# Mixed-Salt-Based Transformational Solvent Technology for CO<sub>2</sub> Capture

### primary project goal

The overall objective of the project is to develop a novel, water-lean, mixed-saltbased transformational solvent technology that will provide a step-change reduction in the carbon dioxide (CO<sub>2</sub>) capture cost and energy penalties. SRI International is developing an advanced mixed-salt process (A-MSP) with the potential for accelerated scale-up to meet the U.S. Department of Energy's (DOE) Carbon Capture Program's transformational technology's goal for a coal-fired power plant. The program goals include  $CO_2$  capture with 95%  $CO_2$  purity and a cost of electricity at least 30% lower than a supercritical pulverized-coal (PC) power plant with  $CO_2$  capture, or approximately \$30 per tonne of  $CO_2$  captured, ready for demonstration by 2030.

### technical goals

- Demonstrate that the A-MSP can:
  - Operate as a solvent-rich system with a very high cyclic CO<sub>2</sub>-loading capacity (greater than 0.10 kilogram [kg] CO<sub>2</sub>/kg of solvent).
  - $_{\odot}$  Regenerate CO<sub>2</sub> at greater than 10 bar at temperatures less than 120°C.
  - Operate continuously in an integrated absorber-regenerator using simulated flue gas with 13–15% CO<sub>2</sub> and balance air.
- Perform thermodynamic modeling and vapor-liquid equilibrium (VLE) measurements of multi-component systems.
- Conduct kinetic measurements of CO<sub>2</sub> absorption of select compositions.
- Conduct solvent degradation and aerosol formation studies.
- Perform bench-scale testing of integrated absorber-regenerator system.
- Develop a rate-based model and process flowsheet and perform a technoeconomic analysis (TEA) to aid identification of development pathways for technology advancement.

### technical content

SRI International, in collaboration with SINTEF, Technical University of Denmark (DTU), OLI Systems Inc., and Trimeric Corporation, are utilizing the knowledge gained during a DOE-funded project (FE0012959) in the design of a mixed-salt process (MSP) that uses a solvent formulation comprised of ammonium (NH<sub>4</sub>) and potassium (K) salt solutions to develop a transformational technology that achieves further improvements in performance. An analysis conducted by SRI indicates that inclusion of a tertiary amine to the mixed-salt formulation will yield a high CO<sub>2</sub>-loading capacity and high-pressure solvent regeneration at low temperature, thus further reducing the energy penalty of CO<sub>2</sub> capture.

Bench-scale testing of SRI's first-generation MSP under FE0012959 showed that the two-component system has significant advantages over single-component systems. In the MSP chemistry, ammonia (NH<sub>3</sub>) plays a dual role—the role of catalyst and the role of the absorbent, due to its high mobility and reactivity with CO<sub>2</sub>. Ammonia absorbs large amounts of CO<sub>2</sub> at low temperature and releases

### program area:

Point Source Carbon Capture

ending scale: Laboratory Scale

## application:

Post-Combustion Power Generation PSC

key technology:

Solvents

### project focus:

Advanced Mixed-Salt Solvent Process

participant: SRI International

project number: FE0031597

predecessor projects: N/A

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OLI Systems Inc.; SINTEF; Technical University of Denmark; Trimeric Corporation

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percent complete: 85% CO<sub>2</sub> at high temperature and pressure, making it a highly useful chemical in CO<sub>2</sub> absorption formulations. By blending NH<sub>3</sub> with other low-capacity and low-reactivity components to suppress the undesirable high vapor pressure of NH<sub>3</sub>, SRI has identified a next-generation A-MSP formulation that can provide a step-change reduction in CO<sub>2</sub> capture costs. Based on preliminary examinations, adding methyl diethanolamine (MDEA) into the MSP formulation significantly improves the capture performance, yielding a regeneration energy of 1.5–1.8 megajoules (MJ)/kg-CO<sub>2</sub> while operating with less than 50% water. The solvent and process parameters are provided in Table 1.

The A-MSP concept includes two isothermal absorbers, a selective regenerator, and auxiliary equipment, as shown in Figure 1. Absorber 1 operates with high-NH<sub>3</sub>/(MDEA+K) solvent composition and absorber 2 operates with low-NH<sub>3</sub>/(MDEA+K) solvent composition, resulting in efficient absorption and minimum NH<sub>3</sub> slip. In the range of 60-80% of the  $CO_2$  in the flue gas stream is absorbed in absorber 1, and the remaining  $CO_2$  is absorbed in absorber 2. The dualstage absorber system reduces NH<sub>3</sub> carryover, resulting in less than 10 parts per million (ppm) NH<sub>3</sub> in the clean flue gas stream exiting the water wash. Both absorbers operate with liquid recycle using heat exchangers to remove the heat of reaction. The bottom stage operates with the highest CO<sub>2</sub> loading (up to 0.7 mol/mol). The CO<sub>2</sub>-rich solutions from the absorbers are then sent to the regenerator through crossflow heat exchangers, which recover the heat from returning lean solutions. The A-MSP uses a selective regenerator to produce two CO<sub>2</sub>-lean salt streams with high and low NH<sub>3</sub> content, drawn from the lower-middle and bottom stages of the regenerator. The regenerator is operated under highpressure isobaric conditions (10–20 bar) and has a temperature gradient in the column (top ~30°C and bottom ~110°C). At high temperature, the NH<sub>3</sub> at the bottom of the regenerator is vaporized along with CO<sub>2</sub>, making a lean, low-NH<sub>3</sub>/(MDEA+K) ratio solution to be used in absorber 2. Vaporized NH<sub>3</sub> gets re-absorbed as the vapor moves up the regenerator column, thereby creating a high-NH<sub>3</sub>/(MDEA+K) ratio solution in the mid-section of the regenerator for use in absorber 1. In the A-MSP design, operating the regenerator at relatively low temperature and high pressure eliminates the water stripping, thus generating an almost-dry CO<sub>2</sub> stream ( $H_2O_{vap}/CO_2 < 0.02$ ) at high pressure. Figure 2 shows equilibrium modeling data comparing MSP and A-MSP systems, illustrating the high-CO<sub>2</sub> regeneration pressure advantage (almost doubled for 0.55 mol/mol CO<sub>2</sub> loading) of A-MSP with the inclusion of MDEA to the solvent. This results in a reduction of regeneration and CO<sub>2</sub> compression energy costs (operating cost reduction) and removal of the expensive first stage of CO<sub>2</sub> compression (capital cost reduction). In addition, the lower regeneration temperature and lower reboiler duty significantly reduce power plant energy loss due to steam extraction, improving the net power output of the plant (Figure 3).



Figure 1: Conceptual process flow diagram for the A-MSP.



Figure 2: CO<sub>2</sub> loading versus CO<sub>2</sub> pressure at 100°C for (i) 10 molal mixed-salt and (ii) 10 molal MDEA-mixed-salt formulations.



Figure 3: Power plant energy loss due to steam extraction.

Following lab-scale and small bench-scale testing, SRI's large bench-scale integrated CO<sub>2</sub> absorber-regenerator system (Figure 4), originally built for testing the MSP, will be used without any modifications for dynamic and steady-state testing.



A: Rich solution inlet locations

B: Discharge locations for high NH<sub>3</sub>/K solution

C: Discharge locations for low NH<sub>3</sub>/K solution

D: Heat exchangers (Cold rich $\leftrightarrow$  Hot lean)

### Figure 4: SRI's large bench-scale integrated absorber-regenerator system (gas flow rates up to 400 standard liters per minute).

Pure Solvent	Units	Current R&D Value	Target R&D Value	
Molecular Weight	mol <sup>-1</sup>	18	18	
Normal Boiling Point	°C	100	100	
Normal Freezing Point	°C	0	0	
Vapor Pressure @ 15°C	bar	0.17	0.17	
Manufacturing Cost for Solvent	\$/kg	—	—	
Working Solution				
Concentration	kg/kg	0.20-0.55	0.30-0.55	
Specific Gravity (15°C/15°C)	_	1.37	1.37	
Specific Heat Capacity @ STP	kJ/kg-K	3.2	3.2	
Viscosity @ 20°C	cP	1.6-35	1.6-35	
Surface Tension @ STP	dyn/cm	73.4	73.4	
Absorption				
Pressure	bar	1	1	
Temperature	°C	20-40	20-40	
Equilibrium CO <sub>2</sub> Loading	gmol CO <sub>2</sub> /kg	1.5-3.5	2.5-3.5	
Heat of Absorption	kJ/kg CO <sub>2</sub>	795-1,136 <1,100		
Solution Viscosity	cP	1.5-3.0	1.5-3.0	
Desorption				
Pressure	bar	>10	10-15	
Temperature	°C	120-180	140-160	
Equilibrium CO <sub>2</sub> Loading	gmol CO <sub>2</sub> /kg	0.2-1	0.2-0.5	
Heat of Desorption	kJ/kg CO <sub>2</sub>	1,500-2,200	<2,000	

### **TABLE 1: SOLVENT PROCESS PARAMETERS**

Proposed Module Design	(for	(for equipment developers)		
Flue Gas Flowrate	kg/hr		—	
CO <sub>2</sub> Recovery, Purity, and Pressure	% / % / bar	90%	95%	—
Absorber Pressure Drop	bar		_	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	\$ kg/hr		_	

### **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 CO<sub>2</sub> 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., CO2-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<sub>2</sub> 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 processdependent (e.g., an monoethanolamine [MEA]-based absorption system has a typical CO<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub> 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 CO<sub>2</sub> in CO<sub>2</sub>-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 <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	<b>O</b> <sub>2</sub>	Ar	SOx	NOx
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

### **Other Parameter Descriptions:**

Chemical/Physical Solvent Mechanism - The reaction involves chemical absorption of CO<sub>2</sub> through gas/liquid phase mass transfer followed by chemical reactions in the liquid phase.

These reactions are as follows:

 $1.CO_2(q) \leftrightarrow CO_2(aq)$ 

2. NH<sub>3</sub> (aq) + CO<sub>2</sub> (aq) + H<sub>2</sub>O (liq)  $\leftrightarrow$  (NH<sub>4</sub>)HCO<sub>3</sub> (aq)

3. 
$$(NH_4)_2CO_3 + 2CO_2 (aq) + H_2O (liq) \leftrightarrow 2(NH_4)HCO_3 (aq)$$

$$4.2NH_3 (aq) + CO_2 (aq) \leftrightarrow (NH_4)NH_2CO_2$$

5. (NH<sub>4</sub>)NH<sub>2</sub>CO<sub>2</sub> (aq) + CO<sub>2</sub> (aq) + 2H<sub>2</sub>O (liq)  $\leftrightarrow$  2(NH<sub>4</sub>)HCO<sub>3</sub> (aq) 6. K<sub>2</sub>CO<sub>3</sub> (aq) + CO<sub>2</sub> (aq) + H<sub>2</sub>O (liq) + catalyst  $\leftrightarrow$  2KHCO<sub>3</sub> (aq) + catalyst 7. R1R2R3N (aq) + CO<sub>2</sub> (aq) + H<sub>2</sub>O (liq) + catalyst  $\leftrightarrow$  (R1R2R3NH)HCO<sub>3</sub> (aq) + catalyst where R1=R2=CH<sub>2</sub>CH<sub>2</sub>OH and R3=CH<sub>3</sub>

### Solvent Contaminant Resistance - High.

Solvent Foaming Tendency - Low.

Flue Gas Pretreatment Requirements - The process is installed downstream of the FGD unit.

Solvent Makeup Requirements – To be determined.

Waste Streams Generated - To be determined.

Process Design Concept - Flowsheet/block flow diagram shown above in Figure 1.

### **TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS**

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO <sub>2</sub>	TBD	39.6
Cost of Carbon Avoided	\$/tonne CO2	TBD	50.2
Capital Expenditures	\$/MWhr	TBD	68.8
Operating Expenditures	\$/MWhr	TBD	47.5
Cost of Electricity	\$/MWhr	TBD	116.4

### **Definitions:**

Cost of Carbon Captured – Projected cost of capture per mass of CO<sub>2</sub> captured under expected operating conditions.

*Cost of Carbon Avoided* – Projected cost of capture per mass of CO<sub>2</sub> avoided under expected operating conditions.

Capital Expenditures - Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures - Projected operating expenditures in dollars per unit of energy produced.

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

**Calculations Basis** – The numbers provided in the table are based on the reference plant provided by NETL for TEA analysis, found in 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*), Revision 3.

**Scale of Validation of Technology Used in TEA** – Technology numbers were validated for use in the TEA analysis by modeling and laboratory testing.

**Qualifying Information or Assumptions** – Detailed qualifying information or assumptions regarding the economic numbers will be understood upon completion of the final TEA.

### technology advantages

- Low NH<sub>3</sub> emissions.
- High CO<sub>2</sub> absorption rate and high CO<sub>2</sub> loading capacity.
- Reduced reboiler energy demand.
- Addition of tertiary amine to NH<sub>4</sub>-based mixed-salt solvent reduces regeneration energy need and water use.
- Lower reboiler duty and regeneration temperature improve net power output, increasing net plant efficiency.
- Low-temperature, high-pressure regeneration of greater than 99% pure dry CO<sub>2</sub> reduces compression requirements.
- Oxidative degradation results show the A-MSP amine is more stable than MEA and other widely used amines.

### R&D challenges

- Precipitation of solids in the absorber during cold weather conditions.
- Residual amine and/or NH<sub>3</sub> in exit gas stream.
- Solvent interaction with acid gases.
- Thermal management of absorber columns and regenerator.
- Volatility and corrosiveness of MDEA.

### status

The project team conducted VLE measurements of various CO<sub>2</sub>-loading levels and compositions for the regenerator side and is conducting lab-scale absorber tests to investigate reaction kinetics and CO<sub>2</sub> absorption capacity. SRI completed the refurbishment of the existing absorber bench-scale unit and has performed parametric testing in the unit with simulated flue gas to determine the rate of CO<sub>2</sub> absorption in the A-MSP solutions as a function of temperature, gas flow rate, solution composition, CO<sub>2</sub> loading, and liquid/gas ratio. After testing 11 different MSP solvent formulations, it was determined that a 9-molal (total) formulation comprised of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), NH<sub>3</sub>, and MDEA exhibited the highest overall carbon capture efficiency. The existing MSP process model was updated to include MDEA in the solvent formulation and VLE data will be used to inform model refinements and process design. DTU has assembled a thermodynamic modeling program for the process to aid with predicting CO<sub>2</sub> and NH<sub>3</sub> isotherms under various test conditions and solvent compositions. Process kinetics assessment has been completed on the bench-scale system. Oxidative and thermal degradation studies have been completed. A preliminary A-MSP process flow sheet was developed, along with a preliminary TEA. The integrated absorption/desorption testing in SRI's large bench-scale system is currently being investigated, and a TEA will be completed in Budget Period 2.

### available reports/technical papers/presentations

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO<sub>2</sub> Capture," presented at 2021 NETL Carbon Management Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG\_PSC\_Jayaweera\_SRII.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO<sub>2</sub> Capture," presented at 2020 BP1 Review Meeting, Pittsburgh, PA, December 2020. *https://www.netl.doe.gov/projects/plpdownload.aspx?id=10454&filename=Mixed-Salt+Based+Transformational+Solvent+Technology+for+CO2+Capture.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO<sub>2</sub> Capture," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Solvent.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO<sub>2</sub> Capture," Project Kick-Off Meeting, September 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10459&filename=Mixed-Salt+Based+Transformational+Solvent+Technology+for+CO2+Capture.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO<sub>2</sub> Capture," presented at the 2018 NETL CO<sub>2</sub> Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Based-Transformational-Solvent.pdf.