Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture

primary project goal

The project goal is to demonstrate the capability of a novel water-lean solvent, comprised of more than 90 wt.% N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (EEMPA), to achieve 90% recovery of carbon dioxide (CO₂) while requiring reboiler duties ≤2.3 GJ/tonne CO₂ for post-combustion capture of CO₂ from coal-and natural gas-derived flue gas. Extended test campaigns are bing performed at approximately 0.5 megawatt-electric (MWe)-equivalent scale for both coal and natural gas to verify its favorable performance characteristics while evaluating the environmental, health, and safety (EH&S) risks of the technology and quantifying its potential to lower the cost of CO₂ capture. Through a previous U.S. Department of Energy (DOE)-funded project (FWP-70924) under the Discovery of Carbon Capture Substance and Systems (DOCCSS) Initiative, EEMPA was validated in laboratory-scale experiments and confirmed as a viable post-combustion capture solvent.

technical goals

- Develop a cost-effective method for synthesizing sufficient quantities of solvent to perform a 0.5 MWe-scale test at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, while evaluating process modifications needed to optimally operate the solvent process.
- Manufacture the solvent and implement equipment modifications at the NCCC.
- Conduct test campaigns with both coal and natural gas flue gas sources and perform techno-economic analyses (TEAs) and an EH&S risk assessment assuming full-scale deployment of the solvent and process at power plants.

technical content

In this project, Electric Power Research Institute (EPRI), along with their partners, are scaling-up and testing the EEMPA solvent, a water-lean single-amine solvent developed by Pacific Northwest National Laboratory (PNNL). The 0.5 MWe-scale testing is being conducted at the NCCC's Pilot Solvent Test Unit (PSTU). This project will verify that EEMPA can capture CO_2 with heat duties lower than advanced aqueous amine solvents, and with low degradation rates when exposed to real flue gas. The tests also serve as a demonstration of several process design elements, including the use of plastic packings and flash regeneration, that can reduce the capital cost of post-combustion capture processes. Knowledge gained from these tests may also benefit other solvent systems.

In Phase I of the project, activities include development of a cheaper solvent synthesis route (\$10/kg cost target) and identification and contracting of a solvent manufacturer, test facility process model development, host site planning, and initial TEA and EH&S risk assessment. Phase II activities comprise the manufacture of the solvent (~2,300 gallons) and modification of the PSTU equipment for the engineering-scale test. Raw material procurement, solvent manufacturing, and quality assurance will be performed and solvent product will be delivered to the test facility. Equipment procurement, permitting, and

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Water-Lean Solvent for Coal and Natural Gas Applications

participant:

Electric Power Research Institute

project number:

FE0031945

predecessor project:

FWP-70924

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partners:

Pacific Northwest National Laboratory; RTI International; Paul M. Mathias Consulting LLC; Gradient; Worley; Southern Company Services

start date:

10.01.2020

percent complete:

30%

construction will be completed. A test plan will also be developed. Phase III activities include test facility commissioning, separate test campaigns on coal and natural gas flue gases, performance and emissions data collection, data reduction and analysis, and test facility demobilization and solvent removal. The project will conclude with the completion of a final TEA, a final EH&S risk assessment, and an update of the Technology Maturation Plan (TMP).

EEMPA (Figure 1) is formulated as a water-lean single-amine solvent, consisting of less than 10 wt.% water. The major advantage of a water-lean solvent is lower water vaporization during the solvent regeneration step, especially compared to the aqueous amines.

Figure 1: Chemical structure of EEMPA

This solvent was developed through discrete placement and orientation of hydrogen bonds at the molecular level. The control over hydrogen bond orientation and strength resulted in the development of a derivative that is greater than 90% lower in viscosity than the reference compound. The low regeneration temperature of EEMPA provides a solvent system with potential for a minimal temperature swing between absorption and regeneration cycles.

In previous lab- and bench-scale testing, EEMPA achieved a 90% capture rate with low specific reboiler duties. The favorable thermal performance is attributable to the low water content (around 2 wt.% or less) and a shift in the ionic character of the solvent with higher temperature, disfavoring the CO₂-bound ionic species. Specific reboiler duties down to 2.0 GJ/tonne CO₂ have been observed in experiments. Cost-optimal designs for coal indicate 2.34 GJ/tonne is achievable.

Although EEMPA is formulated without the water of conventional CO_2 capture solvents, it can be used within a conventional solvent scrubbing process design using packed absorption and stripping columns (Figure 2). High viscosity can be an issue for some water-lean candidates; however, EEMPA has demonstrated only modest increases in the viscosity upon uptake of CO_2 (<12 cP at 40° C, 0.22 mol CO_2 /mol EEMPA) and mass transfer coefficients are comparable to other solvents. EEMPA can use conventional "simple" stripper designs, but because of the nature of its thermodynamic properties, it may be able to take advantage of alternative designs with simpler construction and lower capital costs. Some of these improvements will be tested at the NCCC.

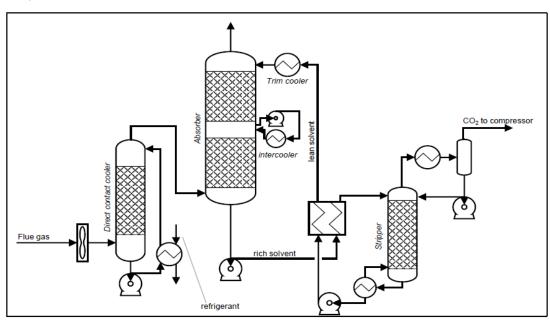


Figure 2: Process flowsheet using a simple stripper arrangement for EEMPA.

Modeling and TEA studies have also estimated 17% lower total equivalent work and 14% lower costs than the National Energy Technology Laboratory's (NETL's) Baseline Study Case B12B (Cansolv), and costs as low as \$39.4/tonne CO₂ in 2018 pricing basis.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value	
Molecular Weight	mol ⁻¹	216.3	_	
Normal Boiling Point	°C	181.0	_	
Normal Freezing Point	°C	°C <0		
Vapor Pressure @ 15°C	bar	bar 5E-5		
Manufacturing Cost for Solvent	\$/kg	13	10	
Working Solution				
Concentration	kg/kg	0.98 (hydrated)	_	
Specific Gravity (15°C/15°C)	-	0.94	_	
Specific Heat Capacity @ STP	kJ/kg-K	1.97	_	
Viscosity @ 15°C	сР	12	_	
Absorption				
Pressure	bar	1	_	
Temperature	°C	45	_	
Equilibrium CO ₂ Loading	mol/mol	0.225	_	
Heat of Absorption	kJ/mol CO ₂	75	_	
Solution Viscosity	сР	25	_	
Desorption				
Pressure	bar	1.8	_	
Temperature	°C	118	_	
Equilibrium CO ₂ Loading	mol/mol	0.045 —		
Heat of Desorption	kJ/mol CO ₂	75		

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO₂ absorption (e.g., monoethanolamine [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 inorganic salt 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 CO₂ 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., a monoethanolamine [MEA]-based absorption system has a typical CO₂ 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 power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. 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 CO₂ loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO₂ in CO₂-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature			vol%			рр	mv
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SOx	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – EEMPA appears to be relatively stable toward oxidative and thermal degradation and hydrolysis in the absence of steel, while sulfur oxide (SO_X) and nitrogen oxide (NO_X) form heat-stable salts.

Solvent Foaming Tendency – EEMPA showed no evidence of foaming during 40 continuous hours of testing with simulated flue gas.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce sulfur dioxide (SO₂) and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively.

Solvent Makeup Requirements – Solvent makeup rates are expected to be at worst comparable to 5M MEA, though preliminary degradation studies indicate higher chemical durability of EEMPA under absorber and stripper conditions.

Waste Streams Generated – Sulfur oxides and NO_x form heat-stable salts, which will need treatment to recover EEMPA in a working process. Preliminary results indicate the addition of polarity-swing assisted regeneration can facilitate regeneration of heat-stable salts, releasing NO_x and SO_x from EEMPA at 60°C and 130°C, respectively.

Economic Values	Units	Current R&D Value	Target R&D Value 37.9			
Cost of Carbon Captured	\$/tonne CO ₂	39.4				
Cost of Carbon Avoided	\$/tonne CO ₂	60.2	58.3			
Capital Expenditures	\$/MW	4,231,000	4,231,000			
Operating Expenditures	\$/MWhr	28.4	27.2			
Cost of Electricity	\$/MWhr	105.7	104.4			

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Definitions:

Cost of Carbon Captured - Projected cost of capture per mass of CO₂ captured under expected operating conditions.

Cost of Carbon Avoided - Projected cost of capture per mass of CO₂ avoided under expected operating conditions.

Capital Expenditures - Projected capital expenditures in dollars per MW of power generation capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced. Operating costs include both variable operating cost and fixed operating costs at an 85% capacity factor.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Values presented are based on a new build supercritical pulverized coal plant with EEMPA-based post-combustion capture at 90% recovery of CO₂. The base power plant design and TEA referenced Cases B12A/B12B provided by NETL, found in Revision 4 of the "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" report (https://www.netl.doe.gov/energy-analysis/details?id=3745).

Scale of Validation of Technology Used in TEA – The models used to perform the TEA were validated with large bench-scale testing of the solvent in an integrated continuous flow system.

Qualifying Information or Assumptions – The capture process was a "simple stripping" design with a conventional packed regenerator column and steam-driven reboiler.

technology advantages

- Significantly lower regeneration energy compared to aqueous amines.
- Single-component, miscible in water.
- Low viscosity gain upon reaction with CO₂.
- Low surface tension.
- Compatible with potentially cheaper materials of construction (e.g., plastics).
- · Low corrosivity.
- · Good thermal and chemical stability.
- Potential for advanced heat integration and regeneration steps that could save costs (e.g., flash regeneration).

R&D challenges

- Potentially costly, and large-scale production yet to be demonstrated.
- Imposes need for careful control of the process water balance.

status

The initial TMP, EH&S risk assessment, and TEA were completed. The project team continues finalization of the best route for solvent production at larger scale. Four alternate synthetic routes were investigated with detailed efforts to identify scalable processes with high conversion rates and lower cost raw materials. In identifying modifications needed to the NCCC's facility to host the EEMPA engineering-scale test, Aspen Plus models' development and verification continues to predict performance in the PSTU equipment. The development of plans and equipment specifications is being finalized for the heat exchanger and chiller for the cooler-condenser, plastic packing for the absorber, and flash regeneration using the existing Advanced Flash Stripper equipment. The project team continues communication with the NCCC concerning updating the design hazard review and required permits. EPRI, Southern Company Services, and PNNL have executed their multi-party nondisclosure agreement.

available reports/technical papers/presentations

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," 2021 NETL Carbon Management Research Project Review Meeting, August 12, 2021. https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Swisher.pdf

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," DOE Project Kickoff Meeting, April 12, 2021. https://www.netl.doe.gov/projects/plp-download.aspx?id=11031&filename=Engineering-Scale+Test+of+a+Water-Lean+Solvent+for+Post-Combustion+Capture.pdf.

"Low-Viscosity, Water-Lean CO₂BOLs with Polarity-Swing Assisted Regeneration," NETL CO₂ Capture Technology Meeting, August 13, 2018. https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf.

"Low-Viscosity, Water-Lean CO₂BOLs with Polarity-Swing Assisted Regeneration," DOE Project Kickoff Meeting, September 15, 2017. https://www.netl.doe.gov/sites/default/files/netl-file/FWP-70924-PNNL-DOCCSS-kickoff.pdf.

D. Malhotra, D. C. Cantu, P. K. Koech, D. J. Heldebrant, A. Karkamkar, F. Zheng, M. D. Bearden, R. Rousseau, and V. A. Glezakou, "Directed Hydrogen Bond Placement: Low Viscosity Amine Solvents for CO₂ Capture." ACS Sustainable Chem. Eng., (2019), 7 (8), pp 7535–7542.

- D. Malhotra, J. P. Page, M. E. Bowden, A. Karkamkar, D. J. Heldebrant, V. A. Glezakou, R. Rousseau, P. K. Koech. "Phase change aminopyridines as carbon dioxide capture solvents." Ind. Eng. Chem. Res., (2017), 56, (26), 7534-7540.
- D. Malhotra, P. K. Koech, D. J. Heldebrant, D. C. Cantu, F. Zheng, V. A. Glezakou, R. Rousseau, "Reinventing design principles for developing low-viscosity carbon dioxide binding organic liquids (CO₂BOLs) for flue gas clean up." ChemSusChem. (2017), 10, 636 –642.