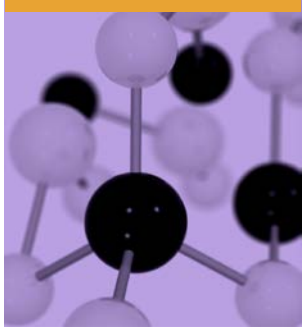


Development of Mixed-Salt Technology for CO_2 Capture from Coal Power Plants

Presented by: Indira S. Jayaweera
Sr. Staff Scientist and CO_2 Program Leader
SRI International, CA, USA

FE0012959 SRI Kick-off Meeting
December 11, 2013

Discussion Topics

- Project Background
  - **Brief overview of SRI & Short discussion of research leading to this award**
- Project Objectives
- Project Team
- Project Structure
- Project Schedule
- Project Management Plan
- Deliverables
- Current Project Status
- Questions
- Closing Comments

Who We Are

SRI is a world-leading R&D organization

- An independent, nonprofit corporation
  - Founded by Stanford University in 1946
  - Independent in 1970; changed name from Stanford Research Institute to SRI International in 1977
  - Sarnoff Corporation acquired as a subsidiary in 1987; integrated into SRI in 2011
- Annual R&D Projects: ~ $600 million
- More than 2,500 employees (~ 700 with advanced degrees)
- More than 20 locations worldwide

Silicon Valley - Headquarters

Washington, D.C.

Princeton, New Jersey

Harrisonburg, Virginia

St. Petersburg, Florida

State College, Pennsylvania

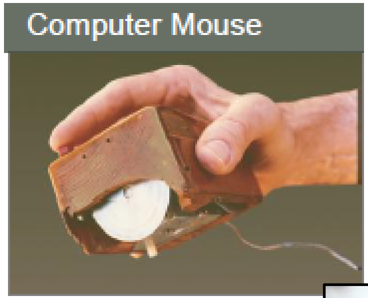
Arecibo, Puerto Rico

Tokyo, Japan

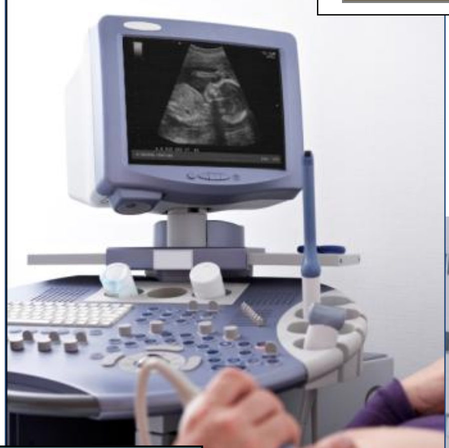
SRI Works on Important Problems

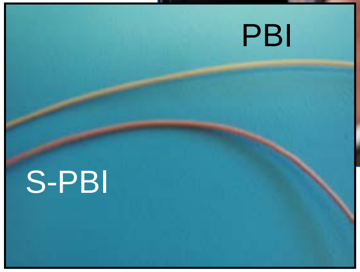
Over 65 years of contributions have changed how we live, work, and play

- SRI has created…
  - New industries
  - Hundreds of billions of dollars in market value
  - Lasting benefits to society
- SRI innovations touch our lives when we…
  - Use the Internet
  - Undergo an ultrasound exam
  - Watch a movie or TV
- Important problems we are working to address include…
  - Global warming
  - Clean water
  - Access to energy



SRI invented this and other foundations of personal computing (1968)





Hollow-fiber membranes for gas and water separation

AHO Facility for waste water treatment plant at The Tokyo Bay, operated by JESCO

SRI Incorporates a Facilitated CO_2 Absorption in the New Mixed-Salt Process

Potassium Carbonate-Based Processes

Pros

- No emissions, long-term experience
- Many options are currently being tested
- Easy permitting

Cons

- Low efficiency and low CO_2 loading
- Energy for solid dissolution
- Energy for water stripping (vacuum stripping)

Ammonia-Based Processes

Pros

- Very high CO_2 loading capacity, ~ 25 MW experience
- Reduced reboiler duty due to high-pressure regeneration
- Fast absorption-reaction kinetics

Cons

- Large water-wash to reduce ammonia emission
- Solvent chilling requirements
- Energy for solid dissolution

SRI's NOVEL MIXED SALT TECHNOLOGY
(Low-Risk Approach: Advancement of known technologies)

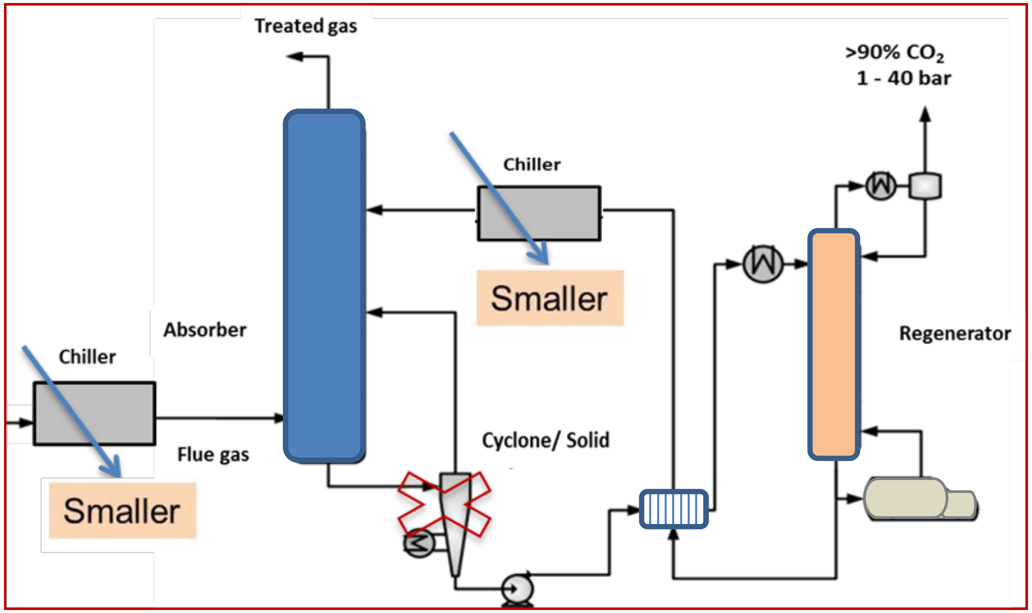
The new process has

Enhanced absorption kinetics
Reduced emissions
High CO_2 loading
High-pressure CO_2
No Solids

Reduced reboiler duty
Reduced auxiliary electricity loads
Reduced water use
Reduced footprint

Reduce the CCS costs

Improving Salt-Based CO_2 Capture Systems



A generic process flow diagram (PFD) for solvent-based CO_2 capture

Need to reduce high energy penalties related to:

- solvent chilling
- solid dissolution (heat requirement for salt dissolution can be up to 1MJ/ kg CO_2)
- water use for ammonia emission control
- sour water stripper

Mixed-Salt Technology Process Conditions

- Process uses mixtures of potassium carbonate and ammonium salts
  - Dual absorber and a selective regenerator
  - Heat of reaction 35 to 50 kJ/mol
- Absorber operation at 20° – 40° C at 1 atm with ~ 38 wt.% mixture of salts
- Regenerator operation at > 120°C at 20-40 atm
  - Produce high-pressure CO_2

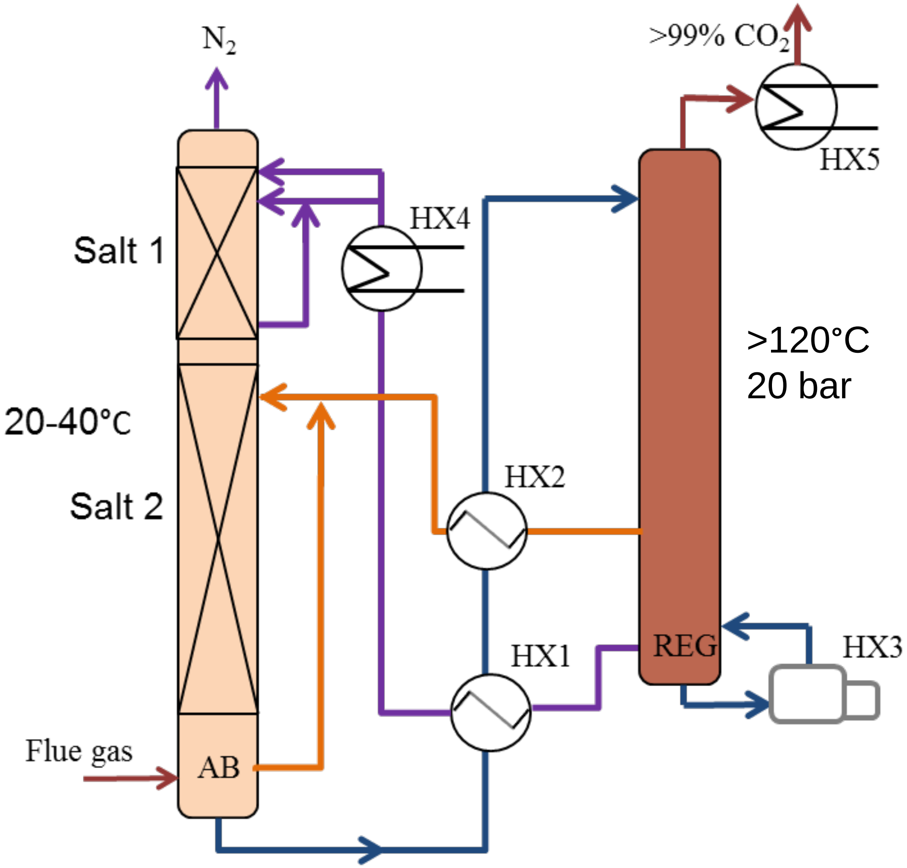
CO_2 Lean

CO_2 Rich

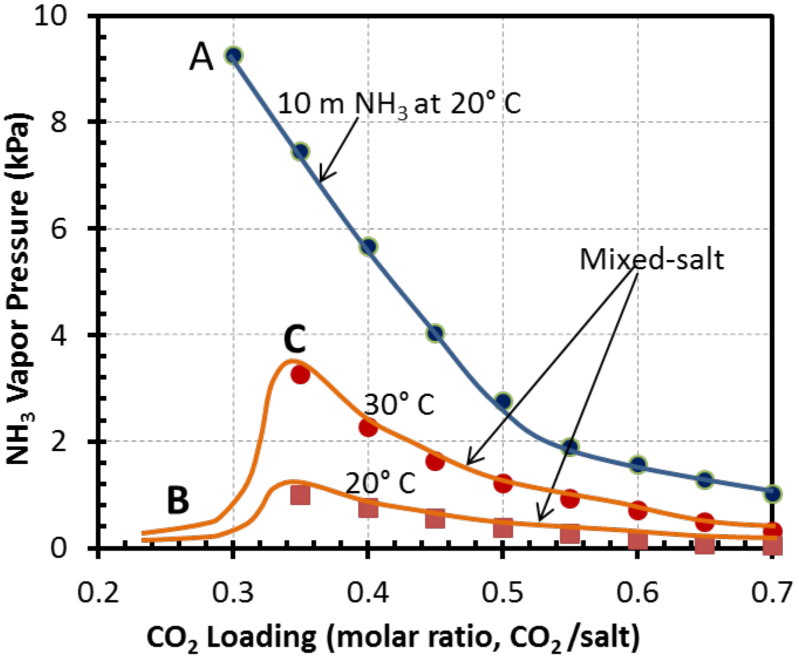
$K_2CO_3–NH_3–xCO_2–H_2O$ system ←→ K_2CO_3 $–NH_3–yCO_2–H2O$ system

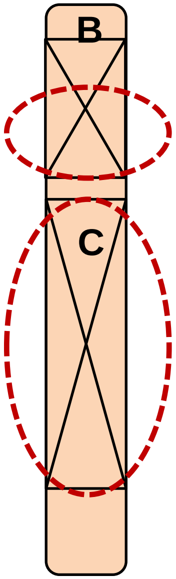
Where $y > x$

Mixed-Salt Process: Simplified Process Diagram



Mixed-Salt has a Reduced Ammonia Emission at the Absorber Exit





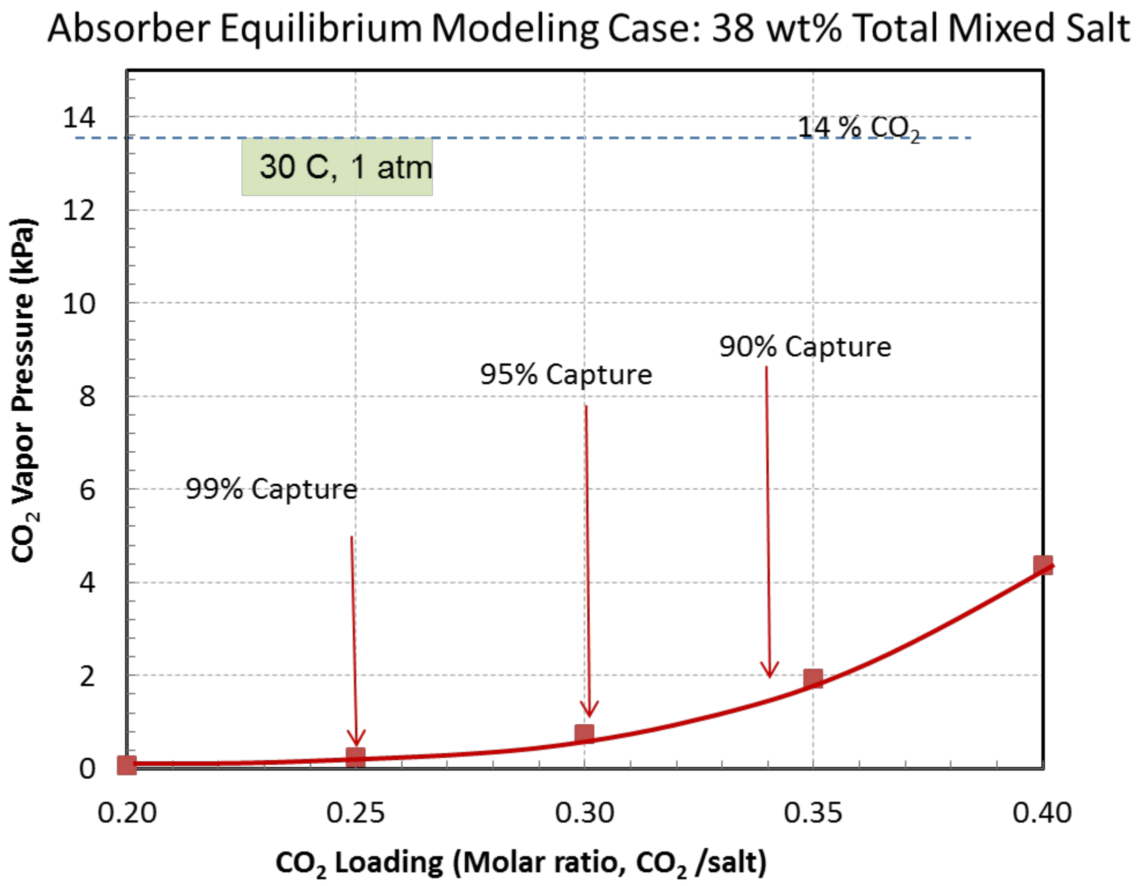
Benefits

- Ammonia emission reduced by more than an order of magnitude

- Absorber-side water use reduced by more than order of magnitude

Ammonia vapor pressure as a function of CO_2 loading. A comparison between mixed-salt and 10-m aqueous ammonia at 20°C is shown.

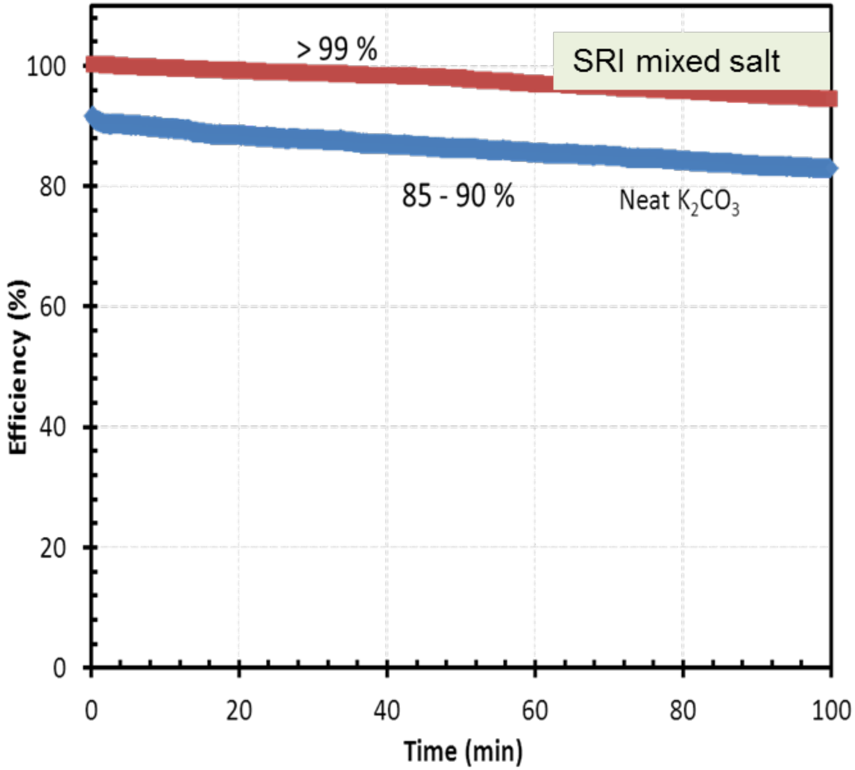
Mixed Salt Can Capture > 90% CO_2



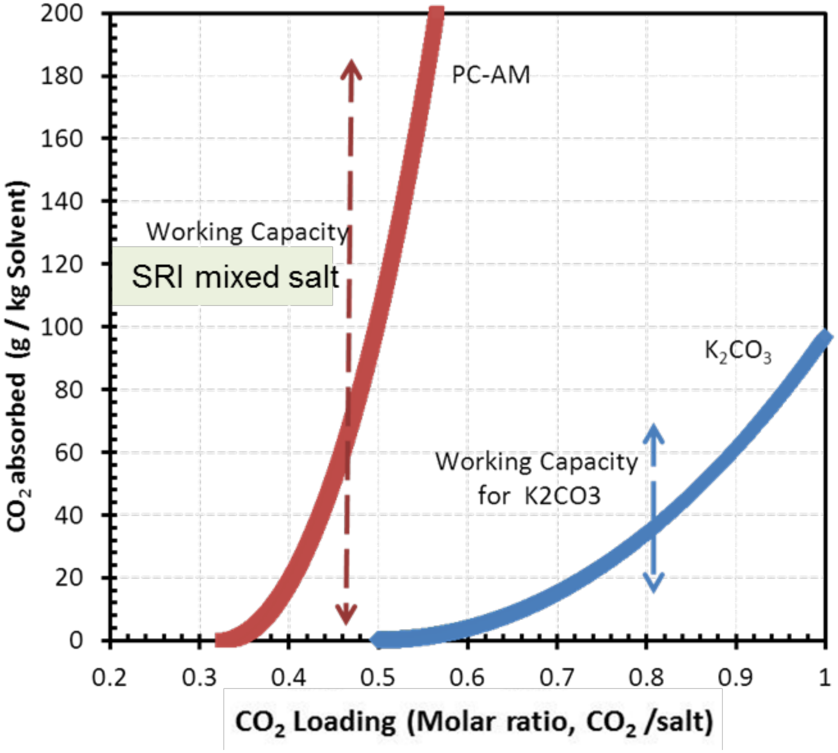
Equilibrium CO_2 vapor pressure at the absorber exit as a function of CO_2 loading

Absorber Data from Lab-Scale Tests: Data at 30°C and 1 atm

Mixed salt has a higher CO_2 capture efficiency



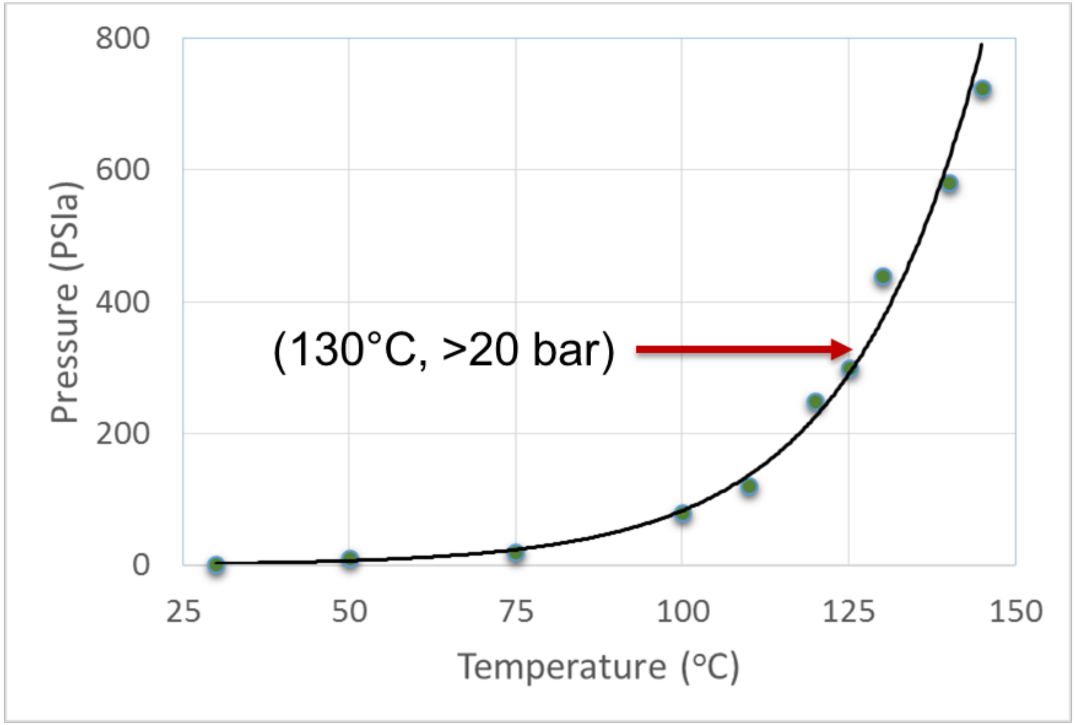
Mixed salt has a higher CO_2-loading capacity



Performance (CO_2 capture efficiency & CO_2 loading) comparison for mixed salt and neat K_2CO_3

SRI WORK PRIOR TO APRIL 2013

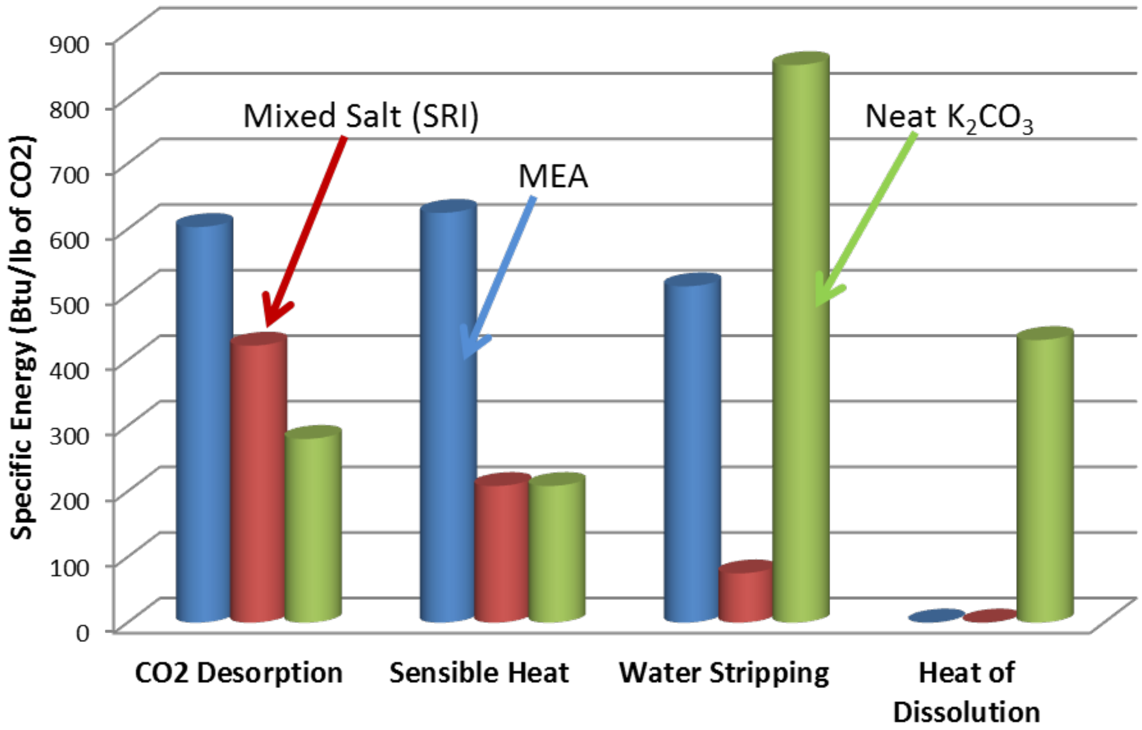
Results from Regenerator Tests: Static Large Bench-Scale Stirred-Tank Reactor Tests



Attainable CO_2 pressure during solvent regeneration: Mixed-salt with CO_2 loading value of 0.6 CO_2/salt

No thermal or oxidative degradation of mixed-salts in the regenerator.

Regeneration Heat Requirement



Estimated regenerator heat requirement for Mixed-Salt system with 0.2 to 0.7 cyclic loading of CO_2. Comparison with neat K_2CO_3 process and MEA is shown

Sources
MEA Data: CSIRO Report (2012). EP116217
K_2CO_3 Data: GHGT-11; Schoon and Van Straelen (2011). TCCS-6

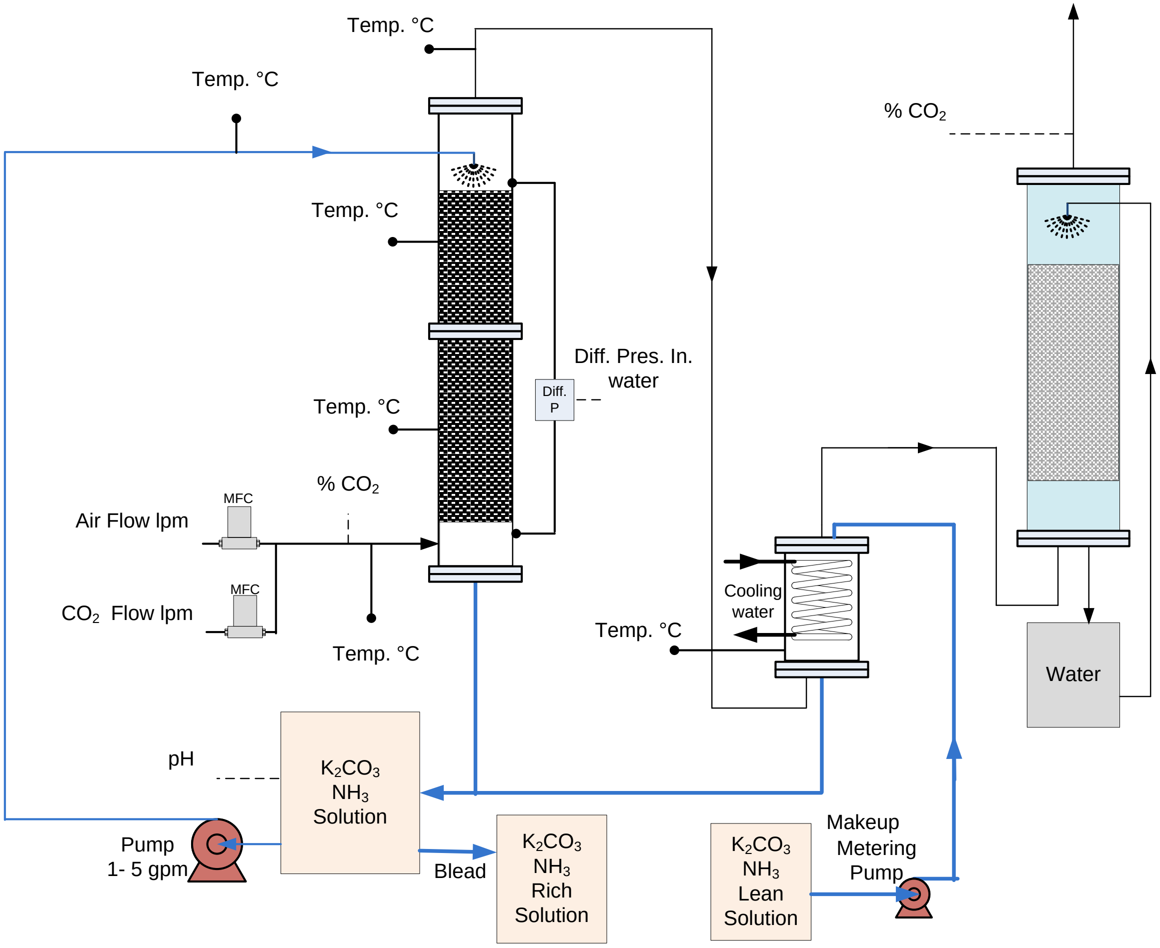
How Does the New Mixed-Salt Process Compare with the State of the Art?

Process Comparison

Parameter	Conventional MEA	SRI Mixed Salt
Solution Circulation Rate	1	0.5
Regeranation Energy	1	0.5
Degradation of the Solvent	1	0
Solvent Loss	1	<0.1
Solvent Cost	1	<0.1
Corrosion Inhibitor	YES	NO
Flue Gas Cooling	YES	YES
FGD Requirement	Deep FGD	light FGD
Hazardous Waste	YES	NO
Oxygen tolarance	NO	YES
CO_2 Loading	1	2
CO_2 Pressure	1	20

New Data: Work Conducted After The Proposal Submission

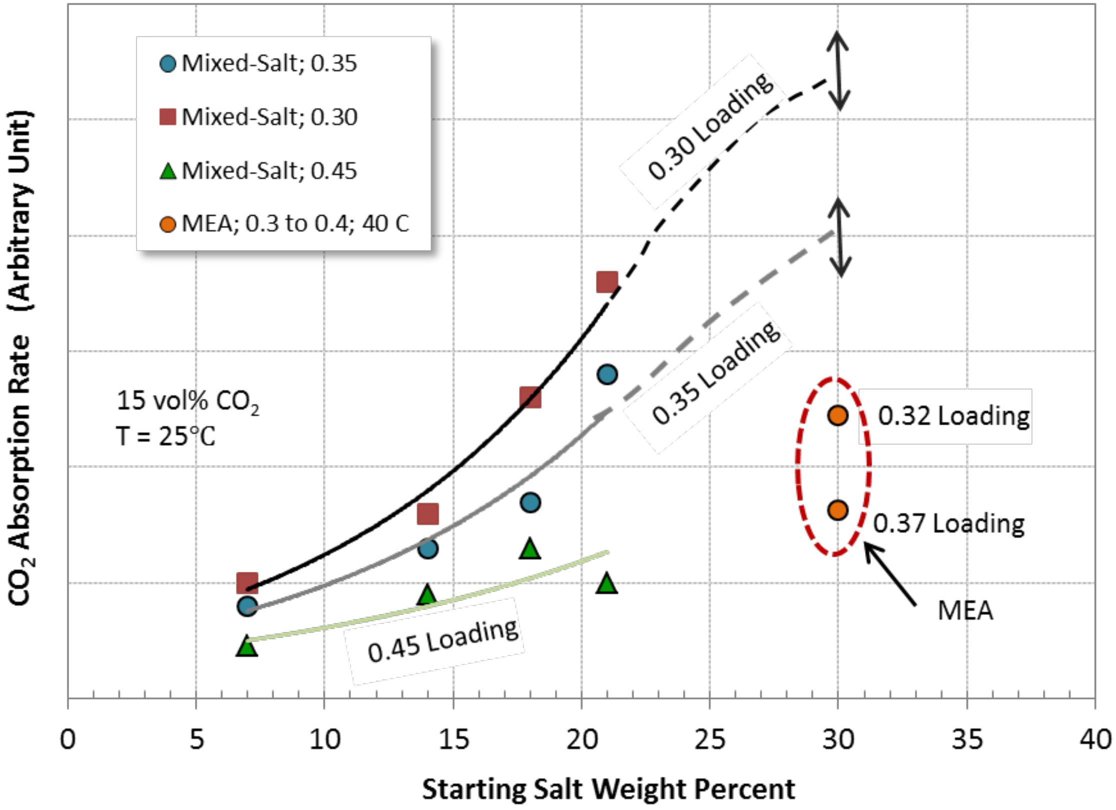
June through October 2013



Built and tested a 4-in single-stage absorber

Gas Flow Rate: 50 - 100 SLPM

Summary results from small bench-scale test data



Source for MEA data: DOE Award No. DE-FC26-02NT41440

Presentations and Publications on Mixed-Salt Technology

- Presented at 25th ACS National Meeting, April 7-11, 2013, **New Orleans**, **LA**
- Presented at 12th Annual CCUS Conference, May 12-16, 2013, **Pittsburgh**, **PA**
- Presented at BIT's 2nd Annual Clean Coal International Symposium of Clean Coal Technology, September 26-29, 2013, **Xian**, **China**
- Filed a provisional patent in August 2012
- Filed the PCT application in November 2013

Discussion Topics

- Project Background ✓
- **DOE Project Objectives**
- **Project Team**
- Project Structure
- Project Schedule
- Project Management Plan
- Deliverables
- Current Project Status
- Questions
- Closing Comments

Project Objectives

The overall objective of the project is to develop and test a solvent-based CO_2 technology that can capture CO_2 from existing or new pulverized coal (PC) power plants at low cost

Budget Period 1:

- Demonstrate the absorber and regenerator processes individually with high efficiency and low NH_3 emission and reduced water use compared to the state-of-the-art ammonia-based technologies

Budget Period 2:

- Demonstrate the high-pressure regeneration and integration of the absorber and the regenerator
- Demonstrate the complete CO_2 capture system with low-cost production of CO_2 stream, optimize the system operation, and collect data to perform the detailed techno-economic analysis of CO_2 capture process integration to a full-scale power plant

Project Team and Organization

Project Team and Technical Leaders

SRI- Indira Jayaweera; OLI Systems (OLI)- Andre Anderko; Stanford University - Adam Brant; Aqueous Systems Aps (ASAp)- Kaj Thomsen; Politechnico De Milano (POLIMI)- Gianluca Valenti; and Eli Gal

Discussion Topics

- Project Background ✓
- Project Objectives ✓
- Project Team ✓
- **Project Structure**
  - **Budget Period (length and cost)**
  - **Description of Tasks by Budget Period**
- Project Schedule
- Project Management Plan
- Deliverables
- Current Project Status
- Questions
- Closing Comments

Project Budget

	Budget Period 1 10/1/13 - 12/30/14	Budget Period 2 1/1/15 - 3/31/16	Total 10/1/13-3/31/16
Total Project Cost	$1,019,650	$1,102,092	$2,121,742
DOE Share	$819,534	$878,113	$1,697,647
Cost Share	$200,116	$223,979	$424,095

Cost share by SRI, OLI Systems, POLIMI, Aqueous Solutions Aps, Stanford University

Budget Period 1 Tasks

Task 1: Project Management and Planning

Task 2: Individual Absorber and Regenerator Testing in a Semi-Continuous Mode

- System design, commissioning and performing parametric tests
- Data analysis to determine the independent relationships between solvent concentration, absorption and regeneration conditions, column packing, CO_2 capture efficiency, ammonia loss, and water usage
- Provide data for process modeling

Task 3: Preliminary Process Modeling and Techno-Economic Analysis.

- UNIQUAC Model development by POLIMI and ASAp based on literature data
- Establish a rate-based thermodynamic modeling database for potassium- and ammonium-based system heat and mass balance evaluations then transferred to Aspen Plus®
- Establishing the basis for techno-economic analysis

Task 4.0 - Budget Period 2 Continuation Application

Budget Period 2 Tasks

Task 1: Project Management and Planning

Task 5: Bench-Scale Integrated System Testing

- System design, commissioning and performing parametric tests (T, P, CO_2 Loading)
- Provide data for process modeling

Task 6 - Process Modeling, Techno-Economic Analysis (TEA), and Technology EH&S Risk Assessment

- A rate-based model for detailed mass-balance and heat-balance calculations for a flue gas feed equivalent to a 550-MWe flue gas stream will be developed
- Aspen Plus® model to develop a process flow sheet of a PC-Power Plant (Cost Estimation Methodology for NETL Assessments of Power Plant Performance DOE/NETL 2011/1455 April 2011, Case 12) system (TEAM)
  - The process modeling and material balance and heat balance calculations will be based on updated rate-based modeling
- Assessment of the environmental friendliness and safety of any future process based on the materials and process being developed (emissions, waste using DOE guidelines)

Bench-Scale Demonstration of Mixed-Salt Technology for CO_2 Capture:

Simulation Studies

Andre Anderko

OLI Systems Inc.

aanderko@olisystems.com

Scope

- Summary of project tasks
- Technology foundations
  - Thermophysical properties
    - Results for selected subsystems of the K_2CO_3 – CO_2 – NH_3 – H_2O system
  - Process simulation tools

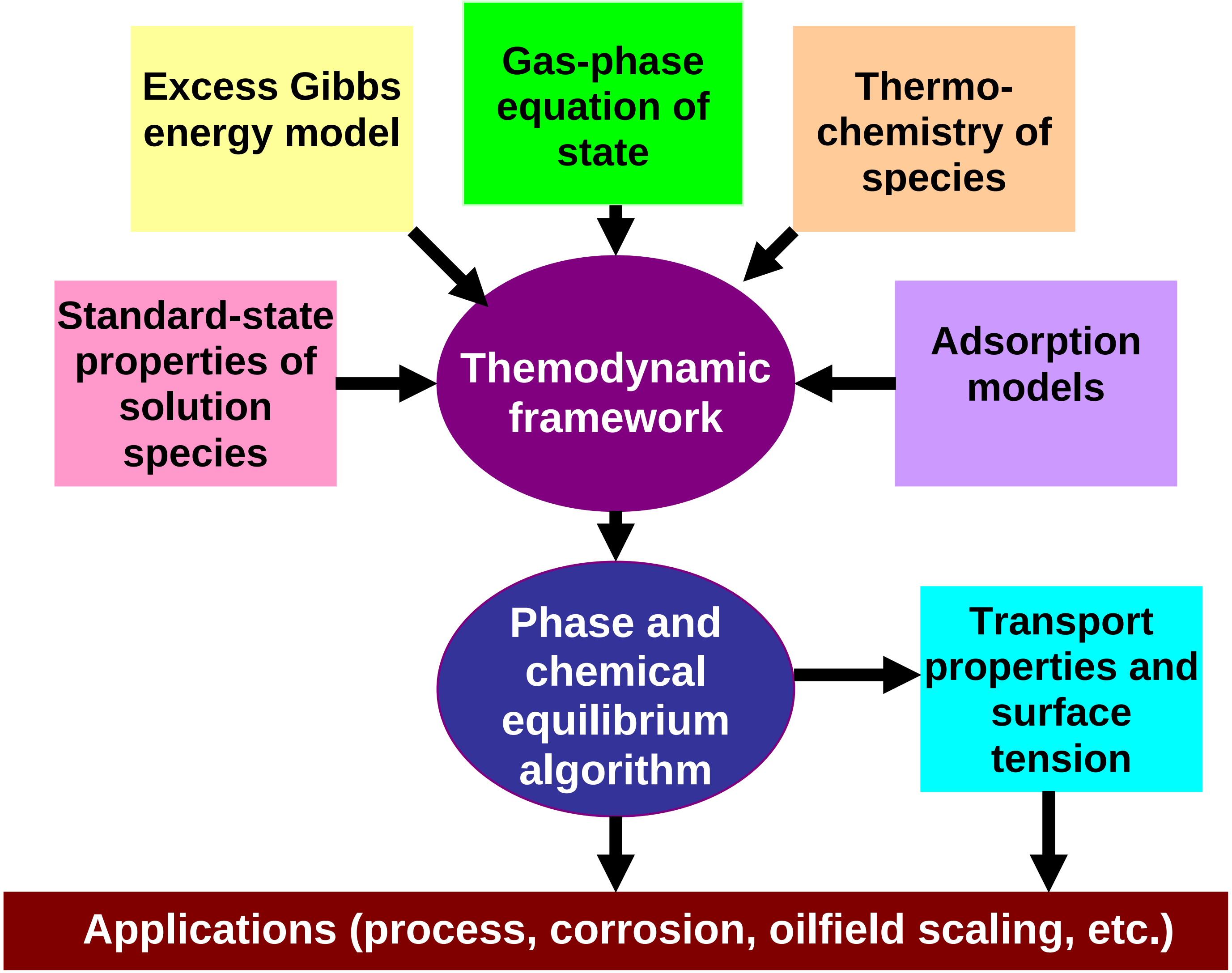
Project Tasks: Period 1

- Thermodynamic model for the system K_2CO_3 – CO_2 – NH_3 – H_2O
- Analysis of SRI test data for thermodynamic modeling
- Process flowsheet using ESP (Electrolyte Simulation Program)
  - Absorber and regenerator modeled as equilibrium unit operations
  - Including mass transfer modeling
- Transfer to Aspen+ for use by other team members

Project Tasks: Period 2

- Heat and mass transfer modeling on the basis of SRI’s bench scale from budget period 1 data
- Model optimization with budget period 2 data for full-scale heat- and mass-transfer modeling
- Detailed rate-based model for mass and heat-balance calculations for flue gas stream

Thermophysical Framework



Excess Gibbs energy model

Gas-phase equation of state

Thermo-chemistry of species

Standard-state properties of solution species

Themodynamic framework

Adsorption models

Phase and chemical equilibrium algorithm

Transport properties and surface tension

Applications (process, corrosion, oilfield scaling, etc.)

Mixed-Solvent Electrolyte Framework

$$\frac{G^{ex}}{RT} = \frac{G^{ex}_{LR}}{RT} + \frac{G^{ex}_{LC}}{RT} + \frac{G^{ex}_{II}}{RT}$$

LR	Long-range electrostatic interactions
LC	Local composition term for neutral molecule interactions
II	Ionic interaction term for specific ion-ion and ion-molecule interactions

MSE thermo

- Standard-state: HKF (direct)
- G^{EX}: MSE no limit on concentration
- Solid phases: thermochemical properties
- 2nd liquid phase: MSE (ionic)

Electrical conductivity

Viscosity

Self - diffusivity

Thermal conductivity

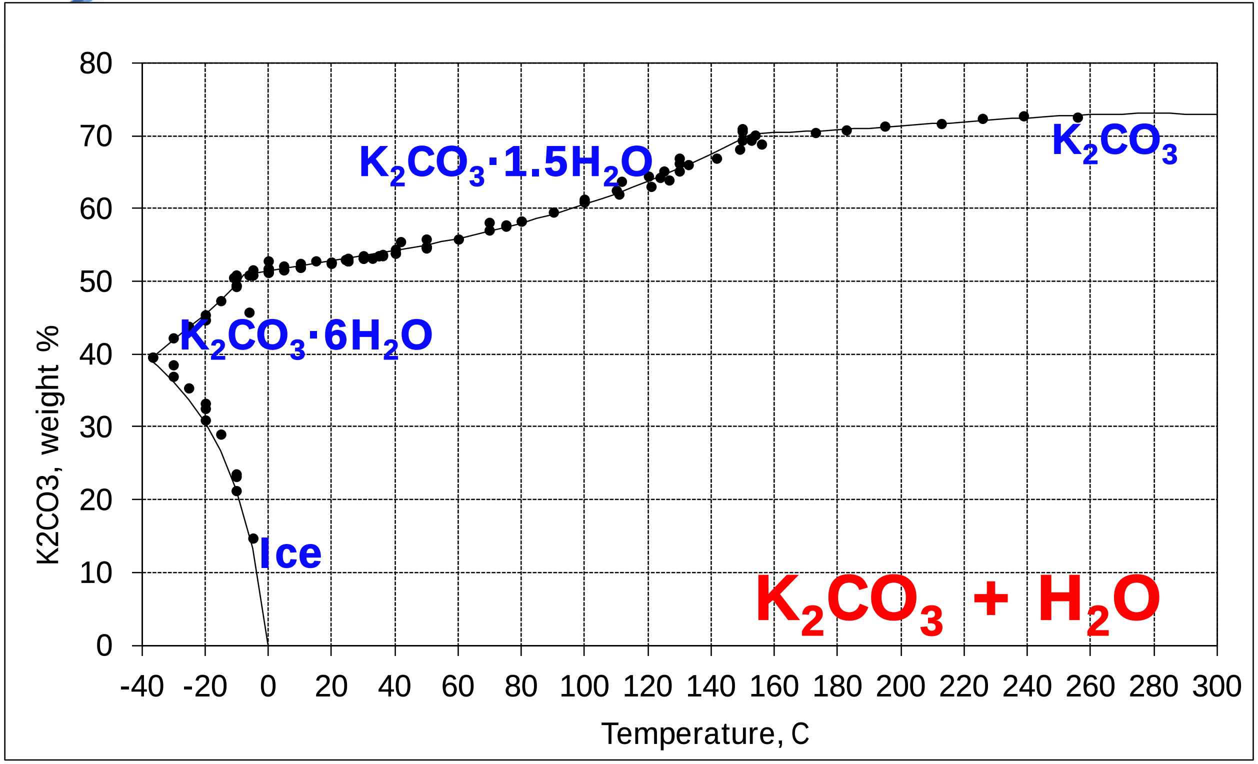
Surface tension

Interfacial tension

Interfacial phenomena: ion exchange, surface complexation, molecular adsorption

Thermodynamic Fundamentals:

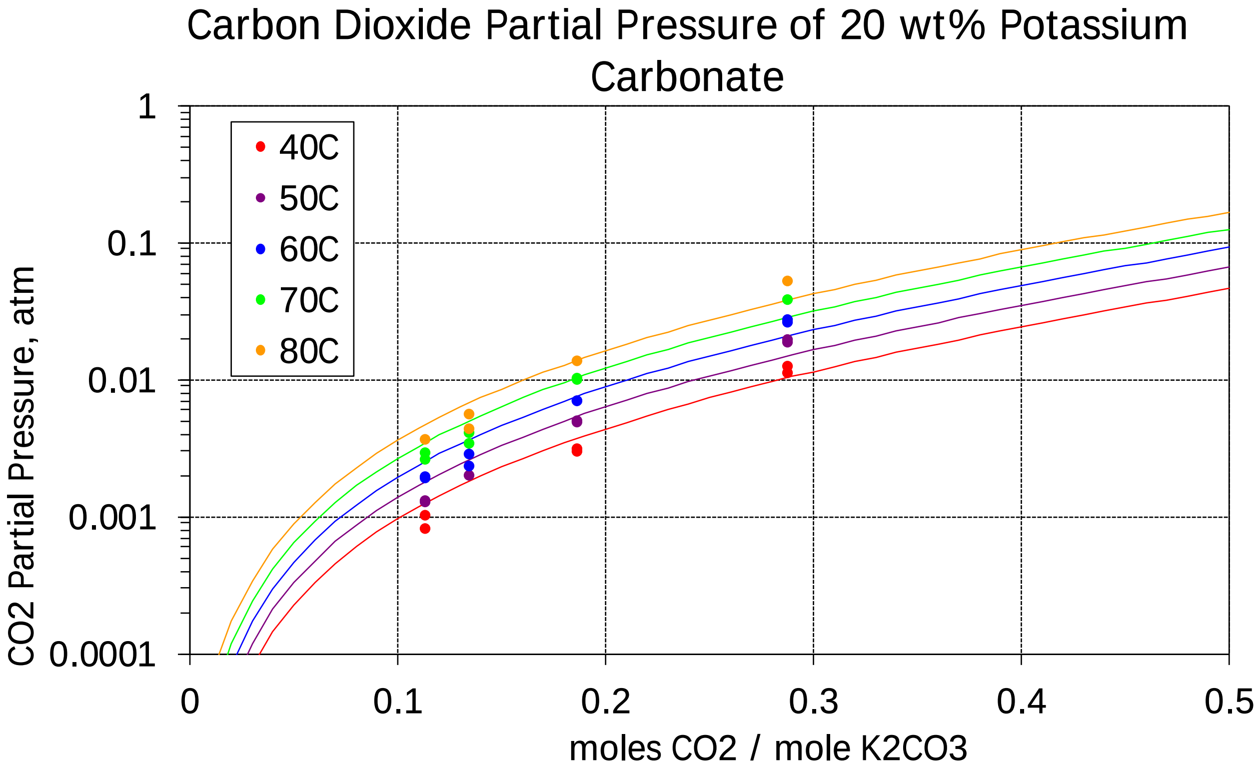
Mixed-Solvent Electrolyte (MSE) Model



- Prediction of phase equilibria and thermodynamic properties in wide temperature and composition ranges
- Example: solid-liquid boundaries for the binary system K_2CO_3 – H_2O

Vapor-liquid equilibria:

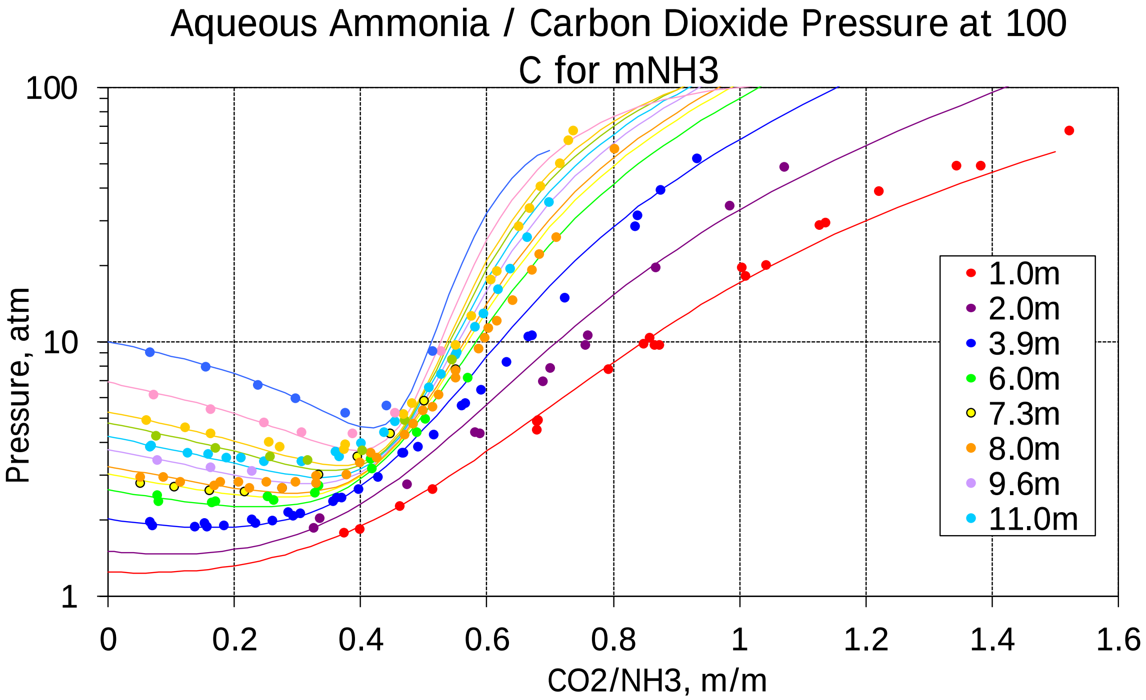
K_2CO_3 – $KHCO_3$ – CO_2 – H_2O

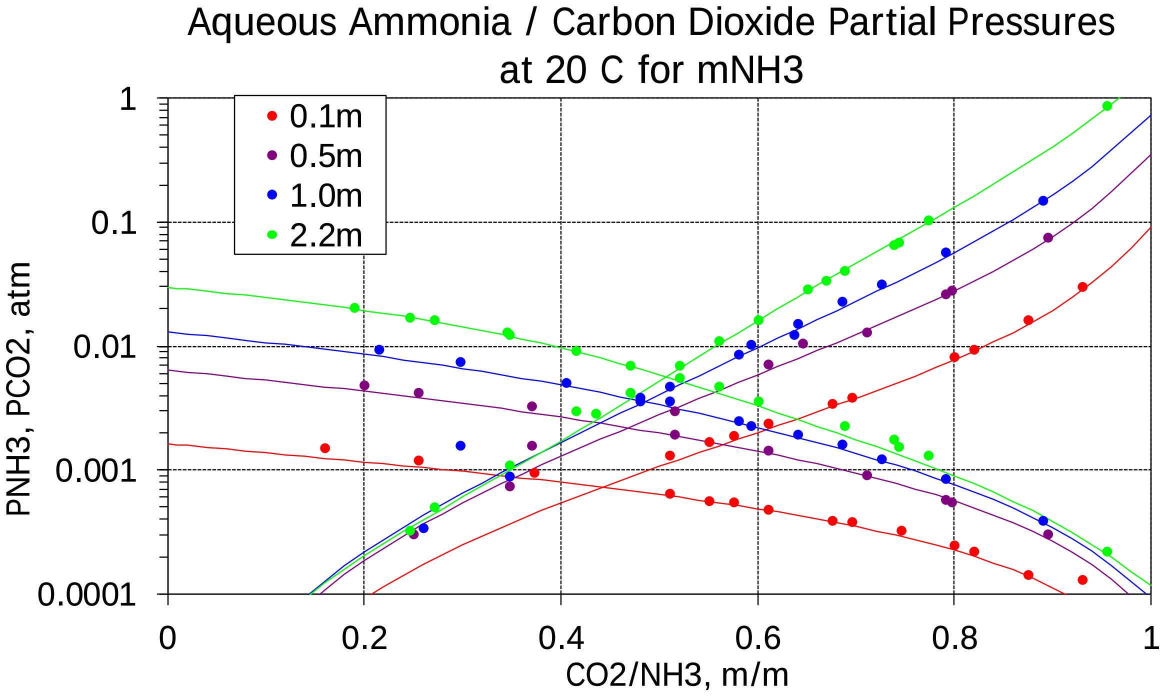


- The model reproduces:
  - VLE
  - SLE
  - Heats of mixing and dilution
  - Heat capacity
  - Density
  - Ionic equilibria

Vapor-liquid equilibria: $NH_3 – CO_2 – H_2O$

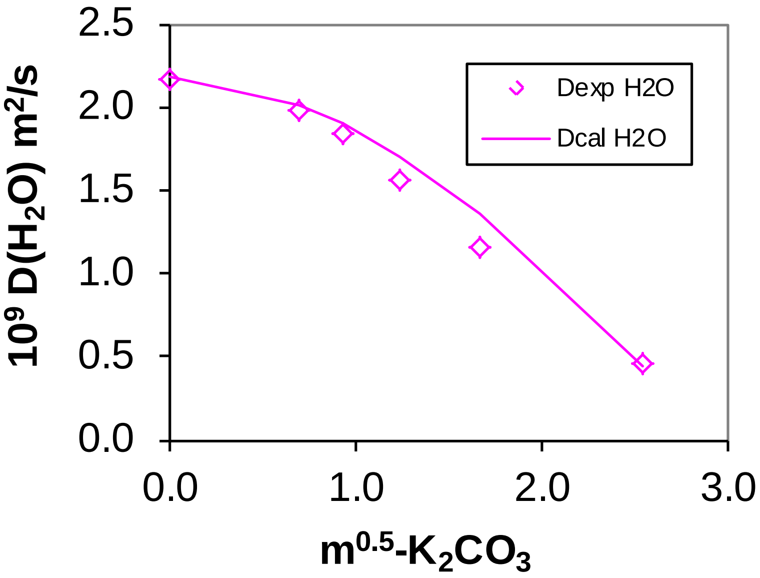
- Total and partial pressures
- Phase equilibria combined with chemical equilibria
  - Acid-base equilibria
  - Complex (carbamate) formation


Aqueous Ammonia / Carbon Dioxide Pressure at 100 C for mNH3


Aqueous Ammonia / Carbon Dioxide Partial Pressures at 20 C for mNH3

Mass transfer separations

- Heat and mass-transfer correlations
- Properties for predicting heat and mass transfer
  - Diffusivity
  - Viscosity
  - Thermal conductivity
  - Surface tension
  - Density

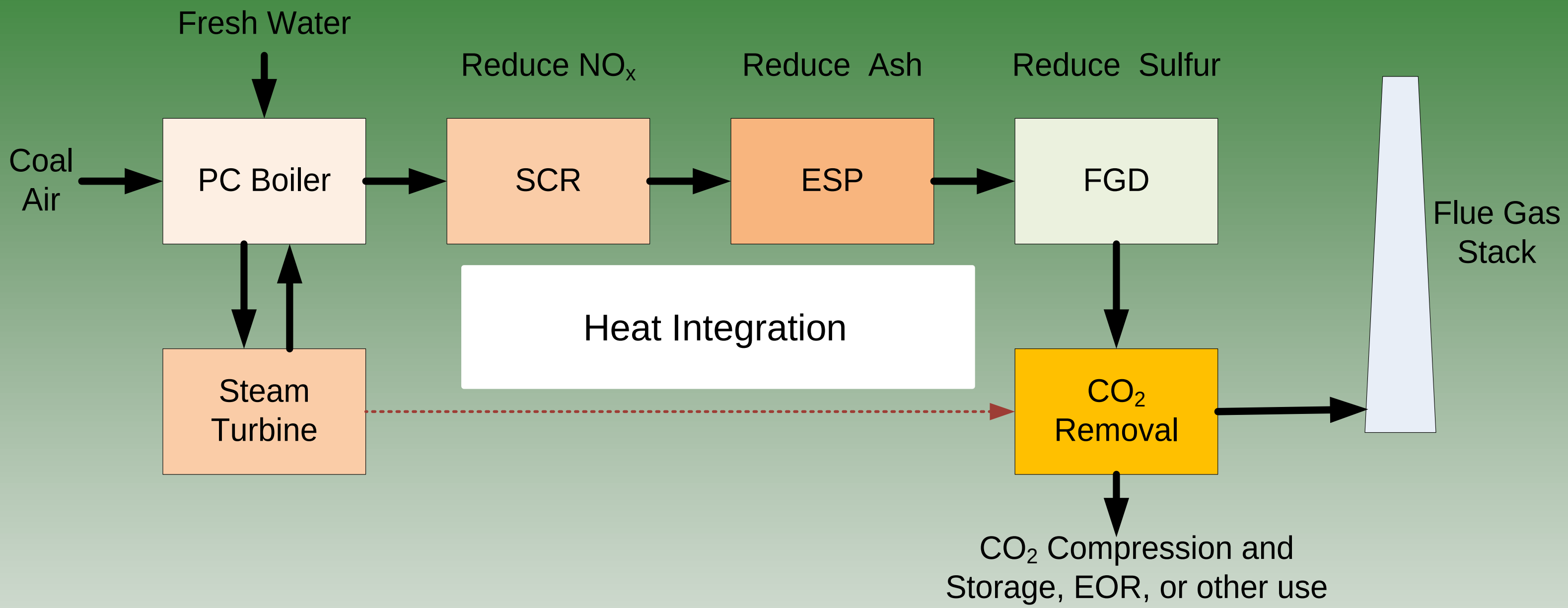


Self-diffusion coefficient of H_2O in K_2CO_3 solutions

Conclusions

- Thermodynamics
  - OLI's MSE model represents the properties of H_2O – CO_2 – salt mixtures up to saturation or fused salt limit
  - Complete parameterization needs to be developed for the K_2CO_3 – CO_2 – NH_3 – H_2O system based on literature and SRI plant data
- Process simulation
  - ESP: A convenient simulator for modeling the process
    - Equilibrium treatment
    - Mass-transfer-based algorithm
  - Interfaces to third-party process simulators

Power Plant Integration with the CC Plant



Heat Integration Alternative Options Ideas: Stanford
Modeling of CC power plant steam cycle integration with the CC plant: POLIMI in support by ASAps

CO_2 Capture Plant and Power Plant Integration

The **CO_2 capture plant** is simulated with **Aspen Plus** and called the **Extended UNIQUAC model**

The **power plant** is simulated with the in-house code named **GS**

The **Aspen Plus and GS integration** is managed manually as follows:

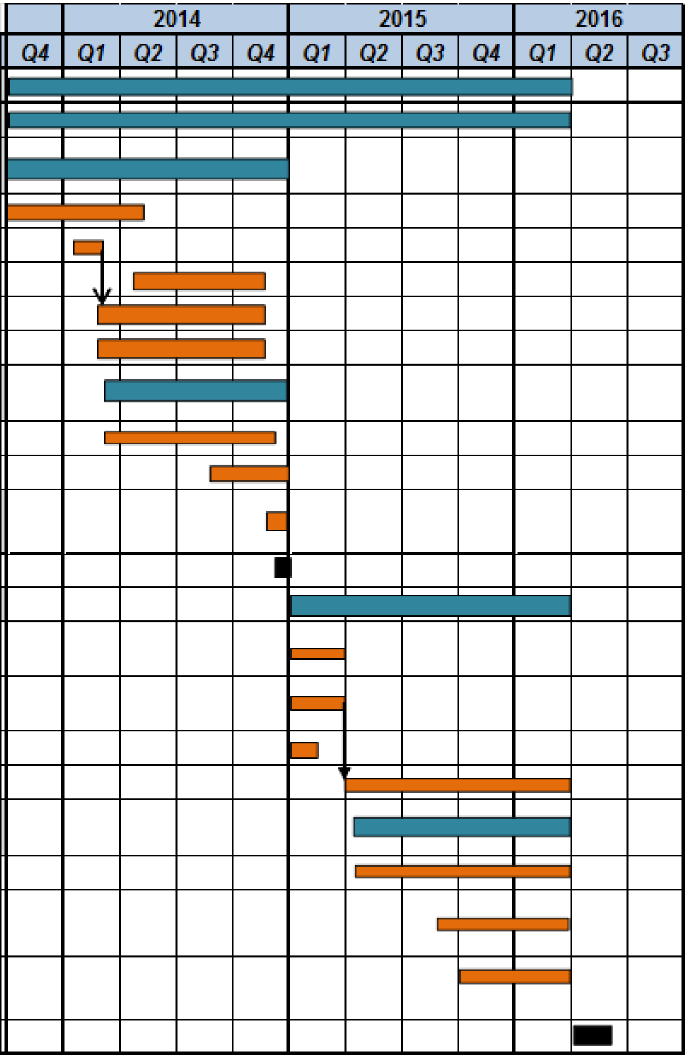
- composition of exhaust gas is calculated in GS and written once in Aspen
- temperatures and flow rates of extracted steam to the reboiler and condensed water from the reboiler are calculated in Aspen Plus
- extracted steam is released to the turbine in GS
- condensed water is released to an appropriate feed water preheater or to the cycle condenser in GS
- net electricity production is computed as the difference between:
    - the electricity production of the power plant from GS (which includes the loss due to steam extraction)
    - the electricity consumption of capture plant from Aspen Plus

Discussion Topics

- Project Background ✓
- Project Objectives ✓
- Project Team ✓
- Project Structure ✓
- **Project Schedule**
- **Project Management Plan**
  - **Milestones**
  - **Risk Management**
- **Deliverables**
- **Current Project Status**
- Questions
- Closing Comments

Project Schedule

Task	Start Date	End Date
Mixed-Salt BP1 and BP2	**10/1/2013**	**3/31/2016**
Task 1.0 - Project Management and Planning	**10/1/2013**	**3/31/2016**
Task 2-0: Individual Absorber and Regenerator Testing in Semi-Continuous mode	**10/1/2013**	**11/30/2014**
Subtask 2.1 - Test Systems Design and Installation	10/1/2013	4/28/2014
Subtask 2.2 - Test Plans	2/1/2013	2/30/2014
Subtask 2.3 - Absorber Tests	4/30/2014	11/30/2014
Subtask 2.4 - Regenerator Tests	2/28/2014	11/3/2014
Subtask 2.5 - Bench-Scale Test Data Analysis	2/28/2014	11/30/2014
Task 3.0 - Preliminary Process Modeling and Techno-Economic Analysis	**3/1/2014**	**12/15/2014**
Subtask 3.1 - Process Modeling	3/1/2014	11/30/2014
Subtask 3.2 - Preliminary Economic Analysis	8/1/2014	12/15/2014
Task 4.0 - Budget Period 2 Continuation Application	**12/1/2014**	**12/30/2014**
Continuation Report Submission	**12/30/2014**	**12/30/2014**
Task 5.0 - Bench-Scale Integrated System Testing	**1/15/2015**	**3/31/2016**
Subtask 5.1 - Design of the Bench-Scale Integrated Test System	1/15/2015	3/31/2015
Subtask 5.2 - Installation of the Bench-Scale Continuous, Integrated Test System	1/15/2015	3/31/2015
Subtask 5.3 - Bench-Scale Test Plans	1/15/2015	2/15/2015
Subtask 5.4 - Bench-Scale Tests and Data Analysis	4/1/2015	3/31/2016
Task 6.0 - Process Modeling and Techno-Economic Analysis	**5/1/2015**	**3/31/2016**
Subtask 6.1 - Process Modeling	5/1/2015	3/1/2016
Subtask 6.2-Techno-Economic Analysis	8/1/2015	3/30/2016
Subtask 6.3- Technology EH&S Risk Assesment	9/1/2015	3/30/2016
Final Report Submission	**4/30/2016**	**5/30/2016**



Project Management Plan

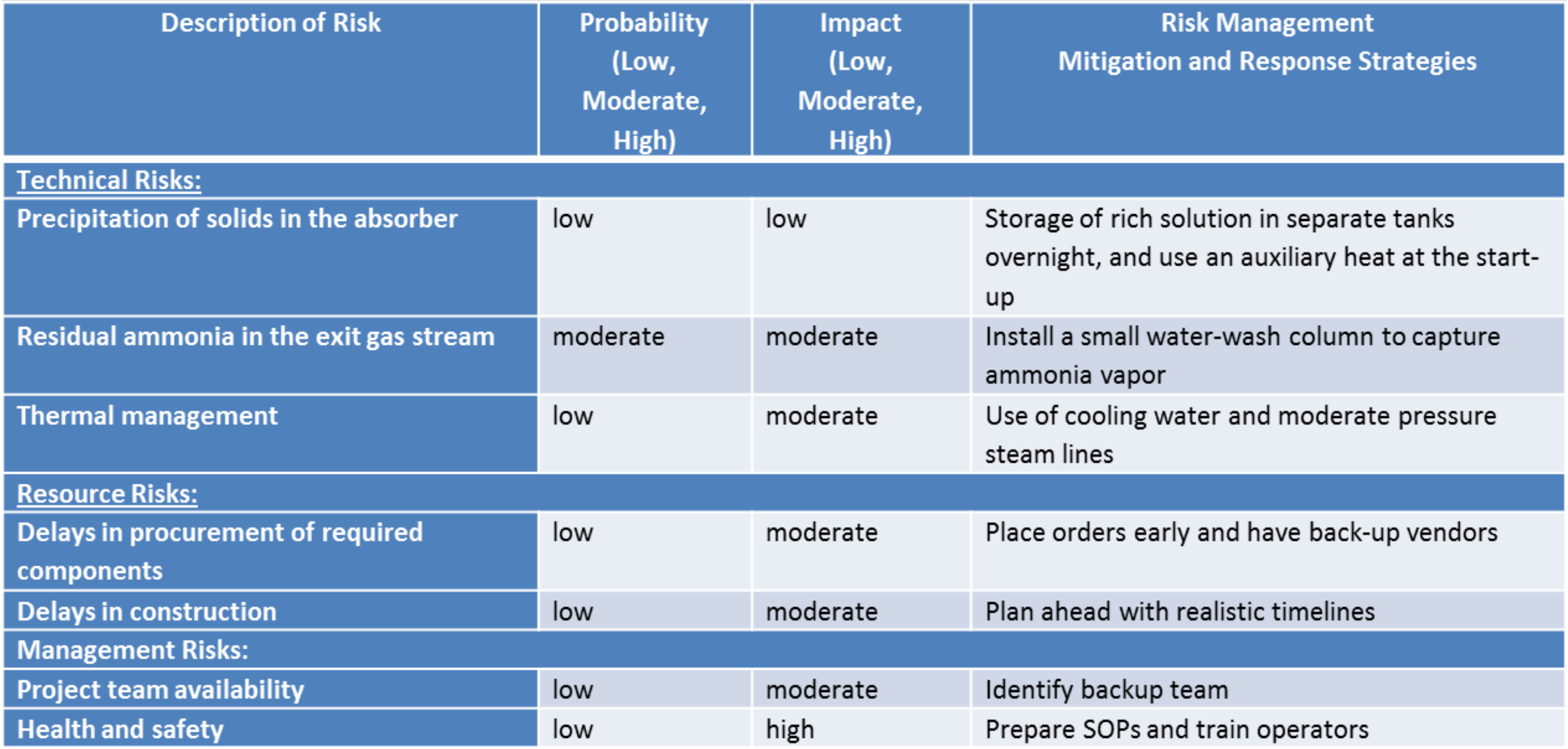
Project Milestones Table

Budget Period	Task/Subtask No.	Milestone Description	Planned Completion
1	1	Updated project management plan	12/05/2013
1	1	Kick-off meeting	12/11/2013
1	2.1	Completion of absorber installation and reactor conversion to regenerator	04/28/2014
1	2.2	Completion of test plan	02/28/2014
1	2.3-2.5	Completion of absorber and regenerator testing including data analysis	11/30/2014
1	3.1	Completion of preliminary process modeling	11/30/2014
1	3.2	Completion of preliminary techno-economic analysis	12/15/2014
1	4	Submission of continuation application	12/30/2014
2	5.1	Completion of the integrated design	03/30/2015
2	5.2	Completion of the bench-scale integrated test system construction	4/28/2015
2	5.4	Completion of integrated system testing and data analysis	03/01/2016
2	6.1	Completion of process modeling	03/01/2016
2	6.2 &6.3	Completion of techno-economic analysis and EH&S Report	03/30/2016
2	1	Budget period 2 final report	05/30/2016

Project Management Plan (cont…)

Risk Management

Risks and risk management strategies



Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Technical Risks:			
Precipitation of solids in the absorber	low	low	Storage of rich solution in separate tanks overnight, and use an auxiliary heat at the start-up
Residual ammonia in the exit gas stream	moderate	moderate	Install a small water-wash column to capture ammonia vapor
Thermal management	low	moderate	Use of cooling water and moderate pressure steam lines
Resource Risks:			
Delays in procurement of required components	low	moderate	Place orders early and have back-up vendors
Delays in construction	low	moderate	Plan ahead with realistic timelines
Management Risks:			
Project team availability	low	moderate	Identify backup team
Health and safety	low	high	Prepare SOPs and train operators

Complexity of the Mixed-Salt Process: The technology uses a two-stage absorber system. The program is structured first to optimize the absorber conditions using two individual absorbers in budget period 1 before attempting to test a single two-stage absorber. This approach is designed to improve the process performance and also to reduce the cost.

Deliverables

Reports Providing

- Absorption/Desorption Isotherms covering the full range of operating pressures and temperatures considered for capturing CO_2 from coal-derived flue gas
- Experimental results from bench-scale activities, including:
  - measured heat and mass-transfer data
  - measured reaction kinetics data
- Updated state-point data table, including measured data
- Identification of flue-gas clean-up requirements upstream of the CO_2 capture process
- Recommended system operating pressures, temperatures, and working capacity
- Fate of solvent
- Identification of suitable process configuration(s) for commercial-scale operations including description of absorption/desorption models used to predict equipment performance and capacity (TEA Report)
- Process hazard evaluation (EH&S Report)

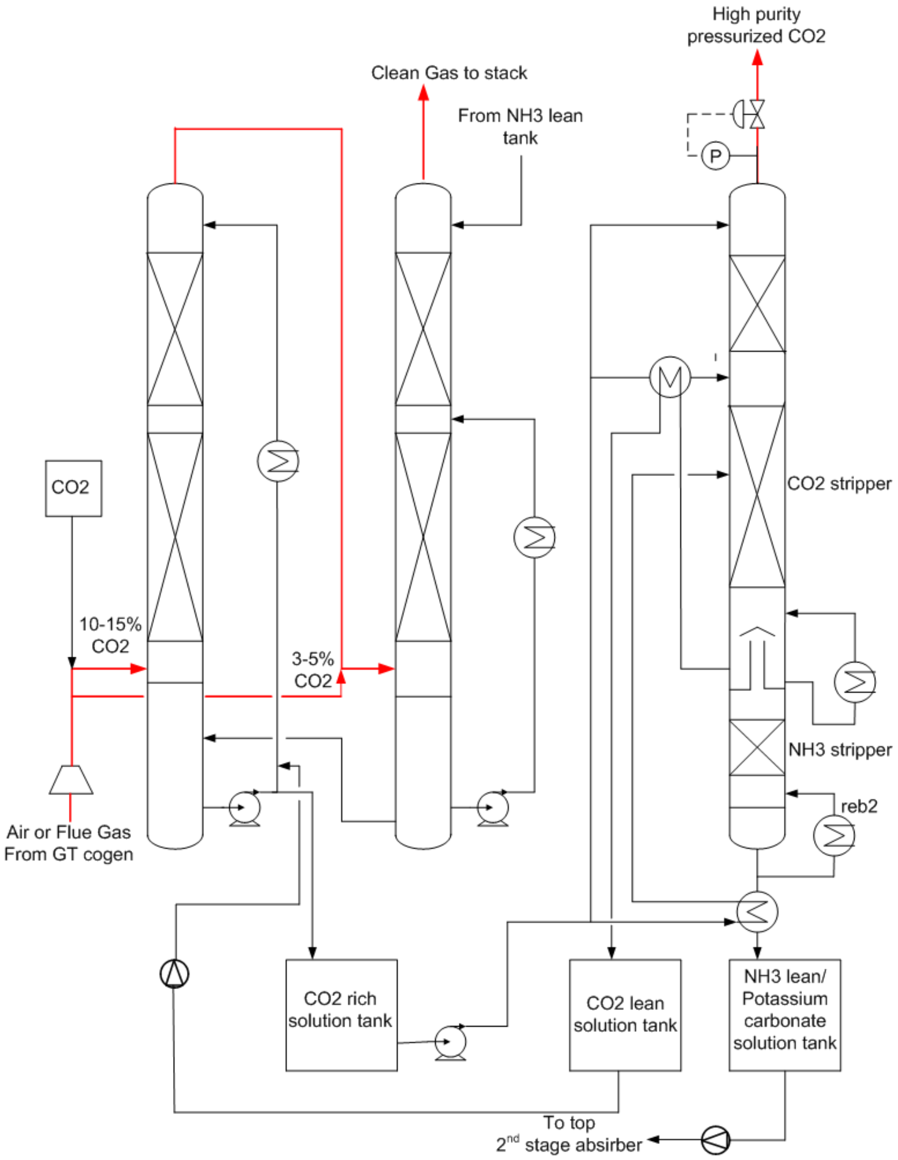
Discussion Topics

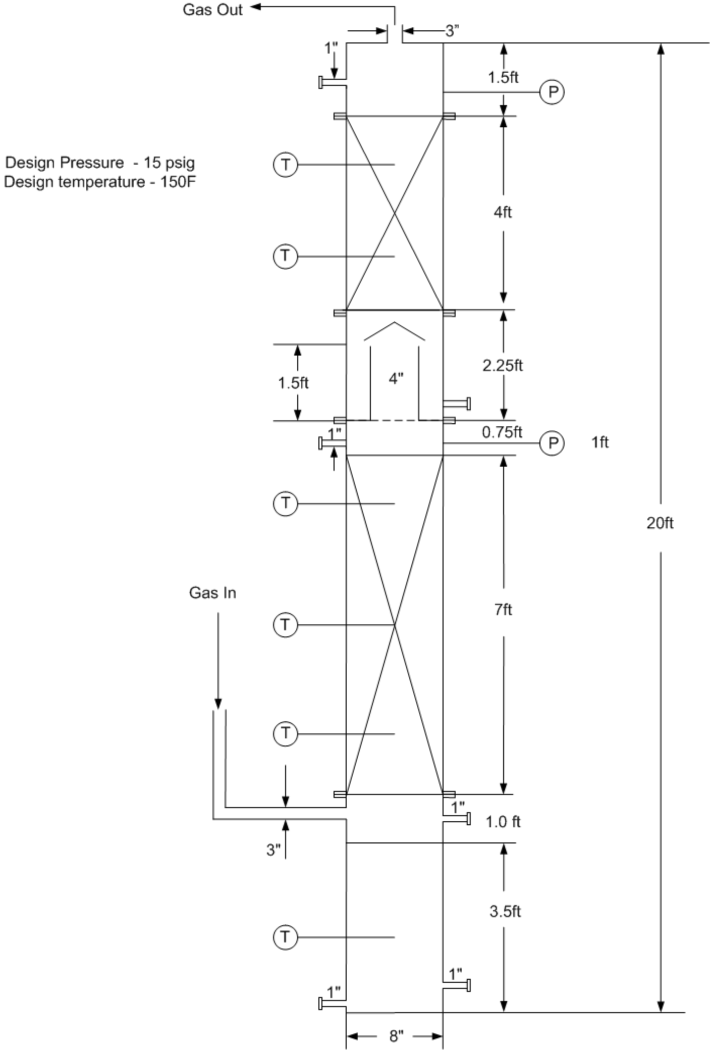
- Project Background ✓
- Project Objectives ✓
- Project Team ✓
- Project Structure ✓
- Project Schedule ✓
- Project Management Plan ✓
- Deliverables ✓
- **Current Project Status**
- Questions
- Closing Comments

Current Project Status

- Subcontracts awards were made last week
- Program management plan updated
- Absorber design in progress
- Regenerator modification design in progress
- Bi-weekly webex meetings to be resumed starting January 13

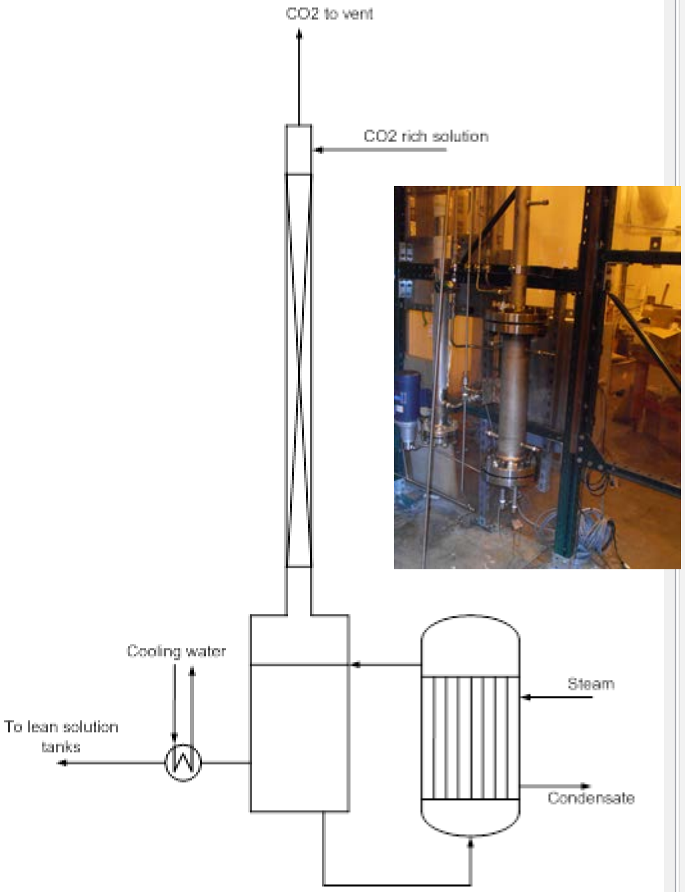
SRI System: Absorber and Regenerator



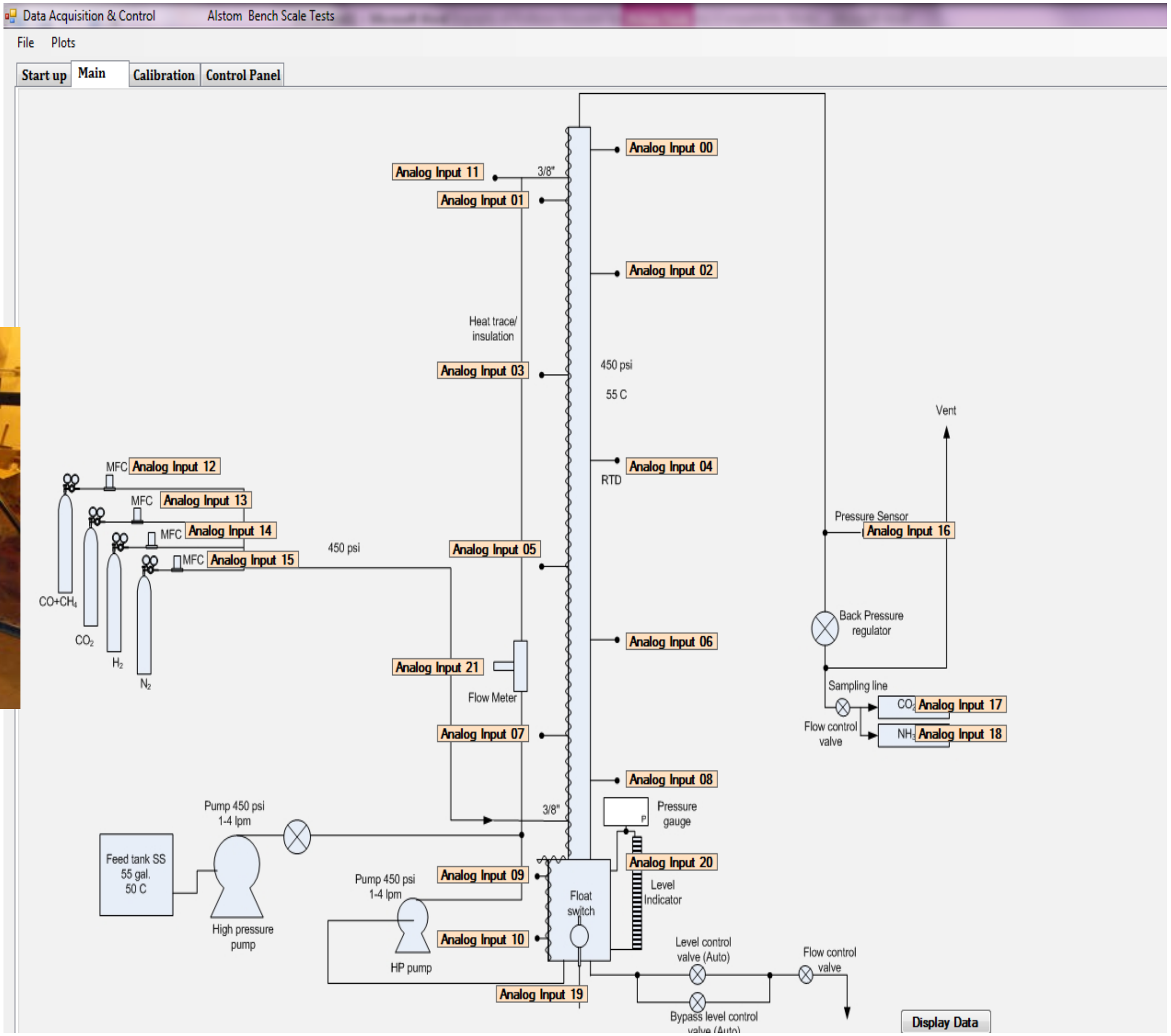


Preliminary absorber design for quotes

Regenerator Modification

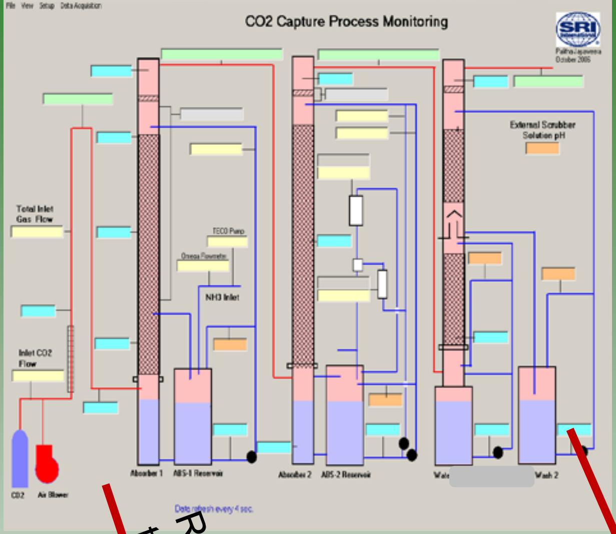


Preliminary Regenerator Design



Existing System

Monitoring Tools and Automation

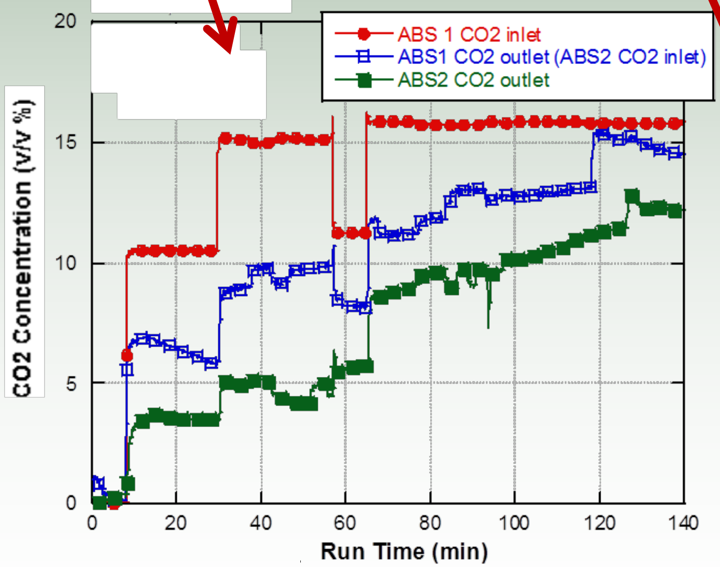


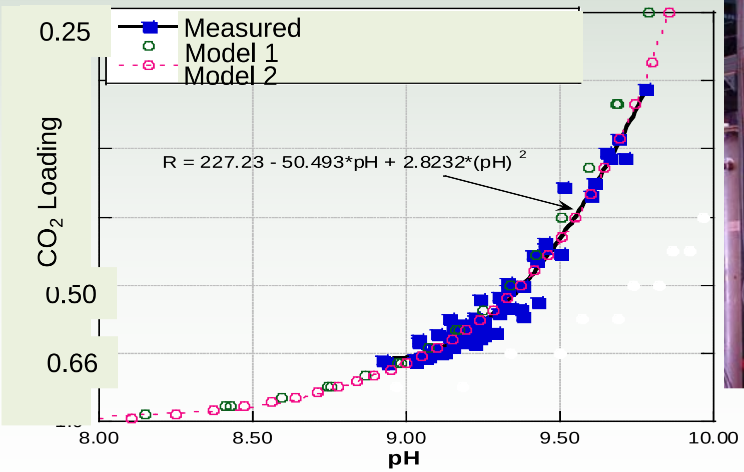
All analyses are done in house

Custom data acquisition

Real time

Real-time Liquid analysis





Project Location

SRI 6 MW Plant

S-Building Building: Large bench and mini-pilot studies

CO_2 yard for mini-pilot testing (up t 100 acfm)

Physical Science Building: Lab-scale tests

SRI's site in Menlo Park, CA (~ 65 acres)
SRI also has a test site near Livermore, CA (480 acres)

Discussion Topics

- Project Background ✓
- Project Objectives ✓
- Project Team ✓
- Project Structure ✓
- Project Schedule ✓
- Project Management Plan ✓
- Deliverables ✓
- Current Project Status ✓
- **Questions**
- **Closing Comments**

Acknowledgements

- SRI Staff
- Eli Gal, OLI Systems, Stanford, Aqueous Systems Aps, Polimi
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