DEVELOPMENT OF CHEMICAL ADDITIVES FOR CO_2 CAPTURE COST REDUCTION

primary project goals

Lawrence Berkeley National Laboratory (LBNL) is investigating a novel mixed solvent system that integrates amine-based, potassium-based, and ammonia-based solvents to provide benefits of three systems while avoiding many of their drawbacks.

technical goals

- Develop chemical additives for solvent systems to reduce the cost of post-combustion capture of carbon dioxide (CO_2).
- Determine the optimal process configuration and operating condition for the transfer of CO_2 in amine solvent to potassium carbonate (K_2CO_3), and then to an ammonium species, resulting in the production of NH_4HCO_3.

technical content

The new solvent system uses a novel solvent transfer approach after the capture of CO_2 from flue gas. Using this approach, the energy demand and the capital cost of solvent regeneration are expected to be significantly reduced compared to the monoethanolamine (MEA) system.

An aqueous solution of amine is used as an absorbent to facilitate favorable CO_2 absorption kinetics. The amine is chosen such that the CO_2 absorbed in an absorber can be readily transferred to potassium carbonate (K_2CO_3) in a recirculation tank to produce $KHCO_3$ solids. Subsequently, $KHCO_3$ solids enter into a regenerator by gravitation, where it reacts with an ammonia catalyst to regenerate K_2CO_3 for reuse and generate a concentrated CO_2 stream suitable for sequestration.

The approach contains the benefits of three solvent systems: amine, K_2CO_3 and ammonia systems. The benefits are: (1) amine's fast CO_2 absorption kinetics; (2) K_2CO_3 and ammonium species' low reagent cost, high chemical stability, and small heat capacity; and (3) ammonium bicarbonate's low decomposition temperature, fast decomposition kinetics, and amenable for high-pressure CO_2 production. The employment of solids significantly reduces the sensible and latent heat consumed by water in solvent regeneration. The low decomposition temperature of ammonium bicarbonate enables waste heat and/or low-quality steam to be used for the production of concentrated CO_2 gas.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Chemical Additives for CO_2 Capture

participant:

Lawrence Berkeley National Laboratory

project number:

FWP-ED33EE

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N/A

performance period:

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TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	100–212	100–212
Normal Boiling Point	°C	165–252	165–252
Normal Freezing Point	°C	(-50)–28	(-50)–28
Vapor Pressure at 15 °C	bar	0–0.0013	0–0.0013
Manufacturing Cost for Solvent	$/kg	30–250	30–250
Working Solution			
Concentration	kg/kg	0.3–0.6	0.3–0.6
Specific Gravity (15 °C/15 °C)	-	0.9–1.7	0.9–1.7
Specific Heat Capacity at STP	kJ/kg-K	3–4	3–4
Viscosity at STP	cP	20–40	20–40
Absorption			
Pressure	bar	1.01	1–1.5
Temperature	°C	40–70	30–80
Equilibrium CO_2 Loading	mol/mol	0.7–0.9	0.7–0.9
Heat of Absorption	kJ/mol CO_2	65–75	65–75
Solution Viscosity	cP	10–15	10–15
Desorption			
Pressure	bar	2.7	1–75
Temperature	°C	80–120	80–300
Equilibrium CO_2 Loading	mol/mol	0.4–0.6	0.4–0.6
Heat of Desorption	kJ/mol CO_2	85–92	85–92
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99%, 75 bar	
Absorber Pressure Drop	bar		

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

Absorber: $\text{Amine} + CO_2 \leftrightarrow \text{Amine-}CO_2$

Recirculation tank: $\text{Amine-}CO_2 + K_2CO_3 + H_2O \leftrightarrow \text{Amine} + 2\ KHCO_3\downarrow$

Regenerator: $2\ KHCO_3 + (NH_4+) \rightarrow K_2CO_3 + H_2O + CO_2\uparrow + (NH_4+)$

Solvent Contaminant Resistance – Sulfur dioxide (SO_2) has little impact to the amine. The amine is regenerated by chemical rather than thermal methods. The amine employed should be much more resistant to oxygen (O_2) and nitrogen oxides (NO_x) than MEA. Nevertheless, the reaction kinetics and products of O_2 and NO_x with amine need to be investigated.

Solvent Foaming Tendency – Solvent foaming was not observed in laboratory experiments.

Flue Gas Pretreatment Requirements – Flue gas from coal-fired power plants equipped with conventional pollution control systems does not require additional pretreatment. Residual SO_2 after dissolution can be separated from the liquid stream as K_2SO_3/K_2SO_4 precipitates. The formation of heat-stable salts with amine should not be an issue, as amine is regenerated by chemical rather than thermal methods involving steam.

Solvent Makeup Requirements – Amine is confined in the low-temperature absorber and recirculation tank loop. As a result, the thermal degradation, chemical degradation (due to the reactions with flue gas trace constituents), and emission loss (due to the volatility) are expected to be insignificant compared to the benchmark MEA process. Absorber is not expected to exhibit a plugging problem resulting in operation breakdown and reagent loss as $KHCO_3$ solid is produced in the recirculation tank located above the K_2CO_3 regeneration tank (i.e., the stripper). A long-term integration test that lasts a significant number of hours will be needed to determine the amine’s makeup requirements. $KHCO_3$ and K_2CO_3 are stable chemicals and do not degrade under high-temperature operation in the regenerator.

Waste Streams Generated – Waste streams from the absorber/recirculation tank low-temperature loop may contain trace amount of fly ash, dissolved NO_x, and amine degradation products. Waste streams from the stripper are expected to contain K_2SO_3 and K_2SO_4, if SO_2 polishing is not equipped ahead of the CO_2 capture system.

Process Design Concept – Shown in Figure 1 below.

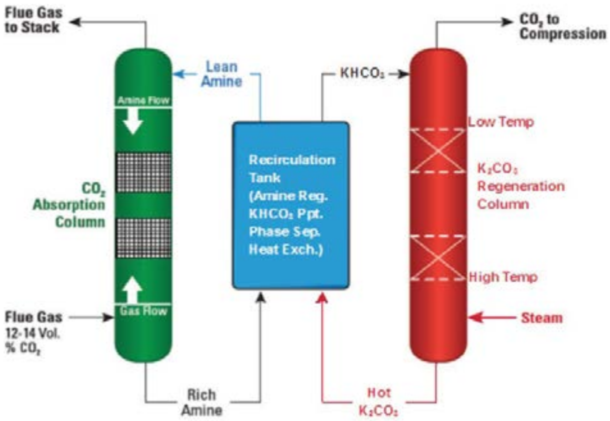

Figure 1: Process Design Concept

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bar, temperature is 57 °C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Possession of high-CO_2 absorption kinetics, resulting in an acceptable absorber capital cost.
- Reduction of processing water, resulting in reduced solvent regeneration energy demands.
- Employment of low-heat capacity $KHCO_3$/K_2CO_3, resulting in reduced sensible heat demands.
- Reduction of reagent loss and equipment corrosion, resulting in reduced operation costs.
- Reduction of emission as $KHCO_3$ can be treated at high temperature without any emissions of heat degradable harmful products.
- Reduction of CO_2 compression ratio, resulting in reduced CO_2 compression energy and compressor capital costs.

R&D challenges

- Development of a new system for the transfer of $KHCO_3$ solid from the recirculation tank to the stripper by the gravitation method and with pressurized steam.
- Determination of the optimal operation condition to regenerate K_2CO_3 and to produce high pressure CO_2 gas for enhanced oil recovery (EOR) or methanol production.

results to date/accomplishments

- Evaluated more than 50 amines and amino acid salts for CO_2 absorption amenable for the new solvent regeneration approach.
- Compared relative CO_2 absorption efficiencies of various lean amines regenerated by chemical methods.

- Investigated conditions required for phase separation and determined phase diagrams following chemical regeneration of lean amine in the recirculation tank in attempt to understand its chemical and physical behaviors.
- Elucidated the kinetics and mechanisms of CO_2 absorption and chemical regeneration involved in the new solvent system.
- Constructed a stripper system equipped with a calorimeter for the determination of K_2CO_3 regeneration rates and energy demands. Preliminary results indicated that K_2CO_3 regeneration energy demand was 2,079 kJ/kg CO_2 at steady-state conditions, which is approximately 40 percent less than that of MEA.
- Performed a semi-continuous integration test encompassing CO_2 absorption in the absorber, amine regeneration in the recirculation tank, and K_2CO_3 regeneration and CO_2 production in the stripper.
- Performed mass and water balances, and developed a stream table of the bench-scale new solvent system.

next steps

Project completed May 31, 2013.

available reports/technical papers/presentations

“Developing Chemical Additives for Aqueous Ammonia to Reduce CO_2 Capture Cost,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants Meeting, Pittsburgh, PA, March 2009.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/CO2capture/presentations/monday/Ted%20Chang-LBNL.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/CO2capture/presentations/2-Tuesday/23Aug11-Chang-LBNL-Additives%20for%20Reducing%20CO2%20Capture%20Costs.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2012. *http://www.netl.doe.gov/publications/proceedings/12/CO2capture/presentations/2-Tuesday/T%20Chang-LBNL-Additives.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/events/2013/CO2%20capture/Y-Li-LBNL-Additives-for-Reducing-CO2-Capture-Costs.pdf*.