent. As mentioned previously, a steam sweep is proposed for the regeneration scheme.

The effect of moisture was examined, both by itself and in combination with CO₂ in the feed gas. Since the sorbent process is targeted to be located downstream of the flue gas desulfurization (FGD) unit in a commercial electric utility, H₂O levels near 8% and 16% were established in the feed gas. To simulate the effect of regenerating with steam sweep gas, H₂O levels near 90% were also established in the gas.

Although equilibrium CO₂ loadings are attained within 15–30 minutes, a much longer period of time is required to achieve equilibrium H₂O loadings, on the order of 3 to 4 more hours. This has the effect of equilibrium H₂O loadings being much greater than CO₂ loadings, by as much as a factor of 10 for FGD simulated conditions. However, this effect can be lessened by engineering the absorber to restrict the solid contact time. This can be seen in Figure 104 for the absorption at 60°C.
For this particular sorbent and within 10–15 minutes initial contact time, the H₂O loading will be approximately twice the CO₂ loading. The effect of moisture on CO₂ loadings is minimal at best, perhaps enhancing CO₂ loadings by 10 to 15 percent. In the case of FGD simulated conditions (16% H₂O), the CO₂ loading increased from approximately 3.3 to 3.5 mol CO₂/kg sorbent under dry versus wet conditions, respectively. When the dry and wet cases are superimposed on top of one another, there is little difference in the time histories of the absorption breakthrough curves and desorption/regeneration breakthrough curves. This suggests that there is little competition for adsorption sites between CO₂ and H₂O.

Reactivation or regeneration of the sorbent was sometimes conducted in two stages: a one-hour isothermal pressure swing desorption under pure helium purge, followed by temperature swing (2°C/min) regeneration. (See Figure 105) With respect to H₂O, the first stage of pressure swing desorption was sufficient to liberate the adsorbed H₂O. However, with respect to CO₂, both stages (pressure swing and temperature swing) were required to liberate the adsorbed CO₂. These results suggest that both weakly bonded and strongly bonded CO₂ sites are present, whereas only weakly bonded H₂O sites are present.
As can be seen in Figure 106, halving the moisture in the feed (from 16% to 8%) caused the absorber H$_2$O loading to drop by roughly 70% (from roughly 30 to 9 mol H$_2$O/kg). This suggests that the equilibrium H$_2$O loading is highly sensitive to the partial pressure of H$_2$O. Even at lower H$_2$O loading, substantial contact time is still required to achieve H$_2$O equilibrium absorption loadings. Therefore, it is still prudent to restrict the solid contact time in the absorber to achieve maximal CO$_2$ performance but minimize H$_2$O pick-up, so as to mitigate regenerative heat duty losses in the regenerator from H$_2$O desorption. It should be noted that in Figure 106, results for another sorbent 184a are shown. This sorbent contains the same PEI loading but is on a PMMA substrate rather than the silica. The moisture loading curves are superimposed for the two sorbents and would indicate that the substrates are not significant contributors to the sorbent moisture pickup.
Along the same lines, the silica support (G-10, HPV) was also examined for its affinity towards individual and combined CO\textsubscript{2} and H\textsubscript{2}O gases. G-10 silica was found to have virtually no affinity for CO\textsubscript{2} using 10% CO\textsubscript{2}/He gas at 60\textdegree C and 105\textdegree C, having loadings of approximately 0.08 and 0.07 mol CO\textsubscript{2}/kg, respectively. The effect of moisture was examined, both by itself and in combination with CO\textsubscript{2} in the feed gas. The test conditions mirrored those performed with sample 196c for simulated FGD conditions, namely H\textsubscript{2}O levels near 8\% and 16\% were established in the feed gas for 60\textdegree C absorption. The silica does have some affinity to absorb H\textsubscript{2}O. The presence of CO\textsubscript{2} in the feed gas makes no difference in the substrates affinity for H\textsubscript{2}O. Roughly 2.5 and 5.0 mol H\textsubscript{2}O/kg loadings are achieved at 8\% and 16\% H\textsubscript{2}O, respectively, a doubling of capacity that is in proportion to the doubling of the feed moisture. During regeneration, the H\textsubscript{2}O is essentially completely liberated during the isothermal desorption phase, and little, if any, H\textsubscript{2}O is liberated during the thermal regeneration phase, again indicative that the H\textsubscript{2}O is more weakly bonded than the CO\textsubscript{2} since temperature swing is required in the case of sample 196C to remove the remainder of the CO\textsubscript{2}. Although the substrate does have some affinity to attract H\textsubscript{2}O, it is obvious that the silica plays a lesser role in moisture absorption compared to the amine. Thus it is the presence of the amine that plays the dominant role in attracting water, presumably through hydrogen bonding. Although it may be possible to engineer a sorbent having a hydrophobic support, the presence of the amine could still dominate and make the sorbent overall hydrophilic.

The effect of simulated steam without CO\textsubscript{2} (0.9 atm H\textsubscript{2}O) on sorbent regeneration was examined and can be seen in Figure 107. However, because of the high moisture content in the feed gas, it was necessary to reduce the dry helium flow rate in the feed gas from 100 sccm to 12 sccm in
order to keep the total gas flow (and hence space velocity through the reactor) within a similar regime as the dry cases. The helium flow rate was kept at 100 sccm for the isothermal pressure swing desorption step. Multi-cycle tests were conducted at 105°C, and the H₂O breakthrough curves occur exceedingly fast, reaching equilibrium capacity within several minutes. The regeneration curve with pure helium is slightly slower despite the higher helium sweep flow rate. Both results suggest that when the regenerator is designed to achieve adequate CO₂ regeneration, because of the very fast nature of the H₂O adsorption, the sorbent will quickly achieve equilibrium moisture loadings when a sweep of steam gas is employed in the regenerator. The best estimates conclude that the sorbent will achieve an equilibrium moisture loading of about 10-15 mol H₂O/kg when exposed to steam-like conditions of 90% H₂O/He at 105°C. This equilibrium moisture estimate does not consider the dead volume of the reactor under these conditions (approximately 0.6–0.8 mol H₂O/kg capacity) and therefore can be subtracted from the above reported H₂O values. However, given the variability in the sorbent measurements under simulated steam, such correction was not implemented. The effect of simulated steam on the silica support yields similar conclusions regarding the hydrophilic character of the amine outweighing that of the support. Seeking to avoid any desorption of water within the regenerator that would thereby raise the regenerator heat duty, manipulation of moisture loadings between the absorber and regenerator is described in greater length while introducing the concept of the BIAS process. Sorbent stability tests suggest that steam contacting the sorbent can cause degradation in the baseline CO₂ loading capacity with this particular sorbent (196c).

Figure 107: Absorption/regeneration with 196c at near total steam conditions at 105°C.
The BIAS Process

Based on the previous findings for the BIAS sorbent (Hoffman et al., 2012a), it was now possible to design the absorber and regenerator in a continuous flow scheme in such a manner so as to manipulate the moisture loadings on the sorbent as it travels around the circulation loop. Balancing the moisture loadings is an attempt to mitigate moisture desorption in the regenerator and ultimately improve the heat duty requirements. For instance, by appropriately restricting sorbent contact time with flue gas in the absorber so as to match the equilibrium moisture loading that will be rapidly attained in the regenerator under steam sweep, desorption of moisture in the regenerator will be lessened. However, some level of dehydration after the regenerator is probably necessary to avoid condensation of water onto the sorbent, since it must be cooled back down to the absorption temperature to repeat the absorption cycle.

Figure 108 shows a conceptual layout of the proposed BIAS process (Hoffman et al., 2012a; Pennline et al., 2013). The basic tenet is to manipulate or control the level of moisture on the sorbent as it travels around the sorbent circulation path between the absorption and regeneration stages. The sorbent is circulated between absorption and regeneration vessels while removing CO$_2$ from flue gas and thereby recovering a concentrated CO$_2$ off-gas from the regenerator. Both CO$_2$ and H$_2$O loadings, as determined for immobilized amine sorbent sample 196c, are depicted along the sorbent circulation loop. To maintain maximum driving force for gas/solid transfer, the absorber and regenerator are configured for countercurrent flow operation using moving bed reactors, with sorbent traveling in downward flow under gravity with an upward flow of gas.

A major key to successful implementation of the BIAS process is effective integration of heat management. Appreciable chemical heats of reaction are encountered during CO$_2$ absorption, and conversely, regeneration. Within a conventional bed of sorbent, the resulting exotherm will be significant and, due to poor heat transfer within the bed, the bed will likely overheat. The opposite effect will occur in the regenerator, with the resulting endotherm cooling the bed. Although the specifics are not detailed in Figure 108, both vessels will require internal heat exchangers with a circulating fluid. In the case of the absorber, the likely fluid to dissipate the heat is cooling water, whereas in the case of the regenerator, indirect steam is a suitable fluid to heat the regenerator. The indirect steam for regeneration is well suited since its temperature closely matches the temperature required for thermal regeneration of the sorbent. The regenerator would most likely rely on using a condensing steam heat exchanger since the latent heat of phase change of steam is large and would transfer considerable heat into the bed of sorbent. The heat removed from the absorber should be recovered as low grade heat within the integrated power plant, such as preheating water for steam generation, etc. Similarly, a condenser is used to separate the moisture from the regenerator off-gas, and this low grade heat is also recoverable.
The above heat considerations account for the chemical energy of removing CO$_2$, namely the heats of reaction. However, there are additional terms that contribute to the overall energy needed to regenerate the sorbent, commonly termed as the regenerative heat duty. (See the second equation in the MATRIX Study Section 4.3.2.) Since temperature swing is employed for regeneration in the BIAS process, with the absorber at 60°C and the regenerator at 105°C, a sensible energy term of the sorbent must be accounted for. This term involves the heat capacity of the sorbent, the CO$_2$ working capacity of the sorbent, as well as the delta temperature swing. To minimize this sensible term, a solid-solid cross flow heat exchanger is shown in Figure 108, whereby the hotter CO$_2$-lean sorbent exiting the regenerator indirectly contacts the cooler CO$_2$-rich sorbent exiting the absorber and exchanges the sensible heat. This method is similar to the cross-flow heat exchanger commonly employed in liquid MEA scrubbing. Actual solid-solid heat exchangers and their relation to CO$_2$ capture with sorbents are described elsewhere (Ziegler, 2010).

Based on the experimental findings with basic immobilized amine sample 196c and the required use of steam sweep gas to maintain sufficient CO$_2$ working capacity, a direct steam sweep gas is fed into the bottom of the regenerator in Figure 108. The amount of sweep gas required is currently not known, but a minimum steam flux will be necessary to allow the exiting sorbent to be in equilibrium with essentially zero partial pressure of CO$_2$ surrounding the sorbent, and thus achieve a maximum level of regeneration and CO$_2$ working capacity. Based on experimental findings using simulated steam, sample 196c is expected to achieve an equilibrium moisture loading of approximately 15 mol H$_2$O/kg of sorbent within the regenerator. It is desired that
moisture desorption be minimized/avoided in the regenerator, to lessen its impact on increasing the regenerator heat duty. Therefore, the sorbent entering the regenerator (or equivalently exiting the absorber), should have the same moisture level of near 15 mol H₂O/kg so as to keep the moisture level constant across the regenerator.

If the absorber is designed correctly for the appropriate gas-solid contact time, the sorbent will absorb roughly 3.5 mol CO₂/kg and 7 mol H₂O/kg from the flue gas. Since the regenerator requires an input of 15 mol H₂O/kg that exits the absorber, the recycled sorbent entering the absorber should have a moisture loading of 8 mol H₂O/kg. Assuming the sorbent moisture content is additive, the moisture loading on the sorbent will increase from an entrance level of 8 mol H₂O/kg to an exit level of 15 mol H₂O/kg across the absorber while in contact with moist flue gas (approximately 17 volume percent moisture) for a restricted period of time.

The sorbent exiting the regenerator will have an equilibrium water loading of 15 mol H₂O/kg at 105°C by being contacted with steam sweep gas. Equilibrium with respect to moisture is reasonable since sorbent residence time in the regenerator will be large as compared to the absorber. It is necessary to cool the sorbent back down to 60°C to repeat the absorption cycle. However, such cooling could cause condensation of absorbed water on or within the sorbent. It is also conceivable that residual steam within the pore structure could also condense with cooling. This should be avoided from the perspective of sorbent stability, given that liquid water could possibly impact the amine in the substrate matrix. Thus a dehydration step is first incorporated before lowering the sorbent temperature so as to avoid the possibility of moisture condensation.

A sample conditioner is depicted in Figure 108 to accomplish partial dehydration of the sorbent exiting the regenerator. Any inert sweep gas could be used, and it could need to be preheated to avoid contacting the hot sorbent with sweep gas at ambient temperature causing condensation on the sorbent. If the sorbent is stable with respect to oxygen at elevated temperature, then preheated dry air can be used as the sweep gas. Calculations indicate that this heat penalty will be minor. The contact time in the sample conditioner should be designed to achieve partial drying of the sorbent such that 7 mol H₂O/kg are removed from the sorbent and transferred to the air sweep gas. This will balance the moisture loading on the sorbent around the circulation loop, by lowering the moisture loading from 15 mol H₂O/kg to 8 mol H₂O/kg across the conditioner.

From a thermodynamic perspective, the BIAS process avoids moisture desorption within the regenerator but instead results in partial moisture desorption within the conditioner. The desorption of water will be endothermic regardless of which location it occurs and is an energy penalty on the heat duty. However, the enthalpy of the sweep gas needs to be considered. In the case of the regenerator, the sweep gas is steam. In the case of the conditioner, the sweep gas is preheated air. The steam has higher heat value (enthalpy) than preheated air and is therefore more valuable (or costly) to produce and use. Therefore the use of sweep air in the conditioner is more preferable to control the moisture loading. It should also be noted that most of the experimental results are for one sorbent (sample 196c) and that more recent sorbents adsorb considerably less moisture in the absorber and regenerator.
Sorbent Stability Under Moisture Conditions

These types of immobilized amine sorbents will be exposed to moisture in a post-combustion application in both the absorption step (moisture in the flue gas) and in the regeneration step (steam temperature swing). Some researchers indicate that it is critical to have moisture present (Sayari et al., 2010). From experimental work, moisture in the absorption and regeneration gases stabilizes the sorbent, unlike the zeolite and activated carbon sorbents. With the amine-based sorbents, moisture presence prevents the formation of urea that would diminish the CO\textsubscript{2} capture performance of the sorbent.

As suggested in the above testing (Hoffman et al., 2012a), the sorbent may be impacted by steam regeneration. Other researchers using immobilized amine sorbents have reported various results. Researchers at Georgia Tech (Li et al., 2010a) reported that little degradation in CO\textsubscript{2} performance occurred with a Class 1 PEI-silica sorbent that was steam stripped during the regeneration step over three cycles. However, the same group found that exposing amine supported on foamed silica to steam conditions in an autoclave for up to 24 h resulted in a decrease in the CO\textsubscript{2} sorption capacity of the sorbents, a decrease postulated to be due to a collapse of the structure of the support (Li et al., 2010b). Thus, changes to the support could play a role in the decrease in performance of the sorbent, although it must be noted that the silica support that NETL research typically used with the basic immobilized amine sorbents is different than the foamed silica support used in the Georgia Tech study.

Since steam regeneration is a needed step with the BIAS sorbents and since there are few studies that have investigated this step, a more recent study at NETL has furthered this knowledge base (Hammache et al., 2013). The sorbent used was PEI immobilized on silica. The sorbent was synthesized by impregnating SiO\textsubscript{2} (Fuji Silysia Cariact grade G-10 HPV, size 75–500 μm) with polyethyleneimine (PEI) (Aldrich PEI Mn-423). Similar to past fabrications, a homogeneous solution of PEI and methanol was added to SiO\textsubscript{2} to form a slurry. The slurry was then placed in a rotary evaporator set to 60°C and rotated for 2 h. The methanol was gradually removed using a vacuum pump once the slurry was fully mixed. The resulting solid was then refrigerated. The target PEI loading within the sample was 50 wt%. A silanated sorbent was prepared following the same procedure except in this case PEI was mixed with aminopropyltriethoxysilane (Aldrich) \[\text{[H}_2\text{N(CH}_2)_3\text{Si(OC}_2\text{H}_5)_3\text{]}\] and methanol to form the homogeneous solution. The targeted wt % was between 40 and 45 organic with 5 wt % being the silane agent (aminopropyltriethoxysilane). The silane agent was added to promote stability and to possibly improve the interaction of PEI with the support, thus improving the dispersion of the amine and therefore the efficiency of the sorbent.

The testing was conducted in a laboratory-packed bed reactor system that has been described previously (see Figure 91). Typically, 1 g sorbent was loaded into a stainless steel tube (3/8 in O.D.). The sample was held in place using quartz wool plugs. The baseline performance of the sorbent was established by testing under dry cycles. A gas stream with a composition of 10 vol% CO\textsubscript{2}/He is passed through the sorbent at 60°C. Once near equilibrium CO\textsubscript{2} uptake is reached, the sorbent is isolated using two three-way valves. Helium is then used to purge the system after which the reactor is brought back on-line for regeneration. The regeneration consists of two steps: an isothermal pressure swing desorption at 60°C followed by a temperature swing desorption in which the remaining CO\textsubscript{2} desorbs by ramping the sorbent temperature to 105°C at 2°C/min. When steam regeneration was used, the reactor temperature was first increased to 105°C under stagnant conditions and then the sorbent was swept with 90 vol% H\textsubscript{2}O/He. Helium
was added to the steam as a reference gas for the mass spectrometer, used to analyzed reactor exit gas. After the steam regeneration, the sorbent was dried at 105°C under He. The sorbent temperature was then decreased to 60°C. The impact of long exposure time to steam conditions was also investigated. The sorbent was first tested under a full dry cycle, followed by a cycle where adsorption of CO$_2$ occurred under dry conditions at 60°C and desorption occurred using a stream of 90 vol% H$_2$O/He at 105°C held for 5 h. The sorbent was dried with a helium sweep at 105°C after steam regeneration. The sample was then tested under a dry cycle to determine its performance after exposure to the steam conditions.

Figure 109: Impact of steam regeneration on the performance of PEI/silica (PEI-Si) and PEI/silica with silane (PEI-Sil-Si). In cycles 1 and 8, the sorbents were regenerated in 100% He using the two steps of regeneration: a pressure swing at 60°C followed by a temperature swing to 105°C. In cycles 2 to 8, the sorbents were regenerated in 90 vol% H$_2$O/He at 105°C.

Figure 109 shows the variation in CO$_2$ loading on the sorbent candidates with the number of cycles. For the PEI/silica (PEI-Si) sample, the initial and final cycles (cycles 1 and 8) are dry cycles. The CO$_2$ uptake on the fresh sample was found to be 3.2 mmol/g sorbent, similar to PEI-containing sorbents discussed earlier. The trend is towards a decrease in CO$_2$ capture. A slight decrease in CO$_2$ uptake from 3.2 to 3.0 mmol/g sorbent (cycle 3) can be seen after one complete cycle with steam regeneration. After two additional cycles with steam regeneration, CO$_2$ uptake
decreased to 2.7 mmol/g sorbent (cycle 4). Subsequently a leveling in CO$_2$ uptake occurred at 2.8 mmol/g sorbent (cycles 5–7). CO$_2$ uptake in the final cycle (cycle 8), measured at dry conditions, was found to be 2.8 mmol/g sorbent, a decrease of 12% from the CO$_2$ uptake measured on the fresh sorbent under the dry cycle. Most of the loss in CO$_2$ loading occurred in the first three cycles, with a concomitant loss in overall sorbent performance. The same experimental protocol was applied to silane PEI/silica (PEI-Sil-Si) sample and can be seen in Figure 109. CO$_2$ uptake of the fresh PEI-Sil-Si was 3 mmol/g sorbent. A similar trend occurred with PEI-Sil-Si as seen with PEI-Si under steam regeneration – a decrease in CO$_2$ loading by about 10%, (3 mmol/g sorbent to 2.7 mmol/g sorbent). The CO$_2$ loading appears to quasi-stabilize after the 4th cycle, although a slight decrease in CO$_2$ loading continued.

The amount of moisture adsorbed and desorbed by the sorbents at 105°C was found to be in the range of 6 to 8 mmol/g sorbent for both sorbents, consistent throughout all six cycles. Water uptake may occur either on SiO$_2$, on the amine, or both. In order to discriminate between the contribution of SiO$_2$ and the amine, moisture loading on bare SiO$_2$ was determined at 105°C using a gas stream composition of 90 vol. % H$_2$O/He, and was found to be only 2.7 mmol/g SiO$_2$. These results coupled with the previous conclusions of Hoffman (Hoffman et al., 2012), suggest the majority of the water was taken up by the amines. The presence of 5 wt. % aminopropyl-triethoxysilane appears not to alter the water uptake of the sorbent.

Two additional modes of steam addition were investigated to further elucidate the impact of steam. In one instance the steam addition was similar to the standard technique except that the sorbent was cycled once and held continuously under steam at 105°C for 5 h. In the other case, the sorbents were exposed to six steam cycles consisting of only H$_2$O adsorption and desorption (drying steps) and every cycle was held approximately 30–40 min resulting in a total time of about 3 hour. No CO$_2$ adsorption occurred during the six cycles. Results allow for separation of the impact of adsorbed CO$_2$ on the interaction of the sorbent and H$_2$O during regeneration. Cycling a sample through six cycles of steam without CO$_2$ sorption resulted in a similar loss in the performance of PEI-Si as before. Holding the sorbent at 105°C for 5 hour under the continuous steam condition resulted in a loss of only 3 % CO$_2$ loading. The impact of steam was more significant for the cyclic cases where the sorbent was exposed to H$_2$O for a total time of around 3.5 h rather than when exposed continuously to H$_2$O for 5 h. The H$_2$O adsorption/desorption cycle appears to have impacted the loss in CO$_2$ loading, possibly suggesting that the drying step degrades the PEI-Si sorbent. The results with the PEI-Sil-Si were not the same as with the PEI-Si sorbent suggesting that the steam exposure impacts the sorbent somewhat differently.

Several possible causes for the decline in the CO$_2$ uptake of the sorbent after steam treatments were speculated: 1) the effect of the support, 2) a change in the nature of the amine, 3) a thermal effect, 4) a leaching of the amine by water, and 5) a change in the distribution of the amine on the support (Hammache et al., 2013). From using various analytical techniques, such as TGA, SEM, BET, and DRIFTS, results were obtained that led to the conclusion that the steam regeneration for the PEI-Si sorbent only impacted the distribution of the amine on the support. Upon steam treatment, the surface area and the pore volume of PEI-Si decreased. The decrease in the BET surface area for this sorbent was most prominent when the sorbent was cycled through six steam cycles, whereas a similar decrease is seen for the pore volume, when either the sorbent was exposed to six steam cycles or six steam regenerations. TGA results showed no decrease in the amount of organics on the support, consistent with the decrease in the BET
surface area and pore volume. These results tend to suggest that a re-agglomeration of the amines on the support occurred resulting in a partial blockage of the pores. The decrease in available amines will thus explain the decrease in CO$_2$ loading. However, for PEI-Sil-Si, no significant change was found in the BET surface area and pore volume between the fresh and the spent sorbents, and the cause of the loss in the CO$_2$ capacity for PEI-Sil-Si remains undetermined.

It is projected that these BIAS sorbents will use a sweep of steam for regeneration. The impact of this steam is extremely important. As the research effort shows, PEI-containing sorbents can have an initial loss in CO$_2$ capacity after successive steam regenerations. In the above study, silane addition did not appear to have a stabilizing effect on the CO$_2$ capture capacity of the PEI containing sorbent. Although the CO$_2$ capacities of these particular sorbents did appear to level off, numerous absorption/regeneration cycles of the sorbent are needed to substantiate conclusions about these sorbents. Only few studies in the area of steam regeneration have been conducted. The one above has been unique and directs that additional work in this area is critically needed.

4.4.3 Effects of Trace Contaminants in Flue Gas

With respect to Lewis acid/base chemistry, the amine-containing sorbents are very basic. This is a reason CO$_2$ is attracted to them. When coal is burned and subsequently flue gas is produced, sulfur in the coal is oxidized to form sulfur dioxide. Similarly in combustion, nitrogenous compounds in the coal are oxidized to form fuel-NO$_x$ whereas nitrogen in the incoming combustion air can be oxidized at high temperatures to form thermal-NO$_x$. The sulfur dioxide (SO$_2$) and nitric oxides (NO$_x$)—precursors to acid rain—are acidic, and it was speculated that they would react with the amine-enriched sorbents. Thus scrubbing of these components would be needed upstream of the CO$_2$ capture system.

From the past work with monoethanolamine (MEA) wet scrubbing, it was known that SO$_2$ would deleteriously impact the activity of the MEA towards CO$_2$ capture performance (White et al., 2003). It has been proposed that the SO$_2$ concentration within the inlet flue gas should be kept to less than 10 ppm. Roughly, uninhibited combustion of a high sulfur coal will produce 3,000 ppm of SO$_2$ and 600 ppm of NO$_x$, of which roughly 95% is NO and 5% NO$_2$. A deep scrubbing flue gas desulfurization system would be needed to scrub the SO$_2$ in the flue gas and would be located upstream of the CO$_2$ capture system. Low NO$_x$ burners and other combustion modifications would be needed to sufficiently reduce the NO$_x$. Determining the impact of these compounds on the basic immobilized amine sorbents (BIAS) in the event of upstream failure of the scrubbing systems was of interest. The extent of the reaction of these compounds with the sorbents was not known, and this directed studies with these gases in the presence of BIAS sorbents.

In the following, tests of the sorbents were typically conducted at elevated SO$_2$ and NO$_x$ levels within the simulated flue gas. Reasoning was two-fold. If a sorbent was situated in a real application in a power facility that burns coal, the possibility exists that, due to an upset in the main flue gas desulfurization unit, a possible polishing unit, or low NO$_x$ burners upstream, the sorbent may be exposed to high concentrations of SO$_2$ and/or NO$_x$. Additionally, the higher levels of SO$_2$ and NO$_x$ would represent an accelerated exposure of these contaminants with the sorbent (a worse case scenario). If the low levels of SO$_2$ and NO$_x$ (10 ppm) were used in the testing, many hundreds of cycles would be needed before an irreversible poisoning of the sorbent could be detected.
Initial Results with Immobilized Amine Sorbents

One of the first studies conducted in this research area was in collaboration with the University of Akron using a silica-based aminated sorbent that was described previously in Section IV.B.1. Some of the objectives of the study (Khatri et al., 2006) were to investigate the nature of adsorbed CO$_2$ species on the amine-grafted SBA-15 sorbent and on a commercial polymer amine-based sorbent, and to evaluate the SO$_2$ capture capacity of the amine-grafted SBA-15 sorbent and its effect on CO$_2$ adsorption capacity. SBA-15 was used as the support because of its high hydrothermal stability as well as its large pores and high surface area for amine grafting. CO$_2$ and SO$_2$ adsorption and desorption were studied by a transient technique and temperature-programmed desorption with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectrometry (MS).

The sorbent investigated was APTS-SBA-15 or SBA-15 grafted with gamma-(aminopropyl)-triethoxysilane. Preparation of the sorbent was described in Section 4.2.1. A commercial sorbent (SA9-T), which is an amine immobilized on a polymer support and which has been utilized in CO$_2$ capture from closed habitats, was used as a reference for comparison. The experimental setup was also described previously (see Figure 63). A DRIFTS reactor filled with 30 mg of the sorbent was followed by a tubular reactor filled with 300 mg of the sorbent; a mass spectrometer was used for effluent analysis. The adsorption of CO$_2$ was carried out by switching the inlet flow from an inert gas stream (argon) to the adsorbing gas stream (10 vol% CO$_2$ in argon). Upon saturation of the sorbent with the adsorbing gas, the inlet stream was switched back to the inert gas stream. The SO$_2$ adsorption was carried out in a similar way with 2% SO$_2$/4% H$_2$O in helium. The spent sorbent containing adsorbed CO$_2$ was regenerated via temperature-programmed desorption (TPD) by heating the DRIFTS and tubular reactors simultaneously from room temperature to 120°C in an argon stream at a rate of 10°C/min. The CO$_2$ concentration profile during TPD was monitored by the MS, and the amount of CO$_2$ was quantified by calibrating the CO$_2$ (m/e = 44) response on the MS. The calibration factor was obtained by injecting 1 ml of CO$_2$ gas in a flowing argon stream and calculating the area corresponding to the amount of CO$_2$ injected. SO$_2$ TPD was carried out in a similar way, and the calibration factor was obtained by injecting 1 ml of SO$_2$ in a flowing He stream and monitoring the SO$_2$ (m/e = 64) response on the MS.

With respect to the adsorption of CO$_2$, the formation of carbonates and bicarbonates on the surface of the sorbent occurred, as determined from the DRIFT analysis. Desorption of the carbonate and bicarbonate species led to the formation of gas-phase CO$_2$, as observed from the MS intensity for CO$_2$. The CO$_2$ adsorption capacity of APTS-SBA-15 was calculated to be 728 micromol/g of sorbent at a desorption temperature of 120°C from the MS TPD profile for CO$_2$. Similarly, the CO$_2$ adsorption capacity of SA9-T was calculated to be 440 micromol/g of sorbent. Capacities of both sorbents were low.

The DRIFTS IR spectra during 2% SO$_2$/He adsorption in the presence of H$_2$O are shown in Figure 110. The adsorption of SO$_2$ on APTS-SBA-15 led to an increase in IR bands at 1,108, 1,200, 1,250, 1,342, 1,533, and 1,633 cm$^{-1}$ and a decrease in IR bands at 2,867, 2,993, 3,308, and 3,358 cm$^{-1}$. The bands at 1,108, 1,200, and 1,250 are assigned to the S=O stretching vibrations of sulfates and sulfites formed on the surface of APTS-SBA-15. The sharp decrease in the IR bands at 3,308 and 3,358 cm$^{-1}$ for N-H symmetric and asymmetric stretches and that in the IR bands at 2,867 and 2,933 cm$^{-1}$ for C-H symmetric and asymmetric stretches are due to the reaction of surface amine with SO$_2$ and the formation of sulfates and sulfites on the surface.
DRIFTS IR spectra and the MS intensity during a TPD study of the adsorbed SO\textsubscript{2} on APTS-SBA-15 in the presence of H\textsubscript{2}O were also obtained (Khatrî et al., 2006). The increase in temperature led to a minor decrease in all of the sulfate/sulfite IR bands, while there was no significant change in the N-H and C-H stretching bands, indicating a strong irreversible interaction between SO\textsubscript{2} and the surface amine species. The amount of SO\textsubscript{2} desorbed from the surface was calculated to be more than 1,040 micromol/g of sorbent from the MS intensity profile of SO\textsubscript{2} during the TPD. The SO\textsubscript{2} desorbed from the surface only after the sorbent temperature reached 60°C, and the peak desorption temperature was at 120°C. The visual analysis of the sample after the TPD study showed the change in the color of sample from white to yellow, which might be due to the formation of irreversible sulfates/sulfites on the surface. CO\textsubscript{2} adsorption on this sample after regeneration from the SO\textsubscript{2} study showed a negligible CO\textsubscript{2} adsorption capacity, revealing that no free surface amine species were available for bonding with CO\textsubscript{2}.

From this study, it can be concluded that the adsorption of SO\textsubscript{2} led to the formation of sulfates and sulfites and an irreversible decrease in the C-H and N-H IR band intensities. The regenerated
APTS-SBA-15 sorbent after SO$_2$ adsorption showed a negligible CO$_2$ adsorption capacity. These results would confirm the NETL projection that the amine-based CO$_2$ absorption reactors would have to be placed downstream of a SO$_2$ scrubber. SO$_2$ in the flue gas will react irreversibly with the sorbent.

At the same time, a study was conducted at NETL with a BIAS sorbent (Fauth et al., 2006; Fauth et al., 2007). The unit used at NETL could perform multiple absorption/desorption cycling of the sorbent. Specifically, a BIAS formulation using reaction-modified tetraethyleneamineacyrilonitrile (TEPAN) and N, N’-bis(2-hydroxyethyl) ethylenediamine impregnated (BED) within a high surface area, polymethylmethacrylate (PMMA) support was investigated. The effect of trace flue gas constituents (moisture, NO/NO$_x$, and SO$_2$) on the performance of amine-enriched sorbent was evaluated. To immobilize the amines within the pores of the polymeric support, a solvent evaporation method was used. Initially, PMMA beads were uniformly dispersed in methanol within a rotary evaporator flask. Equal amounts of TEPAN and BED (dissolved in methanol) were then added to the beads, and the solution was rotated at room temperature for 5–10 minutes producing a homogeneous slurry. Subsequent removal of methanol was a short time by heating the rotary evaporator flask in a heated water bath. The procedure produced a BIAS sorbent with a high percentage of its theoretical pore volume filled with liquid amines. Specifics of the fabrication can be found in Section 4.2.1. (Fauth et al., 2007).

Testing occurred in the bench-scale packed bed reactor system that was previously described and can be seen in Figure 92. Results for certain conditions can be seen in Table 39. Typically, after the simulated flue gas was introduced to the reactor, the adsorption of CO$_2$ continued until the exit CO$_2$ stream asymptotically approached the inlet concentration. Upon reaching inlet CO$_2$ concentration, input delivery of CO$_2$, O$_2$, and H$_2$O was terminated. In switching to pure N$_2$, CO$_2$ rapidly desorbed from the sorbent. Thermal regeneration was accomplished by raising the bed temperature to 90–100°C as evidenced by an additional quantity of CO$_2$ being liberated from the BIAS sorbent. Clearly, the cyclic operation illustrates the reversibility of the BIAS sorbent, and CO$_2$ adsorption capacity was determined from the cyclic data generated within the bench-scale packed bed flow system.
Table 39: Test conditions and results for selected TEPAN/BED sorbent experiments where inlet gas composition in vol% is 9.0% CO₂, 3.5% O₂, ppmv NO, ppmv SO₂, and N₂ balance

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O concentration (vol%)</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>SO₂ concentration (ppmv)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>750</td>
<td>750</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>NO concentration (ppmv)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>750</td>
<td>750</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Adsorption**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature (°C)</td>
<td>40</td>
<td>38</td>
<td>38</td>
<td>39</td>
<td>41</td>
<td>40</td>
<td>39</td>
<td>40</td>
<td>41</td>
<td>37</td>
</tr>
<tr>
<td>Exotherm (°C)</td>
<td>25</td>
<td>27</td>
<td>29</td>
<td>27</td>
<td>34</td>
<td>35</td>
<td>27</td>
<td>29</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>Breakthrough time (min)</td>
<td>14</td>
<td>12</td>
<td>12</td>
<td>13</td>
<td>12</td>
<td>11</td>
<td>14</td>
<td>11</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>CO₂ adsorbed (liter)</td>
<td>2.51</td>
<td>2.36</td>
<td>2.22</td>
<td>2.15</td>
<td>1.98</td>
<td>1.97</td>
<td>2.47</td>
<td>1.71</td>
<td>1.64</td>
<td>1.57</td>
</tr>
<tr>
<td>CO₂ adsorption capacity</td>
<td>3.1</td>
<td>2.9</td>
<td>2.7</td>
<td>2.7</td>
<td>2.4</td>
<td>2.4</td>
<td>3.0</td>
<td>2.1</td>
<td>2.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

**Desorption**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Exotherm (°C)</td>
<td>13</td>
<td>12</td>
<td>14</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>14</td>
<td>14</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>CO₂ desorbed (liter)</td>
<td>2.36</td>
<td>2.17</td>
<td>1.75</td>
<td>1.87</td>
<td>1.71</td>
<td>1.69</td>
<td>2.18</td>
<td>1.72</td>
<td>1.53</td>
<td>1.51</td>
</tr>
</tbody>
</table>

**Thermal Regeneration**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CO₂ desorbed (liter)</td>
<td>0.14</td>
<td>0.46</td>
<td>0.42</td>
<td>0.40</td>
<td>0.42</td>
<td>0.44</td>
<td>0.71</td>
<td>0.17</td>
<td>0.17</td>
<td>0.14</td>
</tr>
<tr>
<td>Total desorbed CO₂ (liter)</td>
<td>2.50</td>
<td>2.63</td>
<td>2.17</td>
<td>2.27</td>
<td>2.13</td>
<td>2.12</td>
<td>2.89</td>
<td>1.90</td>
<td>1.70</td>
<td>1.65</td>
</tr>
</tbody>
</table>
The presence of water vapor appears not to influence CO₂ uptake for the sorbent. Results indicate steady performance with time-on-stream over fifteen cycles initially conducted. The average CO₂ adsorption capacity with an inlet gas composition of 9 vol% CO₂, 3.5% O₂, N₂ balance with 2% (and 4%) water vapor was 2.8 mol CO₂/kg of sorbent. This capacity is slightly better than the TGA experiments with this TEPAN/BED sorbent where the capacity was 2.3 mol CO₂/kg sorbent at 25°C (Fauth et al., 2007).

The effect of nitrogen oxide (NO) on the performance of the immobilized amine sorbent was examined using an inlet NO concentration of 750 ppmv. Adsorption of NO was found to be negligible during testing at 750 ppmv NO. Both CO₂ and NO (> 5 ppmv maximum) are simultaneously desorbed upon thermal regeneration at 90°C. A CO₂ adsorption capacity of 2.4 mol CO₂/kg sorbent was achieved with 750 ppmv NO present in the simulated flue gas mixture over consecutive adsorption/desorption/regeneration cycles.

The effect of sulfur dioxide (SO₂) on the performance of the BIAS material was examined utilizing 750 ppmv SO₂ present in the simulated flue gas steam. In these experiments with 750 ppmv SO₂ present, the sorbent was found to lose activity in incremental amounts with each consecutive cyclic adsorption/desorption/thermal regeneration operation. The BIAS material was found to adsorb both CO₂ and SO₂ simultaneously. As in CO₂ adsorption, an instantaneous drop in SO₂ concentration within the exit gas stream was observed. However, during the desorption process at 90–100°C, there was no indication of SO₂ being eliminated from the exterior surface of the BIAS material. A CO₂ adsorption average capacity of 2.0 mol CO₂/kg sorbent was achieved with 750 ppmv SO₂ present in the simulated flue gas mixture. An additional test without any SO₂ present in the gas stream revealed incremental loss in sorbent performance. (See Table 39.) During periods between experiments, visual inspection of the sorbent within the fixed bed revealed progressive degrees of “staining” or “discoloration” to the material. Upward delivery of the simulated flue gas mixture into the quartz column showed the lower portion of the sorbent bed to be darker in color compared to the upper section. In an attempt to desorb SO₂ from the sample at 120°C, loss of the BED component of the sorbent was observed. As in the previous study, the presence of sulfur dioxide in the flue gas will have a deleterious effect on the CO₂ capture capacity of an immobilized amine sorbent.

**PEI-Containing Sorbents**

More recent testing to determine the impact of contaminants on immobilized amine sorbents was conducted with PEI-based sorbents (Fauth, 2012). The objective was to determine if similar trends with the previous sorbents would be seen with PEI-containing sorbents that are excellent candidates for sorbent-based CO₂ capture technology. Again, bench-scale packed bed reactor studies with polymeric- and silica supported PEI-impregnated sorbents centered on investigating the sorbent interactions with flue gas constituents CO₂, O₂, and SO₂ over a multiple progression of temperature adsorption swing cycles. The sorbents were produced similar to the procedure outlined previously. PEI was introduced into polymeric and silica substrates prepared by wet impregnation. Linear PEI (average molecular weight 423, ρ = 1.03g/ml, Sigma-Aldrich) was impregnated into the respective support, (Diaion®HP2MG, methacrylic ester copolymer, Mitsubishi Co.) or silica (Cariact®G10, Fuji Silysia Chemical). All materials were characterized by N₂ adsorption-desorption isotherms at 77K using a Micromeritics ASAP 2020 automated volumetric instrument. BET surface areas were analyzed by the Brunauer-Emmett-Teller method. The total pore volumes and pore size distributions were calculated from analysis of the desorption branch of the respective isotherms using the BJH method. PEI loading was verified
by thermogravimetric analysis (TG) (Pyris®1, Perkin Elmer). Scanning electron microscopy (SEM) for particle morphology and energy dispersive X-ray spectroscopy (EDXS) for resolving the elemental composition of both fresh and SO₂-exposed supported PEI sorbents were performed using an ASPEX PSEM 2000™ electron microscope. As determined by TGA, the estimated quantities of PEI deposited within the applicable polymer and silica supports rendered polyamine weight loadings of 40 and 45%, respectively.

Carbon dioxide adsorption, desorption (in N₂ at adsorption temperature), and thermal regeneration measurements were performed utilizing the bench-scale packed bed reactor system as previously used (see Figure 92). Experiments were conducted by first loading a sample/inert diluent mixture (weight ratio 1:3) of ca. 100 g onto a fritted disc positioned in the center of a 400 mm length quartz reactor. The sample/inert diluent mixture was heated to 105°C and held overnight under a N₂ flow. After pretreatment to remove adsorbed H₂O and CO₂, the temperature was decreased to 60°C in N₂. The dry CO₂ concentration in the inlet gas was monitored at 10% by volume with 3.5% O₂ in nitrogen. Gas flows were held constant at 1.5 slpm. Desorption and thermal regeneration of the sample was conducted at 60°C and 105°C respectively, for 3 hr under N₂ flow (1.5 slpm). Bed temperatures were monitored with a series of K-type thermocouples positioned at ½-in increments upward from the center of the bed. The effluent gas was analyzed using gas analyzers downstream as previously explained.

A series of CO₂ and SO₂ uptake profiles were obtained by breakthrough experiments utilizing the silica-supported PEI sorbent. The results for this series of breakthrough experiments of silica supported PEI sorbent are shown in Figure 111. Throughout this specific set of experiments, nineteen adsorption/desorption/thermal regeneration cycles were completed. The CO₂ adsorption progression consisted initially of five adsorption cycles under dry 10% CO₂, 3.5% O₂ in nitrogen; followed by 11 additional cycles utilizing a reactant gas stream of 10% CO₂, 3.5% O₂ balance N₂ containing 1,000 ppm SO₂; followed immediately by three additional cycles identical to the first five cycles (i.e., dry 10% CO₂, 3.5% O₂ in nitrogen). Experimental values of initial CO₂ adsorption were high near 84 mmol. However, SO₂ poisoning of the sample initiated by adsorption of SO₂ onto the multiple active sites during each adsorption, desorption, and thermal regeneration cycle was also correspondingly high (near 7.15 mmol). The impact of the silica-supported PEI sorbent with SO₂ was further explored by scanning electron microscopy with energy dispersive X-ray analysis. SEM with EDXS was performed to identify the degree of sulfur deposited throughout the sorbent particles after repeated exposure from an SO₂-laden simulated flue gas stream. SEM micrographs of the fresh and SO₂-exposed sorbent particles are given in Figure 112. Sulfur was found to be uniformly deposited throughout the spent, SO₂-laden sorbent particles.
Figure 111: Summary data of CO\(_2\) and SO\(_2\) uptake profiles of silica supported PEI sorbent, using simulated flue gas of 10 vol% CO\(_2\), 3.5% O\(_2\), balance N\(_2\) containing 1,000 ppmv SO\(_2\).

Figure 112: Scanning electron microscopy micrographs of PEI/silica sorbent particles (A) before SO\(_2\) exposure, (B) after 1,000 ppmv SO\(_2\) exposure.
Similar poisoning results occurred with the PEI/polymer (polymethylmethacrylate or PMMA) sorbent. As can be seen in Figure 113, discoloration of the various sorbents occurred after exposure with SO$_2$ in the flue gas as compared to the original color of the sorbent.

![Figure 113: Pictures of sorbent. To the left, PEI/PMMA before exposure to SO$_2$. The middle and right photos depict PEI/silica and PEI/PMMA, respectively, after various cycles with 1,000-ppm SO$_2$ in the simulated flue gas.](image)

The PMMA-supported PEI sorbent progressively declined in CO$_2$ sorption upon multiple SO$_2$ exposures, as illustrated in Figure 114. The loss of sorbent performance was found relatively equivalent to the amount of SO$_2$ adsorbed per cycle. The total SO$_2$ uptake was reasonably consistent during each adsorption, desorption, and thermal regeneration cycle, as shown in Figure 114. Desorption and thermal regeneration of SO$_2$ at 60°C and 110°C, respectively, in pure N$_2$ was found ineffective. As a result, SO$_2$ reacts irreversibly with the polyamine, and its presence negatively impacts CO$_2$ sorption capacity by poisoning the sorbent.

Additional tests were conducted with either NO or NO$_2$ in the gas stream with these sorbents (Resnik, 2009). As seen previously with the TEPAN+BED sorbents, the NO did not have an impact after numerous absorption/regeneration cycles with NO in the simulated flue gas. However, NO$_2$ did significantly impact the sorbent in much the same manner as the SO$_2$. Figure 114 shows the results from exposure of SO$_2$ or NO$_2$ with the PEI/silica and PEI/PMMA sorbents. A 1:1 molar ratio can roughly be established, meaning that for every mole of SO$_2$ or NO$_2$ adsorbed onto the sorbent, a loss of one mole capacity of CO$_2$ occurs. (As will be seen later in Section 4.6, ADA studies found a similar correlation.)
For SO₂ and NOₓ, it can be assumed that sorbent deactivation is related to contaminant exposure and nothing else. If a 1-mole CO₂ decrease per 1-mole SO₂ (or NO₂) increase occurs on the sorbent, an approximate lifetime of the sorbent can be calculated for numerous cycles. It is assumed that the sorbent totally absorbs the inlet contaminant irreversibly over each cycle. The conversion of CO₂ will decrease according to the following formula:

\[
\text{Fractional conversion of CO}_2 = 1 - \frac{n}{a/cd}
\]

where \(n\) = the number of cycles

\(a\) = the inlet concentration of SO₂ (or NO₂) in mole fraction

\(c\) = the percentage CO₂ capture desired

\(d\) = the concentration of CO₂ in the inlet gas in mole fraction

As an example, assume the inlet volume concentration of CO₂ is 15%, and 90% overall CO₂ capture is desired for the sorbent system. If the inlet concentration of SO₂ is 20 ppm, then the conversion of CO₂ would reach 93% after 500 cycles and 50% after 3400 cycles. If the inlet flue gas was scrubbed even deeper to 10 ppm, the conversion of CO₂ would reach 96% after 500 cycles and 50% after 6800 cycles. It can be concluded that it is paramount that CO₂ capture sorbents of this type need to be exposed to very clean flue gas.

**TVA External Collaborative Study**

In collaboration with NETL through a memorandum-of-understanding, the Tennessee Valley Authority (TVA) conducted tests using NETL sorbents. Exposure of the sorbent to SO₂ was performed in a packed bed configuration that contained 30 gram of sorbent. The base gas contained 10 vol% CO₂ in nitrogen, and this was spiked with the following: either 1.8–2.0%
water vapor at 20°C or 50°C; 7.5% O₂ with water vapor at 50°C; or 470 ppm SO₂ with water vapor at 20°C. The SO₂ level of 470 ppm was selected to match conditions for a TVA unit near Muscle Shoals at that time. The sorbents used were Samples 186D, 187E and 187F, which contained about 33.4 wt% PEI with 6.6 % glycerol on a PMMA, polystyrene, and PMMA substrate, respectively. Sample 191A contained 33.4 wt% with an APD additive on PMMA; 191E contained 40 wt% PEI on PMMA; and 195A contained 40 wt% PEI on Cariact silica. Results of the SO₂ spiking after 5-cycles can be seen in Figure 115 (Stevens et al., 2008).

![Figure 115: Effect of SO₂ exposure on NETL sorbent containing PEI on silica or polymer supports. Tests were conducted at TVA.](image)

In each case, the presence of SO₂ decreased the capacity of the sorbent, similar to what NETL had found in its laboratories. SO₂ was taking up the active sites for CO₂, and it was speculated that sulfate may be formed in the presence of oxygen.

4.4.4 Kinetics

In the solid–gas reaction with immobilized amine sorbents, determination of the kinetic equation, rate controlling steps, and kinetic parameters provide valuable insight into the mechanism of the process. To optimize the design of an adsorption system removing CO₂ from flue gases, it is also important to establish the most appropriate expression for the equilibrium data. A relationship describing equilibrium data, using either a theoretical or an empirical equation, is essential to interpret and predict the extent of adsorption. Thus, the objective of a more recent study was to
determine the kinetics, equilibrium, and thermodynamic parameters of CO$_2$ removal by an immobilized amine on high surface area mesoporous silica material (Monazam et al., 2013).

A Thermo Cahn Thermomax 300 unit thermogravimetric analyzer (TGA) was used to examine the fundamental kinetics of CO$_2$ uptake information using immobilized PEI sorbent (see Figure 90). This apparatus has a reaction chamber volume of less than 30 ml. For a typical test, a 30 mg of sample was placed in the microbalance quartz sample bowl. Drying under an inert flow of nitrogen preceded the adsorption step. The adsorption was conducted within the temperature range of 40–100°C at five CO$_2$ concentrations: 5, 10, 20, 50, and 100 vol% with the balance nitrogen. The weight of the sorbent sample and the reaction temperature were recorded continuously. In all experiments, the flow rate of reactant gas (CO$_2$) and inert gas (N$_2$) were set at 100 ml/min (at standard rate) and were supplied by Butler Gas Supply of Pittsburgh, Pa with stock gas grade 99.99% purity. The sample size, gas flow rate, and particle size were optimized to minimize measurement artifacts due to dispersion and mass transfer of CO$_2$ to the sorbent particles. At the end of the adsorption step, the sorbent was again exposed to a flow of nitrogen at 105°C to regenerate the sample. A further ramp in temperature to 600°C under inert was conducted to drive off all organic material from the silica substrate and thus determine the loading of the PEI on the sorbent. The sorbent consisted of PEI deposited within a mesoporous silica. Information on sorbent sample “196c” that was used extensively in much of the BIAS testing can be found in Table 42.

To optimize the design of the CO$_2$ adsorption system, it is important to establish the appropriate mechanisms and quantitatively describe the thermodynamic equilibrium. Hence, understanding the equilibrium data is essential to predict the adsorption behavior. Therefore, the equilibrium experimental data for adsorbed CO$_2$ on immobilized PEI/silica sorbent were analyzed using various isotherm models, but the Freundlich and especially the Temkin isotherms best describe the CO$_2$ adsorption (Monazam et al., 2013). The Temkin isotherm describes the behavior of adsorption systems on heterogeneous surfaces, and assumes that (1) the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbent–adsorbate interactions, and that (2) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. From the experimental data, the one constant in the Temkin isotherm reflects bonding energy, which in turn dictates the type of interaction. The low values obtained (0.1–0.25 kJ/mol) indicate that interactions between the sorbate and sorbent are neither purely ion exchange nor purely physisorption. Higher values are indicative of ion exchange while lower values are indicative of physisorption processes. Experimentally, past regenerations with this type of sorbent have seen evidence of two types of bonding sites.

With respect to kinetics, the TGA data on CO$_2$ sorption on immobilized PEI/silica sorbent are illustrated in Figure 116 at different reaction temperatures in 100% CO$_2$. The CO$_2$ adsorption capacity and uptake in g-CO$_2$/g-adsorbent (q) were calculated from the weight gain during adsorption of the sample per initial weight of adsorbent. It can be seen that CO$_2$ uptake increased monotonically with CO$_2$ exposure time and the sorbent reached saturation levels in about 2 min. The rapid uptake of CO$_2$ was preceded by an induction period that resulted in a sigmoidal shaped uptake curve with time. The extent of the induction period depended on the CO$_2$ concentration and sorption temperature. In an atmosphere with 100% CO$_2$, this induction time increased as temperature increased initially up to 70°C and then decreased again. The time required for the sorbent to reach saturation was longer at the higher temperatures. Up to the maximum uptake at 70°C, the longer time to reach saturation was due to longer induction times; however, at 100°C,
the longer uptake time was a result of slower approach to equilibrium after the initial rapid rise. It is important to emphasize that the rate of CO₂ uptake decreased with increasing temperature.

![Figure 116: Effect of reaction temperature on CO₂ uptake for immobilized PEI sorbent particle and CO₂ reaction using 100% CO₂.](image)

In the development of the kinetic expression, the Weibull cumulative distribution function (CDF) displayed many of the necessary characteristics to explain the experimental observations for this type of sorbent. The Weibull function describes the decay rate of a lifetime process. It has the feature that has a memory in that the progress depends on the prior state. In the Weibull CDF, the reaction times are randomly distributed and the reaction curve exhibits a sigmoidal shape. An equation similar to the Weibull distribution function was developed for the reaction time (t) proportional to the fractional uptake (X) where “a” is referred to as the scale parameter and “b” is the shape parameter:

\[
X(t) = 1 - e^{(-at^b)}
\]

Experimental values of “a” and “b” were obtained by curve fitting the uptake data presented in Figure 117 with the above expression using TABLECURVE software. The typical fit of the equation to the CO₂ uptake, X, measurement is also illustrated in Figure 117. Agreement is very good over the entire experiment duration with little overall variance (Monazam et al., 2013).
Figure 117: Comparison of experimental fractional uptake (marker) to Weibull reaction model (lines) at different temperature for 20% CO₂ concentration.

Through mathematical manipulation of the Weibull CDF, an expression for the Arrhenius equation can be determined. A plot of ln(k) versus 1/T for the amine/silica sorbent with particle size of 80 micron according to particle-CO₂ uptake was conducted for each reaction temperature and CO₂ concentrations between 5 and 100%. The values for pre-exponential factor, A, and activation energy, E, for the CO₂ removal were obtained from the intercept and slope of the straight line. The temperature dependence for the activation energy, E, was fairly constant for different CO₂ levels as evidenced by nearly parallel lines. Overall, for all of the CO₂ levels, the rate of reaction decreased as the temperature increased and this yielded apparent negative activation energy. Interestingly, this finding was consistent with the negative temperature dependence observed by others testing the same sorbent sample 196c (Ebner et al., 2011). Incorporating all the equations led to a global kinetic rate expression.

\[
\frac{dX}{dt} = 0.42e^{\frac{6.62}{T}y_{CO₂}^{0.693}(1 - X)\sqrt{-\ln(1 - X)}}
\]

The calculated rate–time (dX/dt versus t) data obtained at different temperatures in Figure 118 show the maximum rate of process obtained at t > 0. In Figure 118, the maximum rate decreased with the increasing temperature as observed in the experimental results. However, the changes in the induction period with temperature were more complex and could not be described as accurately. These variations in the induction period were not a significant contribution to the overall rate. Later calculations with the kinetic model were used to predict the CO₂ uptake at different operating conditions and resulted in good agreement with experimental data. The results of this initial kinetic study validated that immobilized PEI sorbent has considerable potential for the removal of CO₂ from flue gas over a wide range of concentrations.
4.5 CLAY-BASED SORBENTS

4.5.1 More Recent Sorbent Development

The clay-based sorbents are another type of amine-enriched sorbent. The targets for this sorbent are the same as those established in the MATRIC study. Using these sorbents can significantly reduce costs as compared to the energy-intensive MEA scrubbing by eliminating the energy-intensive aqueous solutions and by using a low-cost, readily-available, substitute material with a much lower specific heat capacity. This sorbent concept incorporates amines or other polar liquids in a clay matrix. Clays have the ability to retain large quantities of polar liquids, such as water and amines, between their unit layers that are known to expand and imbibe such compounds. They are naturally occurring, low-cost materials with lower specific heat capacities than water. From the preliminary system analysis described earlier in Section 4.3.1 (Tarka et al., 2006b), the regeneration energy required for a liquid impregnated-clay sorbent can be significantly lower than that for the liquid-amine process. The liquid-impregnated clay sorbent is capable of capturing CO₂ in the presence of water vapor at 30–60°C and can be regenerated at temperatures around 80–100°C. The liquid-impregnated clay sorbent is available in small particle sizes (<200 microns) suitable for fluidized bed operation or in large particle sizes (1mm) suitable for moving bed or fixed bed reactor operations.

Additionally, embedding the amine in the clay matrix eliminates the corrosion problems of liquid amines. This, in turn, allows higher loadings of both amine and CO₂ that are not restricted by corrosion limitations. Adding to the economic benefits of the process is the use of low-cost clay matrices and facile fabrication of the solid sorbent. Preliminary process schemes suggest many operational advantages for the solid sorbent as compared to conventional liquid amine scrubbing.

Figure 118: Effect of temperature on reaction rate using 100% CO₂.
Sorbent Research for the Capture of Carbon Dioxide

systems, as seen in Section 4.3. Several reactor configurations using solid sorbents for CO₂ capture from post-combustion gas streams have been identified. One of these, a dilute-phase, fluidized bed (transport reactor), is projected to have a low pressure drop during the absorption step. The sorbent in the regenerator could then be fluidized by either recycled hot CO₂ or steam. The fluidizing CO₂ is available at high pressure from the product compression process, so that even modest pressure drops can be readily tolerated. With this design, much of the solids transport duty is internally available to the system and the solids handling and transport costs will be minimal (Siriwardane, 2008).

**Pre-Combustion**

The use of the sorbent material was primarily targeted for post-combustion applications, but the potential also existed to use these sorbents in a pre-combustion system, for example IGCC, that could replace the low temperature operation of the Selexol physical solvent scrubbing system (Siriwardane et al., 2007). For testing conducted after the MATRIC study, liquid-impregnated solid sorbent pellets suitable for fixed bed applications were prepared by using the fabrication procedure identified in the patent literature (Siriwardane, 2005). In a collaborative effort, sorbents were prepared by Sud-Chemie. Competitive gas adsorption studies were conducted in a bench-scale fixed-bed reactor at NETL’s Morgantown campus and described previously in the zeolite work in Section 2.2. A 20-cycle bench-scale test was conducted at 19.1 atm with 16 volume percent CO₂ and 84 percent N₂ saturated with water vapor. The regenerations during the 20-cycle test were conducted at 80°C and 19.1 atm with steam and N₂. The space velocity utilized during the bench-scale tests was 1,000 h⁻¹. The reactor bed diameter is 2 inches, and about 350 grams of the sorbent were used to form a 6-inch bed height. The sorbent was also regenerated by lowering the pressure to 1 atm after CO₂ sorption at 30°C.

The results of the CO₂ removal from a gas mixture containing 16 percent CO₂ and N₂ saturated with steam are shown in Figure 119. This test series was continued for 20 cycles of absorption and regeneration at 20 atm. The sorbent removed CO₂ from the inlet 16 percent to ppm levels and achieved 99 percent removal efficiency with stable reactivity during the 20-cycle test. This indicated that the regeneration at 80°C and 20 atm was satisfactory and did not affect the sorbent’s performance. Since regeneration could be performed at 20 atm to produce a concentrated CO₂ stream, this could reduce the cost of compression necessary for CO₂ after the capture step in the carbon sequestration scenario. The capture capacity of the sorbent at 20 atm is significantly higher than that of the Selexol process, which has a capture capacity of less than 1 mole per liter at similar conditions. Since the sorbent performs well at high pressure and with a high concentration of CO₂, this could be suitable for separation of CO₂ from IGCC fuel gas after the shift reactor to produce H₂ (Siriwardane et al., 2007).
Figure 119: Bench-scale tests with NETL liquid-impregnated solid sorbent (Süd-Chemie prepared extrudates) at high pressure (20 atm; 30°C; space velocity 1,000 h⁻¹; feed composition of 16% CO₂, 84% N₂).

These were preliminary results with respect to the application of the sorbent in a pre-combustion system. The impacts of higher pressures and higher concentrations of CO₂ in the simulated fuel gas would need to be determined. However, the more recent programmatic trend in the pre-combustion area is to remove CO₂ and all contaminants with removal processes that can operate at elevated temperatures (~300–700°F) (Pennline et al., 2008). These CO₂ capture sorbents could not perform at these temperatures, and thus work in the pre-combustion area with the clay-based sorbents was concluded.

**Post-Combustion**

The vast majority of recent work with these sorbents has been in a post-combustion application. Liquid-amine impregnated clay sorbent was prepared utilizing the procedures described previously (Siriwardane, 2005). Pellets (1–2 mm, sizes typically used in moving-bed and fixed-bed reactors) and extrudates (2 mm) were prepared for fixed-bed tests. As the laboratory scale preparations showed promising results, the sorbent extrudates suitable for fixed-bed applications were also prepared at Süd-Chemie and can be seen in Figure 120. A liquid-impregnated solid sorbent suitable for other reactor bed applications, such as fluidized-bed/transport reactors, was also prepared. The initial preparations were conducted in the NETL laboratory. More attrition-resistant sorbent formulations were prepared in collaboration with Süd-Chemie (see Figure 121.)
Competitive gas sorption studies were conducted in a bench-scale fixed-bed reactor at 1 atm and at 30–60°C using a gas mixture representative of flue gas (15% CO₂, 82% N₂, 3% O₂, and ~2.6% H₂O). The space velocity used during the tests in the fixed-bed reactor was 1,000 h⁻¹, based on 2-in diameter with a 6-in height of sorbent. The regeneration was conducted at 80°C with a steam/N₂ mixture.

These sorbents were also tested in a laboratory-scale (reactor volume = 1.08 ml) atmospheric flow reactor (Micromeritics Autochem 2910, Norcross, Ga.) with a simulated flue gas mix with moisture (~2.6% by volume) at 30–60°C at a flow rate of 15 cm³/min. Regeneration occurred at
Sorbe
nt Research for the Capture of Carbon Dioxide

80–100°C with steam/nitrogen. The outlet gaseous mixture was analyzed by a Pfeiffer Vacuum Thermostar mass spectrometer. After the CO₂ sorption process, nitrogen was introduced at the absorption temperature to evaluate the amount of CO₂ and water desorbed at the sorption temperature. Then a temperature-programmed desorption study was conducted to understand desorption of CO₂ and water with a heating rate of 5°C/min.

Thermogravimetric analysis (TGA) was conducted using a Cahn 500 Thermomax 500 unit to obtain the fractional CO₂ conversions and rate of CO₂-uptake information. The sorbent sample (~230 mg) was first heated to 100°C in the TGA unit in nitrogen and was cooled back to the sorption temperature (40 and 60°C). Then a 15 vol% CO₂/3% O₂/N₂ gas mixture was introduced at a flow rate of 150 cc/min at either 40 or 60°C.

Heats of sorption measurements were conducted with a Setaram DSC 111 differential scanning calorimeter (DSC). The samples were pretreated at 100°C in helium and cooled to 40°C; CO₂ was then introduced at a flow rate of 15 cm³/min and the exothermic heat curve was measured isothermally at 40°C. The heat of reaction was calculated utilizing the software provided by Setaram instruments.

The sorption reaction of CO₂ with the sorbent is an exothermic reaction, and heat management during large-scale reactor operation is an important issue. Heat management can be more difficult in fixed-bed reactors than that in fluidized-bed reactors during large-scale operation. Fluidized-bed/transport reactor operation appears to be more suitable for the large concentration of CO₂ removal from flue gas streams. Thus, the sorbent was prepared with a particle size less than 200 micron as required for fluidized-bed reactors (see Figure 121).

The CO₂-capture delta capacity or working capacity (the difference between CO₂ sorption capacity at the absorption temperature and the CO₂ sorption capacity at regeneration temperature) is one of the important parameters that affects the regeneration energy, as identified previously in the MATRIC study in Section 4.3.2. If an external heating process is utilized during the regeneration, it is estimated that a large concentration of CO₂ may be present during the regeneration process. Therefore, some CO₂ could remain on the sorbent at a regeneration temperature of 80–100°C.

The sorbent (laboratory-scale preparation with particle size <200 micron) was tested with simulated flue gas in a laboratory-scale fixed bed reactor (Siriwardane, 2005). Results of the testing yielded a 99% removal efficiency of CO₂ and a capture capacity of approximately 2.1 mol CO₂/kg of sorbent at 40°C as shown in Figure 122. As the particle density of the sorbent is ~2 g/cm³ (measured using helium density measurements), the corresponding CO₂ capture capacity on a volume basis is approximately 4.6 mol/l of sorbent. The sorbent can be regenerated at 80–100°C. Since steam will likely be utilized for external heating of the reactor with the sorbent during regeneration, the majority of regenerations were conducted at 100°C. The CO₂ sorption was also conducted at 100°C to determine the CO₂ capture capacity at 100°C utilizing 90% CO₂ in N₂; this would simulate an ideal regeneration scenario (see Figure 123.) The CO₂ delta loading was determined by CO₂ sorption capacity differences between 40 and 100°C. Thus, the delta loading values determined in this study represent the amount of CO₂ that can be recovered at 100°C in the presence of 90% CO₂. The CO₂ delta loading for sorption at 40°C and regeneration at 100°C under a near pure CO₂ surrounding was determined to be 1.6 mol/kg (3.2 mol/l), and for sorption at 60°C it was 1.3 mol/kg (2.6 mol/l). The value obtained at 40°C is very close to the acceptable minimum CO₂ capture delta capacities identified in the Target
Establishment Section 4.3. However, improvements in CO₂ delta loading may be necessary to operate within the 40–60°C temperature range. A six-cycle test performed with capture at 60°C and regeneration at 100°C showed stable reactivity as shown in Figure 124. The deviation in the CO₂ capture capacity data during the multi-test was about 0.15 mol/kg.

Figure 122: CO₂ capacity data for sorption on a spray dried clay-based sorbent. 15% CO₂, 3% O₂, 3% H₂O and 79% N₂ at 40°C, 15 cc/min in atmospheric reactor. Working capacity is 1.7 mol/kg.

Figure 123: CO₂ capacity data for spray dried sorbent from Sud Chemie at 100°C with 90% CO₂ and remainder N₂.
Figure 124: Laboratory-scale flow reactor multicycle test data with sorbent (particle diameter less than 200 micron) at 1 atm; 60°C; space velocity ~500 h⁻¹; feed composition of 16% CO₂, 3% O₂, 82% N₂, saturated with water vapor.

In the testing, the typical amine with additives were diisopropylamine, diethanolamine, ethyleneamine, and TEPA with glycols or glycol ethers – all incorporated into the clay matrix (Siriwardane, 2011). Some of the thermodynamic and physical properties of the sorbent were determined. Heat of reaction of CO₂ with the sorbent measured using the DSC calorimeter was about 650 Btu/lb of CO₂ (67 kJ/mol of CO₂). This was the average of several measurements obtained with both 15% CO₂ and pure CO₂. The heat of reaction values were very similar for reactions with both 15% CO₂ and pure CO₂ (Siriwardane et al., 2009). The heat capacity of the clay substrate was 0.23 Btu/lb°F at 30°C. However, the heat capacity of the sorbent (amine/additive within the clay substrate) is not known at this time.

In collaboration with Süd-Chemie, the sorbent preparations were also made with more attrition resistance. The particle size was in the range of 60–325 micron and the helium density of the sorbent was 1.715 g/cc. Attrition tests of the liquid-impregnated clay sorbent were conducted at Süd-Chemie utilizing the F-Bat attrition method (internal to Süd-Chemie). The 20-hr attrition tests indicated that the material has an attrition resistance (0.71%) similar to that of other materials suitable for fluidized-bed operations. When the fluidization tests were conducted in a 2.5 in diameter tube with air, it was determined that the sorbent was easily fluidizable and the minimum fluidization velocity was approximately 0.0285 ft/s.
4.5.2 Impact of Moisture

The CO₂ sorption tests were conducted in the presence and in the absence of moisture. The CO₂ sorption capacities were similar in both cases, indicating that the sorbent performance was not affected by the presence of moisture. After the CO₂ sorption experiment at 60°C with a gas stream containing 15% CO₂, 3% O₂, 82% N₂ saturated with moisture, the reactor was isolated and the system was flushed with N₂ to remove the residual flue gas in the system. Then pure N₂ was introduced to the sorbent at 60°C, and the amount of CO₂ and water desorbed at 60°C were measured using a mass spectrometer. The desorption data at 60°C are shown in Figure 125 (Siriwardane and Robinson, 2009). A large amount of CO₂ (1.2 mol/kg) and some water (0.5 mol/kg) were desorbed at 60°C. After all the CO₂ was desorbed at 60°C (i.e., when the outlet CO₂ was less than 1%), a temperature programmed desorption (TPD) study was conducted by ramping the temperature from 60 to 100°C. Additional CO₂ (0.56 mol/kg) and water (0.13 mol/kg) were desorbed from sorbent during the TPD study. The desorption peak maximum for CO₂ was around 97°C and for water it was around 100°C. Thus, the amount of water desorbed during the regeneration is lower than CO₂. This indicates that desorption of water is not significant during regeneration and the majority of water can be desorbed at a lower temperature. The CO₂ capture capacity measured at 40°C with and without water were very similar which also indicated that the water is not a major part of the sorption reaction mechanism. Measurements with higher water concentrations similar to that found in actual flue gas after the flue gas desulfurization unit (~ 17% at 60°C) should be conducted.

![Figure 125: Desorption of CO₂ and H₂O at 60°C with nitrogen after sorption at 60°C with 15% CO₂, 3% O₂, 82% N₂, and saturated with water.](image-url)
4.5.3 **Effects of Trace Contaminants in Flue Gas**

As stated before, SO$_2$ is a contaminant present in flue gas, and it is necessary to evaluate how the sorbent performance is affected by the presence of SO$_2$. The likely location of the CO$_2$ removal sorbent reactor will be after the flue gas contaminant removal unit to minimize the contaminant interaction with the sorbent. The SO$_2$ concentration will be less than 10 ppm after deep scrubbing the SO$_2$ in the flue gas desulfurization unit, similar to the scrubbing limits before an MEA wet scrubbing unit (White et al., 2003). The sorbent was tested in the laboratory-scale reactor with 20 ppm SO$_2$, 15% CO$_2$, 3% O$_2$, and 82% N$_2$ at a flow rate of 15 cc/min (Siriwardane and Robinson, 2009). The amount of sorbent used was about 1.2–1.5 g. The results of the 21-cycle test are shown in Figure 126. It is clear that there is no significant change in the reactivity during the 21-cycle test in the presence of 20 ppm SO$_2$. The deviation in the CO$_2$ capture capacity data during the 21-cycle test was about 0.05 mol/kg. Tests at higher concentrations of SO$_2$ to simulate upstream FGD upsets and thus demonstrate stability under these conditions were not conducted.

![Figure 126: Laboratory-scale flow reactor 20-cycle test data with sorbent at 1 atm in the presence of 20 ppmv SO$_2$ at 40°C; space velocity ~500 h$^{-1}$; feed composition of 15% CO$_2$, 3% O$_2$, 20 ppm SO$_2$ in N$_2$.](image)
4.5.4 **Kinetics**

An effort was made to model this sorbent by empirically fitting the information obtained in small-scale units with various types of equilibrium and kinetic models. In all cases of gas absorption, two factors of fundamental importance must be realized: (1) the equilibrium absorption or the maximum possible degree of absorption under given conditions of pressure, temperature, and concentration and (2) the rate of absorption. Both factors exert an important influence on the capacity of a solid supported sorbent and on the amount of sorbent needed in relation to the quantity of gas to be treated. The equilibrium concentration of the reacting gas establishes the driving force for the reaction rate. The sorbent itself has a capacity for the amount of gas that can be reacted that will be dependent on the temperature and reactant concentration. The extent that the sorbent attains that limit will be determined by reacting gas concentration and the equilibrium vapor pressure of the reacting gas over that sorbent. All of these parameters must be defined to describe the behavior of this amine/clay sorbent for absorbing CO$_2$ and being regenerated (Monazam et al., 2011a).

The equilibrium absorption was obtained using a volumetric adsorption apparatus. Approximately 10 ml of the sorbent material was placed in the sample chamber and evacuated to about 5 x 10$^{-5}$ Torr at 25°C before each run. The amount of CO$_2$ adsorbed was calculated using pressure measurements before and after the exposure of the sample chamber to CO$_2$. Pressure measurements up to 103 Torr were obtained. It was possible to obtain more-accurate pressure measurements in the low-pressure region. Details of this unit can be found in the Zeolite Section 2.2.

To examine the fundamental kinetics of the fractional CO$_2$ conversions and rate of CO$_2$-uptake information, tests were carried out using a Cahn 500 Thermomax 500 unit thermo-gravimetric analyzer (TGA). The solid sorbent was a mixture of amine and bentonite with specific gravity of 1.05 and 2.5, respectively. The sorbent sample (50 mg) was placed on the sample pan situated on the sample arm of the balance. This sample size minimized the depth of the sample layer in the pan to avoid any effects of intraparticle diffusion on the rate of weight gain in the sorbent. The mean sorbent particle diameter tested was 70 micron; the specific gravity was ~1.7 using a volumetric mixing law and assuming no change in particle volume; and the surface area was determined assuming spherical particles. Inert gas (N$_2$) was fed into weighing unit of the TGA to prevent the reactant gas from diffusing into the balance chamber. The temperature was ramped from 20°C to 100°C at 2°C/min. These samples were held at 100°C for 2 h before it was cooled back to the desired reaction temperature (30–100°C). The soak time during the pretreatment was increased from 30 to 120 min to obtain more reproducible weight change, presumably a result of loss of residual water that was used during the impregnation of amine onto the bentonite support. The weight loss during the pretreatment soak at 100°C represented about 7.5% of the sample weight. Solid sorbents consisted of spherical particles of bentonite to which diethanol amine (DEA) and ethylene glycolmonoethylether were added (Monazam et al., 2011b).

The maximum CO$_2$ loading on the clay-based sorbent was determined using both the gravimetric and volumetric techniques. The experiments were designed to minimize complicating thermal and mass transfer effects. Using both test data describing the relationship between maximum capacities as a linear function of temperature, an expression was developed.
\[
\ln K_{eq} = 2.978 + \frac{2953.6}{T}
\]

The pressure of CO\(_2\) in equilibrium over the sorbent was measured and the temperature-dependent equilibrium constant was reported. An Arrhenius model for the prediction of CO\(_2\) equilibrium was successfully used to fit a series of experimental data on CO\(_2\) loading at various temperatures (30–100°C) and CO\(_2\) partial pressures (10–760 mm Hg) obtained from the volumetric adsorption apparatus. The capacity of the sorbent to hold CO\(_2\) decreased with reaction temperature, as indicated by the maximum value presented in Figure 127. Thus, the extent of reaction as it approached equilibrium varied inversely with temperature.

This was also confirmed from TGA data and both results, when combined, lead to the formulation of:

\[
\text{Maximum loading} = 1.923 - 0.0048T
\]
This reaction was measured to be exothermic with an enthalpy of reaction 64 kJ/mole of CO₂. The test data seen in Figure 128 indicated an increasing rate with increasing temperature. This was used to extract the temperature-dependent kinetic parameters for both chemical kinetics and the diffusion coefficient. Thus, both chemical kinetic and diffusion resistances were, in fact, found to be lower at higher temperatures.

Figure 128: Effect of reaction temperature on amine/bentonite particle and CO₂ reaction.

The TGA data were used to develop a pseudo first-order rate constant expression using information from Figure 128 (Monazam et al., 2011b). The expression led to the following equation:

\[ \ln k = 1.46 - \frac{1716.5}{T} \]

The kinetic and thermodynamic relationships were combined to demonstrate the ability to predict the overall response at different test conditions (see Figure 129). The kinetic model was used to predict the fractional conversion at three test cases at different temperatures. In general there was good agreement between calculated and experimental results for all of these test cases particularly at lower temperatures. At temperatures 80°C and higher, the first order rate constant
tended to over predict conversion when the fractional conversion was above 0.8. At these higher temperatures, the order of reaction tended toward 1.5. A shrinking core model was also used to interpret absorption data taken between 30 and 120°C in the TGA and equilibrium volumetric sorption apparatuses. Results are summarized elsewhere (Monazam et al., 2011a).

![Graph showing conversion over time at different temperatures](image)

**Figure 129**: Comparison between kinetic model predictions and experimental data at several temperatures in isothermal condition.

### 4.6 ADA RESULTS WITH NETL-DEVELOPED AMINE-ENRICHED SORBENTS

ADA Environmental Solutions (ADA) examined available sorbents as well as process equipment options to assess the viability and accelerate development of solid sorbents for post-combustion CO₂ capture. The work was conducted through a U.S. Department of Energy Cooperative Agreement with supplemental funding from ADA, EPRI, and several power industry partners. During the project, sorbents were acquired from various developers and screened at the laboratory-scale to select materials for testing in a 1 kW slipstream pilot demonstration. Based on the laboratory-scale results, pilot-scale batches of two amine-enriched sorbents originating within the NETL in-house research effort were produced and then tested in the 1 kW pilot. In addition to this effort funded by DOE/NETL, a separate, non-funded collaborative activity, a Cooperative Research and Development Agreement (CRADA, 2010), was formulated and implemented between ADA and the in-house effort at NETL.
**Laboratory-Scale Tests**

ADA screened over 100 materials using a fixed bed system both in the laboratory with simulated flue gas and in the field with a slipstream of actual flue gas. The materials were tested over multiple adsorption/regeneration cycles. The purpose of the screening was to identify materials that exhibit properties that are promising enough to be produced and evaluated at larger scales. The sorbents were categorized as either carbon-based sorbents, zeolites, or supported amine materials. Results from different materials were highly varied, but general conclusions were drawn regarding different sorbent types. For example, sorbents that include amine functionalization generally have a high CO$_2$ capacity (i.e., 5% to 14% by weight), whereas carbon-based materials have been observed to have lower CO$_2$ capacities, but superior cyclic stability (Sjostrom et al., 2011).

All sorbent screenings were conducted using the same test fixture. The laboratory-scale test unit was designed to be used in the laboratory on simulated flue gas as well as in the field on actual flue gas with minimal modifications. A schematic of the system can be seen in Figure 130 (Sjostrom et al., 2010). A programmable logic controller controlling solenoid valves was employed so that the system was completely automated. The flow rate of the simulated or actual flue gas was approximately 255 sccm, and the amount of sorbent tested varied from 0.5 to 2.5 g. The sorbent and flue gas (either simulated or actual) were contacted in a fixed bed. The CO$_2$ analyzer was a continuous NDIR sensor with a 90% response time of 10 seconds. The steps to carry out the adsorption/regeneration cycles were the same whether tests were conducted on simulated or actual flue gas. First, 2.5 g (or less) of sorbent was placed in the fixed bed and was heated to the initial flushing temperature. The initial flushing temperature was set based on the expected regeneration temperature, unless a different temperature was recommended by the sorbent developer. A thermocouple on the outside of the glass fixed bed was used to determine when the bed had reached the desired temperature. When the bed temperature matched the desired adsorption temperature, the sorbent was flushed with dry N$_2$ for 10 minutes or until no CO$_2$ was being evolved (whichever was longer). Then, the simulated flue gas, composed by mixing compressed gas from tanks, was sent through the bypass line, so that it did not contact the sorbent. The composition of the laboratory sample gas, by volume, was approximately 12% CO$_2$, 4% O$_2$, with a balance of N$_2$. The relative humidity, controlled by adding water using a peristaltic pump and then evaporating, was 0% or 90% (0 or ~15% by volume, respectively). When the CO$_2$ monitor reading was stable and represented the correct concentration of CO$_2$ (i.e., baseline reading) the gas flow was directed through the sorbent. After the CO$_2$ levels returned to their original inlet levels (i.e., the sorbent was saturated with CO$_2$), the gas was sent through the bypass, which was the end of the adsorption step. A temperature swing with N$_2$ purge gas was used to regenerate the sorbents and desorb the CO$_2$. The gas passing through the fixed bed was switched from the simulated flue gas to N$_2$ (acting as a sweep gas) and the temperature was gradually increased to the regeneration temperature. This was continued until no additional CO$_2$ was measured in the sweep gas. It is important to note that this type of adsorption/regeneration cycle provided the total CO$_2$ capacity at the adsorption conditions rather than a working capacity, which can be achieved economically in a commercial system. In addition, this system is used to assess cyclic stability by repeating the adsorption/regeneration cycle for more than 100 iterations.
The sorbents that were developed by NETL and screened can be seen in Table 40. All of the sorbents except S contained about 40–50 wt% polyethyleneimine. ADA used various criteria to judge the sorbents, including overall CO₂ capacity and theoretical regeneration energy (Sjostrom et al., 2010). The latter criterion was discussed in the MATRIC study found in Section 4.3.2 and is based on the calculations of Richards (2006a) and Hoffman et al. (2008a).

<table>
<thead>
<tr>
<th>ADA Sorbent Identifier</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>CARiACT® G10</td>
</tr>
<tr>
<td>S</td>
<td>Bentonite</td>
</tr>
<tr>
<td>X</td>
<td>CARiACT® Q10</td>
</tr>
<tr>
<td>Y</td>
<td>Diaion® SP700</td>
</tr>
<tr>
<td>AX</td>
<td>PQ Inc 2129</td>
</tr>
</tbody>
</table>

Figure 130: Schematic of sorbent screening unit.
In general, the supported amines exhibited high CO$_2$ working capacities in the laboratory screening tests as can be seen in Figure 131. It should be noted that the capacities of all these materials varied significantly from cycle to cycle. The figure shows the maximum, minimum, and average laboratory working CO$_2$ capacities of all the sorbents. As can be seen in Figure 131 and as identified in Table 40, the NETL developed sorbents did have some of the better working capacities.

Based on the laboratory-scale testing results, the theoretical regeneration energy was calculated for all sorbents that were able to remove CO$_2$ from the simulated flue gas. Figure 132 shows the theoretical regeneration energy for all the materials and also includes a dotted line for the benchmark aqueous MEA value. The values in Figure 132 are based on the average working CO$_2$ capacity at the highest regeneration temperature tested (i.e., not optimized values). Based on the laboratory tests, several materials included in the screening program exhibited significantly lower theoretical regeneration energies compared to the benchmark. Based on the theoretical energy for regeneration under the laboratory testing conditions, all the supported amines were competitive with aqueous MEA.
Figure 132: Comparison of theoretical regeneration energies based on laboratory fixed bed tests with humid simulated flue gas. These sorbents have been group according to the material type: black bars (left) represent carbon-based sorbents, blue bars (center) represent supported amines, and yellow bars (right) represent zeolites. The red dashed line is an estimate for an advanced aqueous MEA system.

From these results, a down-selection of the NETL sorbents was made by ADA. The BIAS sorbents X and Y did not perform as well as R and AX with respect to CO\textsubscript{2} capacity and were cut from the program. The clay-based sorbent S experienced some difficulty during the operation of the unit. One concern was a liquid that appeared to have been emitted during operation and the possibility that the emission could make the automated field testing unit difficult to operate (ADA, 2009). Further pilot-scale work by ADA with this sorbent was not conducted.

Sorbent R and two other amine-enriched sorbents were chosen for field testing in the laboratory screening unit due to their low theoretical regeneration energy during laboratory tests. The sorbents were exposed to a flue gas, whose characteristics can be seen in Table 41. The average, maximum, and minimum working capacities measured during the field testing are shown in Figure 133. For all three of these supported amines, there was a significant difference between the maximum and minimum values measured. Sorbent R had an average working capacity of 9.7 wt% over the 43 adsorption/regeneration cycles that were completed. One important characteristic that was shared between all the materials was a slow loss in CO\textsubscript{2} capture capacity, which can be attributed, at least in part, to reaction with SO\textsubscript{2} to form heat-stable salts. Earlier tests with amine-enriched sorbents showed a poisoning with SO\textsubscript{2} using the field site gas. Based on SO\textsubscript{2} concentration of 50–250 ppm in the flue gas, a mass balance reveals that if indeed this deactivation can be attributed to reaction with SO\textsubscript{2}, it was reacting with the active amine sites in a 1:1 ratio (i.e., little to no SO\textsubscript{2} passed through the bed unreacted). This also confirms the results for SO\textsubscript{2} poisoning that were concluded at NETL (see Section 4.4.3). Running long breakthrough tests in a fixed bed will exaggerate this behavior because the sorbent is exposed to flue gas for longer adsorption times than possible in a larger-scale system. However, similar to aqueous amine scrubbing, SO\textsubscript{2} will most certainly need to be reduced below the 50 ppm level in a commercial-scale system utilizing supported amine-enriched sorbents (Sjostrom et al., 2010).
Table 41: Key flue gas characteristics for field tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>55–60</td>
</tr>
<tr>
<td>CO₂ concentration (%)</td>
<td>10–12</td>
</tr>
<tr>
<td>Moisture</td>
<td>Saturated</td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>5–6</td>
</tr>
<tr>
<td>NOₓ (ppm)</td>
<td>100–120</td>
</tr>
<tr>
<td>SO₂ (ppm)</td>
<td>50–250</td>
</tr>
</tbody>
</table>

Figure 133: Working capacity during field testing.

**Pilot-Scale Tests**

From the laboratory-scale testing, ADA concluded that amine-enriched sorbents were candidates for the sorbent capture technology. Additionally, they chose two sorbents, R and AX, which were developed in the in-house research effort at NETL for use in their next contractual phase. The sorbents would be tested in a pilot unit, whose schematic can be seen in Figure 134.
The 1 kW pilot system was designed and constructed to characterize the CO₂ capture effectiveness of solid sorbents on coal-fired power plant slipstreams. A circulating fluidized bed-type of entrained flow contactor was selected for the 1 kW pilot-scale apparatus, and ADA worked closely with Southern Company Services to finalize the contactor details. It was designed to evaluate CO₂ sorbents with highly varied physical and chemical properties. The equipment includes a flue gas pretreatment section prior to the capture and regeneration system. Pretreatment options include flue gas pressurization, heating, cooling, SO₂ removal, and moisture reduction. The capture system includes both CO₂ adsorption and sorbent regeneration. The adsorption occurs in the riser, which is a transport reactor (i.e., the sorbent is entrained by the flue gas). Although the riser is only 1 inch in diameter, it is 35 feet tall, which provides a gas/solids contact time of approximately 3 seconds. There is also an added option for sorbent recirculation in the internal fluidized bed if additional contact time is required. The regenerator consisted of a separate fluidized bed. Projected regeneration temperatures were in the range of 210°F to 250°F. For the 1 kW system, electric heaters were used for the heat input, although in a commercial system, indirect steam or some other source of heat would likely be more advantageous. The specified design maximum residence time in the regenerator is approximately 500 seconds. An ID fan is used to extract the enriched CO₂ stream. If any sorbent is carried with the CO₂ gas stream, it is captured in a cyclone or a fines baghouse. After the sorbent is heated and the CO₂ is removed, the sorbent is sent through a cooler that utilized jacketed cooling to
reduce the temperature of the sorbents to approximately the riser temperature. For sorbent R, the immobilized amine sorbent that was evaluated at the first field site, the sorbent circulation rate was 40 lb/hr (Sjostrom et al., 2011).

As mentioned before, the sorbents of interest were developed by NETL. The laboratory-scale screening studies with these basic immobilized amine sorbents (BIAS) at NETL and at ADA have shown the sorbents to be viable candidates for further pilot-testing. The next step on the path to commercialization was to test the sorbent in a process developmental system – one that was described above. In order to proceed, a large batch of sorbent needed to be fabricated and possess similar properties as determined in the earlier laboratory-scale tests. Two large 600 lb batches of the BIAS sorbents were produced at a fabrication facility located in Pittsburgh, PA. The corporation, Pressure Chemical Company, has a unique array of chemical processing equipment and process expertise that aids in the production of specialty chemicals. Under the oversight of NETL, batches of the BIAS sorbent were made in a pan dryer (see Figure 135) following the fabrication procedure formulated at NETL. QA/QC activities were performed on samples from individual batches by experimentally checking the CO₂ loading capacities. The individual batches for each sorbent type were compiled into a large batch that was then sent to ADA for testing within their pilot reactor system.

Figure 135: Pan dryer at Pressure Chemical Company.

Sorbents R and AX were sent for testing in the pilot unit. A compilation of sorbents, their compositions, and their capacities as determined by either TGA or laboratory-scale packed bed reactor systems is shown in Table 42. The sorbents originally sent to ADA for screening showed a high CO₂ capture capacity (3.05–3.52 mol CO₂/kg sorbent). These candidates were chosen based on earlier results from a baseline BIAS sorbent that had been used throughout earlier studies (sample 196C). The key difference between these sorbents was the substrate: both were mesoporous silicas but from different manufacturers. The large batches of sorbent (R and AX) that were sent to ADA for the pilot testing were different from the original samples sent for laboratory-scale testing. The key difference was in the composition and loading of the PEI. For
the large batches, the lower molecular weight PEI was not available in sufficient quantities. Thus the higher molecular weight PEI was used. CO₂ capacities were lower.

### Table 42: PEI sorbent key

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Composition</th>
<th>Capacity NETL-Mol CO₂/kg sorbent</th>
<th>Capacity NETL-Mol CO₂/kg sorbent</th>
<th>Capacity ADA-Mol CO₂/kg sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>196C</td>
<td>Nominal 50% PEI (BASF Mn 423) on Silica (Cariact G10)</td>
<td>March 2011 3.87</td>
<td>Feb 2011 3.85</td>
<td>55°C, Lab, ~12% CO₂ 3.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60°C, Field, 10-12% CO₂ 2.95</td>
<td></td>
</tr>
<tr>
<td>Sorbent “R”</td>
<td>Initially sent to ADA for screening study</td>
<td></td>
<td></td>
<td>55°C, Lab, @~12% CO₂ 3.52</td>
</tr>
<tr>
<td></td>
<td>Nominal 50% PEI (BASF Mn 423) on Silica (Cariact G10-HPV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbent “AX”</td>
<td>Initially sent to ADA for screening study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nominal 50% PEI (BASF Mn 423) on Silica (PQ Inc 2129)</td>
<td>Sept 2011 Composite sample from original batch 2.69</td>
<td>Jan 2010 Composite sample from original batch 2.31</td>
<td></td>
</tr>
<tr>
<td>Sorbent “R” large batch made by Pressure Chemical</td>
<td>Nominal 40% PEI (BASF Mn 2000) on Silica (Cariact G10-HPV)</td>
<td>Sept 2011 8-drum received from ADA, sampled and analyzed Range (2.60-2.87) Avg of 7 = 2.82</td>
<td>Jan 2010 Composite sample from original batch 2.44</td>
<td></td>
</tr>
<tr>
<td>Sorbent “AX” large batch made by Pressure Chemical</td>
<td>Nominal 40% PEI (BASF Mn2000) on Silica (PQ Inc 2129)</td>
<td>Sept 2011 8-drum received from ADA, sampled and analyzed Range (2.60-2.87) Avg of 7 = 2.82</td>
<td>Jan 2010 Composite sample from original batch 2.44</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:**
1. Assume equilibrium loadings obtained from sample test.
2. ADA-ES information obtained from following reports:
   b. CO₂ Sorbent Screening Program: Third Round Screening Results, January 28, 2010. (ADA, 2010)
Based on the superior CO₂ capacity measured in the laboratory, cyclic stability, and ability to be produced at increased scales, sorbent R was one of the first materials selected for evaluation at the 1 kW pilot scale. Luminant’s Martin Lake Station was the initial site for the testing with sorbent R. Using this material, 90% CO₂ removal was demonstrated repeatedly with fresh batches of sorbent at a circulation rate of 40 lb/hr. Note that the flue gas CO₂ concentration was approximately 14% and the flue gas volumetric flow rate was approximately 5 acfm. An example of the CO₂ concentration and the removal level recorded during continuous operation of the 1 kW pilot is provided in Figure 136. Based on the decrease in CO₂ removal, it was determined that the sorbent was not being fully regenerated. To determine if the lack of regeneration was caused by sorbent degradation, the system was operated in batch mode. To operate in batch mode, the flue gas in the riser (adsorption section) was replaced with air, while all other operating parameters, except occasionally the sorbent circulation rate, remained unchanged from the continuous operating conditions. Ten adsorption/regeneration cycles were completed in batch mode using sorbent R. The maximum CO₂ removal levels during these ten cycles are shown in Figure 137. Note that several conditions were varied during the different cycles, such as the time allowed for regeneration and the sorbent circulation rate during regeneration; the difference in the CO₂ removal levels can mostly be attributed to such factors (Sjostrom et al., 2011).

![Figure 136: CO₂ concentrations and removal during continuous 1kW testing of sorbent R.](image)

It was determined that the sorbent could be fully regenerated in batch mode. The lack of regeneration in continuous mode can be attributed to the regeneration conditions in combination with the specific characteristics of sorbent R. This sorbent will not regenerate effectively in a pure CO₂ atmosphere, and as discussed previously, a steam sweep would be needed in an actual operation. In the laboratory-scale fixed bed system, sorbent R regenerated fully in the presence of a N₂ sweep gas. Although N₂ was utilized as a fluidization gas in the fluidized bed regenerator, the contact between the sorbent particles and the fluidization gas in this type of system was inefficient. Therefore, sorbent R regenerated much more slowly in the 1 kW pilot compared to what was observed in the laboratory. Improvements in reactor design could improve the overall process.
Sorbtent Research for the Capture of Carbon Dioxide

Figure 137: Maximum CO₂ removal for sorbent R at Martin Lake and sorbent AX at Sherco.

Sorbent R was tested for 10 adsorption/regeneration cycles in batch mode at Martin Lake. During those tests, sorbent R could not maintain 90% CO₂ removal when operated continuously. However, over 90% CO₂ removal was possible when the system was operated in batch mode. Sorbent AX, which was similar to sorbent R except the substrate was a different porous silica, was operated in batch mode at XCEL Energy’s Sherco Station. The maximum CO₂ removal demonstrated by the two sorbents is provided in Figure 137. Although the removal observed in cycle 5 for sorbent AX was significantly lower than the other cycles, it is believed that this was caused by equipment issues due to extremely low ambient temperatures, rather than a decrease in sorbent performance (ADA, 2011).

When operated in batch mode using sorbent R or AX at Martin Lake or Sherco, respectively, there was no significant difference in the performance of the system or the sorbents. Note that the different removal levels shown in Figure 137 can be attributed to changing conditions, such as the time allowed for regeneration. Because the test conditions were not consistent for the different batch cycles, changes in CO₂ removal are not necessarily related to changes in the sorbent performance.

As was observed consistently at Martin Lake with sorbent R, the CO₂ removal was initially high at Sherco (~80% as sorbent circulation was begun), but decreased to approximately 20% removal at steady state. The lack of continuous removal was due primarily to some deficiencies in the reactor system design: a co-current adsorption system and a fluidized bed for regeneration, a combination which did not provide an adequate driving force for regeneration. In addition, ADA speculated that sorbent R could have mass diffusion limitations related to the CO₂ uptake rate.
Since the contact times in the 1 kW pilot are much lower than those used in the laboratory, the working capacity was likely affected in the 1 kW pilot.

In summary, the materials developed by NETL performed quite well in a screening exercise conducted by an outside entity. A couple of these were prime candidates for CO$_2$ capture in a pilot unit that used an actual flue gas. Large quantities of the sorbent could be produced at relative ease. Further developmental work with these sorbents rest with ADA since the NETL patents were licensed to this company.

4.7 COMPLEMENTARY RESEARCH

During the later time frame of the sorbent research, additional studies in the amine-enriched sorbent area occurred at outside laboratories under contract to NETL. This was through the Regional University Alliance (RUA) initiative that has been discontinued. Investigations at two universities, West Virginia University and Carnegie Mellon University, produced interesting results. A novel technique to deposit sorbent on a substrate was investigated, and the study of a tertiary amine was completed.

With amine-enriched sorbents, researchers at West Virginia University tailored the sorbent structure in an attempt to minimize diffusion resistance during both the CO$_2$ capture and subsequent regeneration. Minimal diffusion resistance would insure that the highest CO$_2$ capacity is achieved in the shortest time, reducing the needed size of reactors and materials handling. Thus, it would be desirable to develop a technique where adsorbent chemistry could be deposited on high surface area supports while creating uniform layers of desired thickness. In regards to this, a proof-of-concept study was conducted that showed that advanced solid sorbents can be fabricated using an evolved nanotechnology or electrostatic layer-by-layer (LBL) nanoassembly. (Li et al., 2011). The LBL technique in principle could be scaled to very large quantities. In this work, a CO$_2$-absorbing amine compound, polyethylenimine or PEI, (that was used at NETL as previously described) was successfully nano-layered into a porous supporting substrate, and the developed solid sorbents showed interesting CO$_2$ capture properties. PEI was adsorbed into a porous supporting substrate of polymethylmethacrylate using LBL nanoassembly technology and then an oppositely-charged polyelectrolyte (polystyrene sulfonate or PSS) was deposited to form a PEI/PSS bilayer. From experimental testing, results show that layers of desired thickness can be deposited such that equilibrium adsorption capacity is proportional to the number of layers, demonstrating excellent control of the deposition process. Although the initial CO$_2$ capture capacities were between 0.8 to 1.7 mol CO$_2$/kg of sorbent, the sorbent exhibited fast kinetics in both the absorption and regeneration steps. A later study investigated the impact of certain LBL fabrication variables (Jiang et al., 2011). Again the PEI/PSS had decent CO$_2$ absorption capacity and the amine-multilayered solid sorbents had fine microstructures and fast CO$_2$ desorption rates.

In the latter project at Carnegie Mellon University, the research focused on CO$_2$ capture with molecular amine systems based on two functionalities of the tertiary amine N-methyltetrahydropyrimidine (MTHP): 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazobicyclo[4.3.0]non-5-ene (DBN) immobilized on activated carbon supports (Alesi et al., 2010). Both DBU and DBN are derivatives of MTHP, with an additional ring extending from the carbon adjacent to the interacting nitrogen. The bicyclic functionality helps to decrease the volatility of the amidine by increasing the molecular weight. Additionally the difference of the 5- and 7-membered rings found in DBN and DBU impose differing strains over the entire ring structure changing the electronic structure of the interacting nitrogen which affects the basicity
of each amidine. The differences in capture capacity exhibited by the two amidine molecules, DBN and DBU supported on activated carbon, were compared through the use of a tubular packed-bed reactor in which the molar concentration of gas passing through the reactor was determined using a mass spectrometer. The capture conditions were chosen to simulate the conditions and gas concentrations expected in flue gas, whereas the final operating conditions consisted of a reduction in the partial pressure of CO₂ by changing to a He or N₂ sweep gas, and an increase in the bed temperature to 80°C.

From the packed-bed adsorption/desorption experiments, it was found that DBN had a higher CO₂ capture capacity than the DBU-based sorbent, although the total absorption capacity (0.8 mol CO₂/kg of sorbent at 29°C) was low for amine-enriched sorbents. It was also seen that CO₂ capture on DBN only occurred in the presence of water, signifying that these tertiary amidines only participate in the formation of bicarbonate species (Alesi et al., 2009). As the water concentration was increased from 2.5 to 3.8%, the capture capacity for the sorbent increased. However, at higher concentrations of water, a reduction in total capacity was discovered, and this was attributed to water sorption to the hydrophilic activated carbon support, in which the water was most likely inhibiting the diffusion of CO₂ to the amidine. Again as found in previous sections, it is apparent that the moisture sorption properties of the sorbent must be considered in CO₂ sorbent designs and the role of moisture is critical with these type of amine-enriched sorbents.
5. **POROUS COORDINATION POLYMERS (MOFS)**

An exciting new family of CO₂ capture sorbents is under investigation at NETL. These sorbents are based on a general class of materials referred to as porous coordination polymers (PCPs) which are more commonly categorized using a variety of terms including: metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and Prussian-blue analogs.

PCPs are crystalline compounds consisting of metal ions or clusters coordinated to organic and inorganic linker molecules to form one-, two-, or three-dimensional structures that are porous. The pores in these materials are stable and can be used for the capture or storage of gases, such as CO₂. An attractive feature of these materials is that by appropriate choice of metal ion clusters and organic/inorganic linker molecules, the pore structure of the material can be engineered into a particular size or shape depending on what works best for the end use application. Furthermore, the organic linker molecules that comprise the pores can be functionalized with polar groups (OH, C=O, R-NH₂, etc.) to increase their affinity for CO₂ or any other gas that needs to be stored or separated. Combining the ability to engineer pore size/shape with the additional ability to control the presence of functional groups creates a working platform where a balance can be struck between physisorption-type interactions controlled by the pore size/shape and chemisorption interactions that are dictated by functional groups on the linker molecules. (NETL/Catacel, 2009).

Using this combined approach, the adsorption/desorption kinetics and energetics can be controlled by rationally synthesizing a sorbent with a particular pore size and functional group. This synthetic approach is an improvement over trial-and-error type methods that simply synthesize sorbents, characterize their porosity/functionality, and then test them under a variety of conditions until an optimal application is found. A generalized synthetic scheme is illustrated in Figure 138 and shows how a PCP can be constructed using metal ions/clusters, which are linked together with an assortment of organic/inorganic linker molecules to logically produce a CO₂ capture sorbent.

![Figure 138](image)

Figure 138: A generalized synthetic scheme showing how a PCP can be formulated using metal clusters and inorganic/organic linkers. Variation of the ligand size and any functional groups contained on the linker can enable researchers to rationally engineer pore size/shape and chemical affinity towards CO₂ giving improved control over the adsorption/desorption kinetics and energetics of the sorbent system.
NETL has been involved in fundamental research on PCPs, and an assortment of PCPs have been synthesized, modeled computationally, and tested for storage and separation applications. Studies with pillared layer nickel cyanide PCPs have illustrated that storage capacities and isotherm behaviors can be manipulated simply by using the different ligand architectures illustrated in the synthetic scheme outlined in Figure 139 (Culp et al., 2008). In particular, these materials can sorb up to ~ 30 weight % of CO₂ below 25 atm of pressure and near ambient temperature conditions. As illustrated in Figure 139, changing the functionality associated with the organic linker molecule used between the Ni[Ni(CN)₄]₆ sheets can dramatically change the material’s capacity towards CO₂ from a) high capacity, type I isotherms (red dots), b) a highly unique hysteretic behavior (black dots), and c) a nearly collapsed, nonadsorbing materials (blue dots). The power of changing the linker on the affinity of the sorbent towards CO₂ capture is clearly illustrated.

Figure 139: Isotherms at 293ºK for 3 linkers used with the Ni[Ni(CN)₄]₆. The linker structure shown and isotherm data points are color coordinated. Solid dots are associated with the adsorption branch of the isotherm, while open dots illustrate the desorption branch.
Part of the current research effort at NETL is focused on further changing the organic linkers to contain functional groups such as OH, C=O, C-O-C, and R-NH$_2$ in an effort to increase the affinity of the sorbent to capture CO$_2$. The objective is to find a trade-off between engineering the pore size/shape by adjusting the size of the linkers in combination with modulating the chemical affinity of the linker towards CO$_2$ by adding functional groups. This combined approach allows better control for adsorption/desorption kinetics and energetics for capturing CO$_2$ from, for example, low pressure flue gas. In this fashion, some of the technical barriers associated with the regeneration of CO$_2$ sorbents can be overcome by adding extra layers of control over the kinetics and energetics associated with the adsorption/desorption process.

In addition to the high CO$_2$ capacities and the flexibility of engineering the sorbent, the PCPs currently being studied are non-toxic and require little energy to create, making them an attractive possibility for carbon capture and storage. The porous structures can be heated to reasonably high temperatures (above 150°C), making them suitable for possible use in post-combustion or pre-combustion applications. Furthermore, the images shown in Figure 140 illustrate that these materials can be affixed to metal-oxide based supports and, as such, are good candidates for testing as sorbents in an actual process. Although PCPs represent a newer and emerging sorbent technology, they do not have the lengthy applications track record of some of the other CO$_2$ capture sorbent families and are a riskier technology in terms of commercialization and long term performance. However their inherent CO$_2$ sorption efficiency can make them valuable as a practical means to capture CO$_2$.

![Image of PCP material](image-url)

**Figure 140:** A) Surface and B) cross-sectional images of a NETL synthesized Cu-based metal organic framework material successfully grown on a metal oxide support.

As mentioned, the PCPs lend a great deal of structural versatility to gas separation applications, especially those for pre-combustion applications. A combination of organic and inorganic building blocks, these multi-dimensional hosts can be tailored for selective adsorption of one guest over another via methods, such as pore size exclusion, mesh-size adjustable sieving, and guest-dependent structural dynamics. The numerous reports on structurally dynamic PCPs illustrate the potential of these materials for adsorption applications, yet there are only a few reports demonstrating actual gas separations using these sorbents. A structural breathing phenomenon in the MIL-53 family of MOFs was found to have a significant role in the ability of this sorbent to separate CO$_2$ and CH$_4$. Despite the detailed studies of MIL-53, there are few experimental or theoretical methodologies to predict gas selectivities in other structurally dynamic systems or to indicate how generally applicable the MIL-53 separation mechanism may
be. Additional studies with actual gas mixtures have been conducted at NETL that advance the theoretical and empirical understanding of structurally dynamic PCPs (Matranga, 2011).

Much of the literature on selective adsorption in PCPs is based on the prediction of a gas separation extrapolated from pure gas isotherms or calculations from the ideal adsorbed solution theory, and not from actual experimental observations of gas separations. The use of ideal adsorbed solution theory to predict selectivities in structurally dynamic PCPs can be complicated by the possibility of cooperative adsorption effects, indicating the need for new fundamental insight into how specific structurally dynamic PCPs selectively adsorb gases. While one computational study has investigated the role of stepped isotherms in the separation of CO₂/N₂ mixtures, most models on structurally dynamic MOFs and PCPs displaying stepped isotherms only address single component adsorption, leaving a void in understanding the mechanisms responsible for selective adsorption from mixtures. This paucity of fundamental understanding of gas selective adsorption in these sorbents indicates the need for experiments and theoretical calculations to shed light on this important phenomenon.

Perhaps the most crucial mechanistic issue to address in structurally dynamic systems surrounds what happens to gas interactions with the sorbent before and after the transition between states of differing porosity. The gas- and temperature-dependent threshold pressures, above which a rapid rise in gas uptake is noted in most structurally dynamic PCPs, has led many researchers to hypothesize that this process could be used to selectively adsorb gases. Yet others have speculated it could lead to a cooperative adsorption mechanism where all gases in the mixture have access to the pore network following the transition, thus negating the selective aspect of the threshold pressure/temperature. Few theoretical or empirical formalisms exist that can be used to predict when this cooperative adsorption may occur. Understanding the interaction of gases with structurally dynamic PCP systems is required to advance the use of these materials in pre-combustion separation applications and has been the recent focus at NETL in investigating these sorbents.

The research effort at NETL to study the selective adsorption of CO₂ in structurally dynamic MOF systems has incorporated the use of certain unique instrumentation and procedures (Matranga, 2011). First, an in situ infrared method has been developed that allows researchers to monitor the adsorption of gas mixtures containing CO₂ and obtain quantitative information about how the other gases (e.g. H₂, N₂, CH₄) impact adsorption. This infrared method can also be used to monitor the structural changes and determine whether adsorption and binding sites are altered by the presence of gas mixtures, in comparison to pure gas adsorption. Second, a specialized high pressure cell coupled with gas chromatography can quantify the selective adsorption of CO₂ from a gas mixture. Measurement can be conducted up to ~100 bar (1,475 psi). The technique has been used to quantify the change in gas composition during the adsorption of CO₂/N₂, CO₂/CH₄, and CO₂/N₂O mixtures. Third, as part of a collaborative effort with the U.S. Dept of Commerce’s National Institute of Standards and Technology (NIST), a neutron science facility was used to do in depth structural studies on dynamic MOFs during the adsorption of actual gas mixtures, such as CO₂/N₂ and CO₂/CH₄. How the structure of these dynamic MOFs is impacted during the adsorption of mixtures is evaluated and practical details on how and where gases adsorb in the pore systems is provided. This data better quantify selectivity and design new selective sorbents. And fourth, a measurement system was used to address more practical aspects of selective adsorption, that is, how these MOFs can be incorporated into an industrial process.
for separating syngas mixtures. Simple breakthrough measurements on structurally dynamic MOFs were made up to ~100 bar and at realistic syngas separation conditions.

One of the initial materials chosen for study was the linear chain coordination polymer catena-bis(dibenzoylmethanato)-(4,4′-bipyridyl)nickel(II), commonly referred to as Ni-DBM-BPY. This system has been shown to be selective for the separation of CO₂ from a variety of light gases. The synthesis of the material is detailed elsewhere along with the analytical techniques used to investigate the gas adsorption mechanism in the flexible porous coordination polymer: a pressure-composition isotherm measurement system, a thermogravimetric analyzer, and an in situ attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) (Culp et al., 2010).

The diverse host-guest behavior of Ni-DBM-BPY was investigated by first observing its gas adsorption properties. The CO₂ adsorption-desorption versus pressure isotherms collected at 0 and 25°C are shown in Figure 141. The data are plotted in relation to both gravimetric uptake and a normalized adsorption of CO₂ per mol of Ni-DBM-BPY formula unit. Adsorption isotherms at both temperatures showed relatively low CO₂ uptake below a certain threshold pressure (P_th). Above the threshold pressure, a rapid rise in uptake was seen followed by a gradual trend toward saturation. The coverage at the threshold condition appeared consistent within experimental error. The subsequent desorption isotherms showed a marked hysteresis, with a wider hysteresis loop observed in the higher temperature isotherm.

![Figure 141: Adsorption (solid symbols)/desorption (open symbols) isotherms for CO₂ on Ni-DBM-BPY at 0°C (diamonds) and 25°C (circles). The units of “mol/mol Ni” refer to the moles of gas adsorbed per mole of the Ni(DBM)_2(Bpy) formula unit.](image-url)
The adsorption of CH\textsubscript{4} followed a similar trend as seen with CO\textsubscript{2} with a low initial uptake followed by a rapid rise above \textit{P}th and a subsequent large desorption hysteresis. The similarity in isotherm shape between CO\textsubscript{2} and CH\textsubscript{4} is supportive of a structural phase change occurring in Ni-DBM-BPY at the threshold pressure, since the type of guest-guest interactions that are known to occur with CO\textsubscript{2} would not be expected to occur with CH\textsubscript{4}. It should be noted that analysis of the CO\textsubscript{2} adsorption isotherms measured at several temperatures gave an enthalpy of 26 kJ/mol at the threshold condition, and this enthalpy is lower compared to certain other CO\textsubscript{2} capture sorbents.

The step-shaped adsorption isotherms in Ni-DBM-BPY have attractive features for high pressure capture of CO\textsubscript{2} and for gas separation applications, and thus it was desirable to further understand the highly dynamic adsorption behaviors for CO\textsubscript{2} in Ni-DBM-BPY. In this effort, gas adsorption in the Ni-DBM-BPY material was investigated by using in situ ATR-FTIR spectroscopy. Infrared spectra were collected for Ni-DBM-BPY without CO\textsubscript{2} present; after exposure to CO\textsubscript{2} and then after desorption; and then as a function of increasing pressure. A detailed correlation was established between the structural phase transition in the material and the sorption of CO\textsubscript{2} by monitoring in situ the adsorption of the gas via ATR-FTIR. A spectral transition in the host spectrum occurs simultaneously with a sharp increase in both the intensity and band splitting of the adsorbed CO\textsubscript{2} species. By associating the changes in the host spectra that occur in the region typically assigned to aromatic ring bending and puckering modes with the width of the adsorbed CO\textsubscript{2} band split, the mechanism of the Ni-DBM-BPY structural phase transition can be determined as arising from a reorganization of the DBM ligand conformation in order to allow an enhanced ring interaction with the adsorbed CO\textsubscript{2} (Culp et al., 2010).

The Ni-DBM-BPY material was further investigated using additional analytical techniques. The objective was to further understand the mechanism behind the thermodynamic driving force for the selective inclusion of CO\textsubscript{2} into Ni-DBM-BPY over both N\textsubscript{2} and CH\textsubscript{4} (Kauffman et al., 2011a). Molar mixtures (50:50) of CO\textsubscript{2} with either N\textsubscript{2}, CH\textsubscript{4}, or N\textsubscript{2}O were used. A high pressure cell, previously described, verified selective adsorption using gas chromatography of the headspace composition before and after equilibration with the sorbent. The change in headspace composition after equilibrium with Ni-DBM-BPY for 50/50 mixtures of CO\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4}, and CO\textsubscript{2}/N\textsubscript{2}O is shown in Figure 142. The amount of CO\textsubscript{2} in the headspace decreased for mixtures of CO\textsubscript{2} with N\textsubscript{2} and CH\textsubscript{4}, indicating preferential adsorption of CO\textsubscript{2} from the gas phase into the Ni-DBM-BPY pore network. Mixtures of 80/20 CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} showed complementary decreases in CO\textsubscript{2} composition. Conversely, changes in the headspace composition were not statistically significant for the 50/50 and 80/20 mixtures of CO\textsubscript{2}/N\textsubscript{2}O, confirming the highly competitive adsorption process between CO\textsubscript{2} and N\textsubscript{2}O as seen in Figure 142. Results from the compositional measurements were in agreement with the predicted equilibrium CO\textsubscript{2} composition for all three mixtures investigated, further confirming the behavior of this sorbent system.
Additionally, through the collaboration with NIST, small angle neutron scattering (SANS) was performed on the material. The in situ SANS data, in combination with the results above, confirm that changes in the lattice spacing and porosity of Ni-DBM-BPY brought about by the CO\textsubscript{2}/N\textsubscript{2} mixture are initiated by CO\textsubscript{2}. Pure N\textsubscript{2} is not capable of initiating or stabilizing a structural transition at these pressures and temperatures. The SANS result for the 50/50 mixture of these gases shows no change from that of pure CO\textsubscript{2}, illustrating that the presence of N\textsubscript{2} in the mixture has no effect on the porosity of the opened Ni-DBM-BPY structure. Since the IR data on the ligand vibrations will be sensitive to both interlayer spacing variations as well as conformational changes, the two sets of data clearly indicate that CO\textsubscript{2} is solely responsible for initiating and stabilizing the equilibrium structure of Ni-DBM-BPY in CO\textsubscript{2}/N\textsubscript{2} mixtures when the partial pressure of CO\textsubscript{2} is in excess of the threshold pressure. Furthermore, the adsorption and separation mechanism involves a lattice expansion in the (002) direction with associated conformational rearrangement of DBM ligands to accommodate the expansion and selective incorporation of CO\textsubscript{2}. This mechanism appears unchanged when comparing pure CO\textsubscript{2} adsorption to that occurring from mixtures (Kauffman et al., 2011a).

In a similar study, the linear chain coordination polymer Cu\textsubscript{2}(benzoate)\textsubscript{4}(pyrazine)\textsubscript{n}, or CuBzPyz was investigated (Kauffman et al., 2011b). The spectroscopic experimental methods attenuated total reflectance-Fourier transform-infrared (ATR-FTIR) and transmission FTIR were used primarily in the investigation. The molecular vibrations of CO\textsubscript{2} are fairly sensitive to their local environment and as such can be used to gain insight into porosity, binding sites, and adsorption mechanisms in CO\textsubscript{2} capture materials. The vibrational bands of CO\textsubscript{2} occur in spectral regions that typically do not interfere with the infrared features from the sorbents, making it fairly easy to deconvolute the spectra of the sorbent from the adsorbate. The combination of existing crystal structure data for CuBzPyz along with the infrared information produced a case study for this system. When the CO\textsubscript{2} adsorption isotherm is monitored in situ with both ATR-FTIR and transmission FTIR spectroscopy, the onset of new spectral features can be well correlated with the onset of CO\textsubscript{2} accessing known adsorption sites observed in the reported crystal structure.
There is a clear progression in the spectral data that shows CO$_2$ first accessing sites associated with the benzoate ligand. The CO$_2$ loading at this point in the isotherm of one CO$_2$/unit cell agrees closely with the occupation of one CO$_2$/unit cell that occurs for the CO$_2$ positions located at the unit cell edges. As the crystal phase transition occurs at or above the isotherm step, additional CO$_2$ IR absorption bands arise which can be assigned to CO$_2$ interactions with the pyrazine ligand. As the CO$_2$ loading tends toward saturation, additional spectral bands appear as CO$_2$-CO$_2$ interactions and additional CO$_2$-host interactions become important. The availability of detailed high quality CO$_2$-loaded structural data for CuBzPyz made this system a case study. Future studies with PCPs that can associate infrared spectral features with CO$_2$ adsorption sites should prove valuable for interpretations of CO$_2$ host-guest and guest-guest interactions when X-ray quality structural data are unavailable. Further detailed studies to elucidate the behavior of these dynamic materials are continuing and will include the impact of moisture, ubiquitous in both pre- and post-combustion applications, and the effects of certain trace contaminants.
6. **ACTIVATED CARBON**

Activated carbon is a good physical adsorbent for removal of certain species from a gas mixture. With respect to carbon sequestration, activated carbon has been proposed as a sorbent for the removal of \( \text{CO}_2 \) from flue or fuel gas. One of the main advantages is that it is less costly than other proposed sorbents, such as synthetic zeolites. Kikkinides et al. (1993) investigated pressure swing adsorption (PSA) of \( \text{CO}_2 \) from flue gas by simulating a predictive PSA model. Calgon BPL activated carbon was used in the study. In a later modeling effort, Chue et al. (1995) compares the use of activated carbon versus zeolite 13X. In general, zeolites have higher adsorption capacities for \( \text{CO}_2 \) as well as higher equilibrium selectivities for \( \text{CO}_2 \) over \( \text{N}_2 \) than activated carbon. On the other hand, the heat of adsorption of \( \text{CO}_2 \) on activated carbon is lower than on zeolite, so that the use of activated carbon in a PSA process may result in less severe heat effect on the PSA performance. The temperature excursion due to heats of adsorption and desorption is detrimental to the separation performance of a PSA process. In this study, the average calculated values of heat of adsorption for \( \text{CO}_2 \) over the adsorbed concentration ranges were 33 kJ/mol on zeolite 13X and 21 kJ/mol for activated carbon (Chue et al., 1995).

The carbon capture in-house research effort at NETL briefly investigated activated carbon as a sorbent that could eventually be used in a PSA application (Siriwardane et al., 2001a). G-32 H activated carbon (4 x 10 mesh), was obtained from Sud Chemie Inc. Isotherms were obtained in a volumetric adsorption apparatus; competitive adsorption studies were conducted utilizing an atmospheric microreactor; and various physical and chemical properties were obtained using a surface area and pore volume analyzer, X-ray photoelectron spectrometer, and scanning electron microscope. Details of these systems and analytical instruments can be found in Section 2: Zeolites of this document. It should also be noted that the activated carbon reactivity was also compared to two zeolites, 13X and 4A.

The adsorption isotherms of \( \text{CO}_2 \) on activated carbon are shown in Figure 143. It is interesting to note that all the isotherms were extremely reproducible, which indicates the excellent reversibility of adsorption. Nitrogen and hydrogen adsorption isotherms on activated carbon were also very reproducible. The final \( \text{CO}_2 \) adsorption cycle (cycle 10) was very similar to the first cycle, which indicated that the \( \text{CO}_2 \) adsorption capacity of the sorbent was not affected by the adsorption of other gases. The \( \text{CO}_2 \) uptake of activated carbon was lower than that for the two molecular sieves at lower pressures (<30 psi), but at higher pressures the \( \text{CO}_2 \) uptake of activated carbon was higher than that of the molecular sieves. This can be seen in Figure 144 where the isotherms of the three different sorbents are compared at near room temperature (25°C).

Results of the competitive gas adsorption studies conducted utilizing 14.8% \( \text{CO}_2 \) and 85.2% \( \text{N}_2 \) on activated carbon in the atmospheric microreactor are shown in Figure 145. An excellent separation of \( \text{CO}_2 \) from the \( \text{CO}_2 + \text{N}_2 \) gas mixture was obtained with activated carbon (0.5 g) as shown. It was necessary to lower the flow rate (5 cm\(^3\)/min) to increase the contact time to utilize the full equilibrium adsorption capacity for \( \text{CO}_2 \) adsorption. This indicated that the rate of adsorption of \( \text{CO}_2 \) on activated carbon at 1 atm was lower than that for the molecular sieve 13X.

With respect to physical and chemical properties of the sorbent, the activated carbon in this study (Siriwardane et al., 2001a) had a very high surface area 897 m\(^2\)/g and may have contributed to the high \( \text{CO}_2 \) uptake at higher pressures. However, based on surface area, the molecular sieve 13X has a better affinity for \( \text{CO}_2 \) than the activated carbon. Correlations between the surface
composition of the activated carbon with CO$_2$ reactivity were indeterminate. From the isotherms for activated carbon, an isosteric heat of adsorption was calculated. The average value over various surface coverages was 20 kJ/mol, which was similar to that previously found for an activated carbon (Chue et al., 1995).

The selectivity with respect to CO$_2$ versus N$_2$ and H$_2$ was skewed more favorably to the zeolites as compared to the activated carbon at pressures below 150 psi. If the sorbent was to be used in a PSA or TSA application in flue gas or fuel gas, there are other components that could impact the reactivity/selectivity of the sorbent. Moisture is one that will impact both sorbents and can be in appreciable amounts in both applications. It is known that activated coke, similar to activated carbon, will remove SO$_2$ and NO$_x$ from flue gas in the Mitsui process (Olson et al., 2000), and other components in the gas stream are known to adsorb on the carbon and thus make separation more convoluted. The findings coupled with internal recommendations impacted the research direction with respect to activated carbon, and further CO$_2$ capture investigations with activated carbon have not proceeded at NETL since this study was conducted.

Figure 143: Adsorption isotherms of CO$_2$, N$_2$, and H$_2$ on activated carbon at 25°C.
Figure 144: Adsorption isotherms of CO$_2$ on three sorbents at 25°C.

Figure 145: Microreactor data on CO$_2$ separation with activated carbon – 14.8 vol% CO$_2$/85.2% N$_2$ mixture.
7. REFERENCES


DOE/NEL Advanced Carbon Dioxide Capture R&D Program: Technology Update; May 2011.


Fauth, D. J. SO$_2$ Concentration Influence on the Adsorption of Carbon Dioxide by Polymeric- and Silica Supported Polyethylenimine Sorbents; DOE/NELT Internal Report, 2012b.


Hoffman, J. S. Carbon Dioxide Capture with a Dry, Regenerable Sorbent Scrubbing Technology: Zeolite Testing in the Modular CO₂ Capture Facility; NETL Internal Report, March 31, 2005.


Siriwardane, R. V. Peer Review Information; DOE/NRL Internal Communication, March 14, 2011.


Sorbet Research for the Capture of Carbon Dioxide


Vora, S.; Ciferno, J.; Murphy, J.; Munson, R. DOE/NETL Advanced Carbon Dioxide Capture R&D Program Accomplishments, April 2012.

White, C. M.; Strazisar, B. R.; Granite, E. J.; Hoffman, J. S.; Pennline, H. W. Separation and Capture of CO$_2$ From Large Stationary Sources and Sequestration in Geological


