Bench-Scale Development of a Non-Aqueous Solvent (NAS) CO_2 Capture Process for Coal-Fired Power Plants (DE-FE0013865)

Jak Tanthana, Mustapaha Soukri, Paul Mobley, Aravind Rabindran, Thomas Gohndrone, Tom Nelson, Markus Lesemann, James Zhou, and Marty Lail

RTI INTERNATIONAL

Devin Bostick, Stevan Jovanovic, and Krish Krishnamurthy

THE LINDE GROUP
Linde

Andreas Grimstvedt, Solrun Johanne Vevelstad

SINTEF

Steve Mascaro

NETL

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Non-Aqueous Solvent (NAS) Development Pathway

	Previous Work			DOE ARPA-E Project	DOE NETL Project (Current)	Future Development		
Yr	2009-10			2010-13	2014-15	2016-20		2020+
TRL	1	2	3	4	5	6	7	8 & 9

Proof of Concept/Feasibility

Pre-Commercial Demonstration

Lab-scale Development (*Previous*)

- Solvent screening to identify promising solvent formulations
- Lab-scale evaluation of NAS Process
- Preliminary technical and economic assessments

Large Bench-scale System / Relevant Environment Testing (*Current*)

- Finalize NAS formulation
  - Address evaporative losses and solvent costs
- Develop critical process components
  - NAS wash / recovery section
  - NAS regenerator
- Bench-scale testing with in a process unit with major process components
- Demonstrate ≤ 2,000 kJt/kg CO_2 using bench-scale system
- Detailed solvent degradation and preliminary emissions studies
- Detailed Techno-Economic & EH&S Assessments
  - Demonstrate T&EA competiveness and environmental permitability

R&D Strategic Approach

Breakdown of the Thermal Regeneration Energy Load

$$q_R = \left[\frac{C_P(T_R - T_F)}{\Delta\alpha} \cdot \frac{M_{sol}}{M_{CO_2}} \cdot \frac{1}{x_{sol}}\right] + \left[\Delta H_{V,H_2O} \cdot \frac{p_{H_2O}}{p_{CO_2}} \cdot \frac{1}{M_{CO_2}}\right] + \left[\frac{\Delta H_{abs,CO_2}}{M_{CO_2}}\right]$$

Reboiler Heat Duty — Sensible Heat — Heat of Vaporization — Heat of Absorption

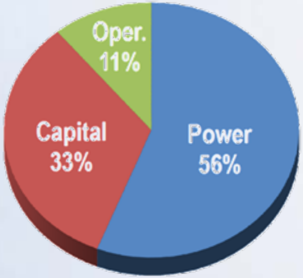
Solvent	C_p [J/g K]	Δh_{abs} [kJ/mol]	Δh_{vap} [kJ/mol]	X_{solv} [mol solv./ mol sol'n]	$\Delta\alpha$ [mol CO_2/ mol solv.]	Reboiler Duty [GJ/tonne CO_2]
MEA (30%)	3.8	85	40	0.11	0.34	3.22
Lower Energy Solvent System	↓	↓	↓	↑	↑	↓
NAS	1.3	65	1	0.3	0.3	1.71

For NAS, heat of vaporization of water becomes a negligible term to the heat duty

Process capable of achieving these criteria will have a lower energy penalty than SOTA processes

Path to Reducing ICOE and Cost of CO_2 Avoided

- Primarily focus on reducing energy consumption – reboiler duty
- Reduce capital expenditure
    - Simplify process arrangement
    - Materials of construction
- Limit operating cost increase



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[1] Rochelle, G. T. Amine Scrubbing for CO_2 Capture. *Science* **2009,** 325, 1652-1654.

Project Objectives and Technical Challenges

Objective: Continue the advancement of the NAS CO_2 Capture Process

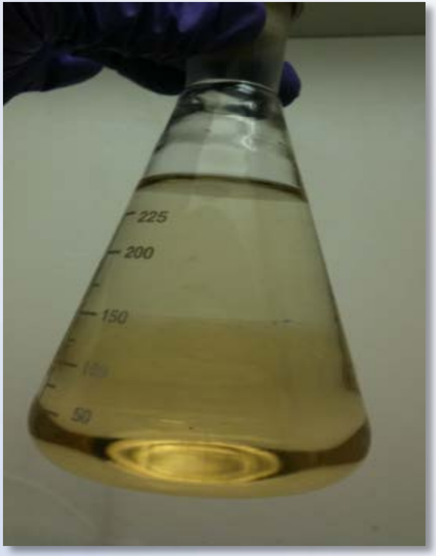
- Address specific challenges facing technical and economic potential
- Bench-scale demonstration of the potential to reduce the energy penalty to <2,000 kJ_t/kg of CO_2 captured

Specific Challenges

- Minimize solvent losses and make-up
- Solvent degradation and emission studies
- Develop and evaluate process modifications
- Bench-scale evaluation of the NAS CO_2 capture process

Timeframe: 10/1/13 to 03/30/15 (BP1, 18 months) 04/1/15 to 06/30/16 (BP2, 15 months)

Cost: $1.51 M BP1, $1.55 M BP2



RTI NAS Solvent

Brief Recap of BP1 Achievements

BP1 Achievements	Select Points
Incorporated non-volatile hydrophobic diluent with suitable properties	• Vapor pressure <0.13 kPa, 25°C • Low cost • Low viscosity (~2 cP)
Formulated diluent with hydrophobic amines	• Low heats of absorption • No precipitates • Low viscosities (25-30 cP rich) • Reasonable CO_2 capacity • Cost is <$50/kg
Demonstrated emissions of NAS below 10 ppm	• Designed wash section at lab scale • ~20 ppm emitted without wash section
Performed long-term evaluation of NAS at lab scale with simulated flue gas containing 13.3% CO_2, 7.5% H_2O, 2% O_2, 50 ppm SO_2, and balance N_2	• Capture efficiency (~90%) • Long-term, stable operation demonstrated (~100 hrs)
Completed long-term thermal and oxidative degradation studies at SINTEF	• Five week evaluations • Single components of diluent are thermally stable • Carbamate polymerization products not formed • Corrosion results promising (Fe, Ni, Cr) • Eliminated one NAS amine due to severe oxidative degradation

BP2 Focus: Bench-scale Testing of Refined Solvents

Absorber

3" Sch. 10 SS316 (8.5 m height)

Mellapak 350X

Temp: 30-55° C

Pressure: Up to 200 kPa

Gas Vel: 0.33-1.5 m/s

L: 15-75 kg/h

Regenerator

3" Sch. 10 SS316 (7.1 m height)

Mellapak 350x

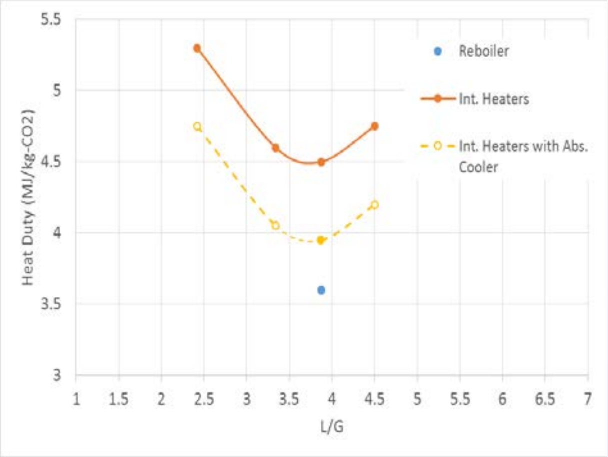
Temp :Up to 150° C

Pressure: Up to 1MPa

~185 kg CO_2/day

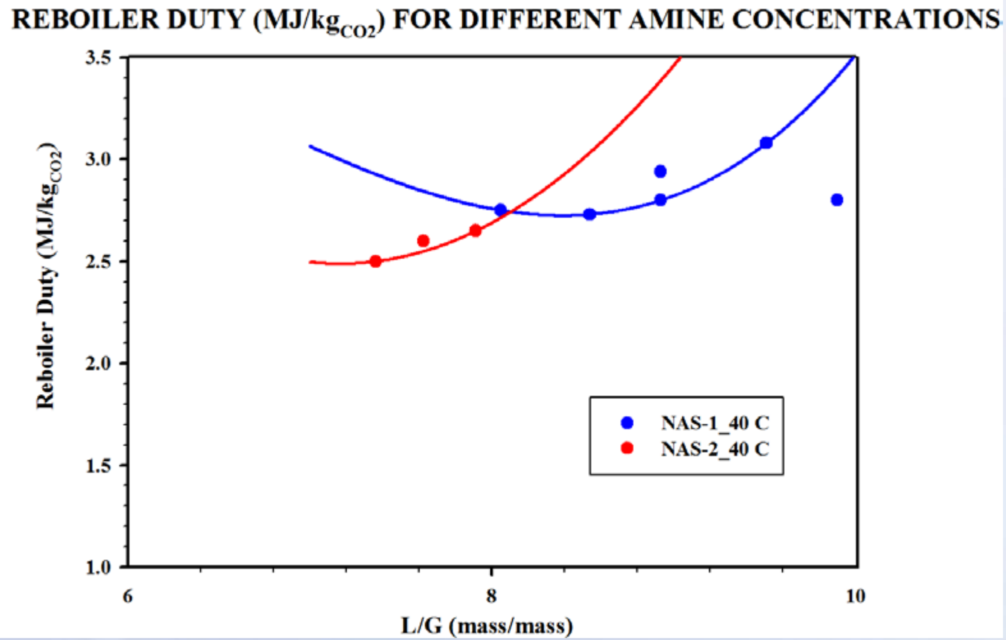
75 Liter Solvent

Simulated Flue Gas Properties	
FG Flow Rate:	100 to 485 SLPM
CO_2 Feed Rate:	1.8 to 8.6 kg/h
Feed Temp.:	30 to 50°C
Target Comp:	CO_2: 13.3%; H_2O: 6.1%; O_2: 2.35%; N_2: bal.
CO_2 Content:	up to 20 %vol
Water Content:	~0 to 12.3%vol



Baseline testing with aqueous MEA

Bench Scale Test Unit Results with Dry Flue Gas



Experimental Conditions

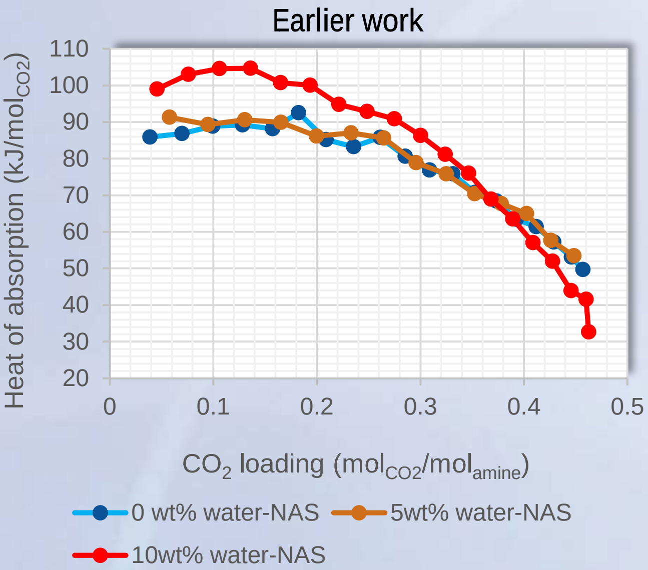
Feed Composition:
15.4% CO_2
Balance N_2.
100 SLPM
Liquid flows: 0.8-1.9 kg/min
Gas Flows: 0.1-0.21 kg/min
Regenerator Pressure 2.5 bar
90% CO_2 capture efficiency

NAS-1
Absorber: 40° C
Regenerator: 115° C
Interstage Heater Regeneration

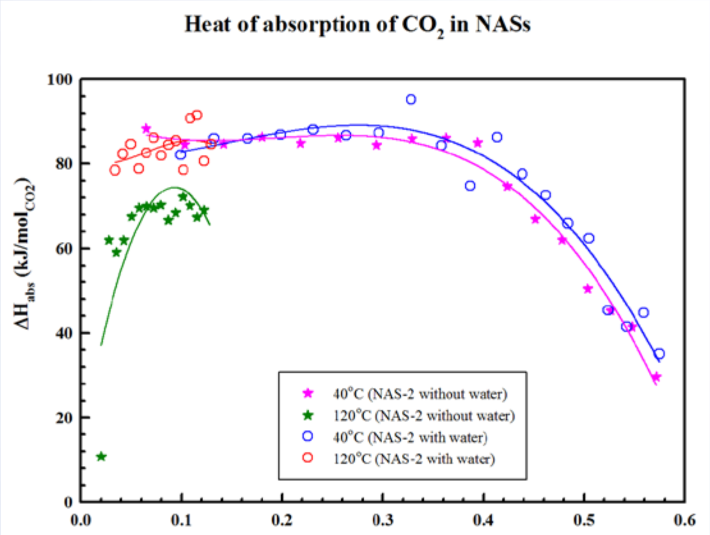
NAS-2
Absorber: 37-40° C
Regenerator: 120-122° C
Interstage Heater Regeneration

- Working capacities were lower than anticipated, ~0.15-0.21 moles CO_2/ mole amine for NAS-1
- Improved slightly for NAS-2 due to slightly lower absorber temperature and higher regenerator temperature
- Still higher than expected based on theoretical values and not a major improvement over other technologies
- Early in our experience at operating the NAS system

Impact of Water

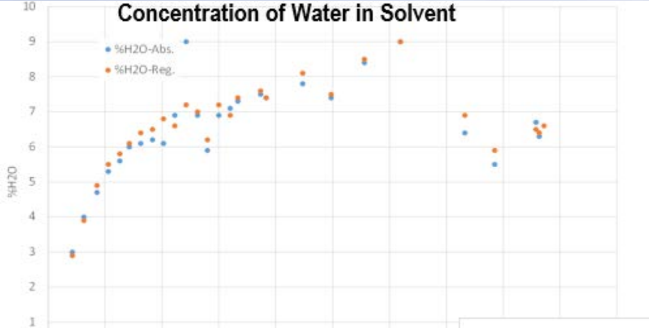


- Observed impact on enthalpy of reaction in earlier NAS formulation
- Measurements at 40° C
- Concentration of water at 10% raised heat of absorption substantially
- Concerns about this impact on reboiler heat duty



- Measured heat of absorption of dry NAS-2 vs. "wet" NAS-2 at 120° C
- Observed increase in heat of absorption when NAS was saturated with water at 120° C
- Expect reboiler duty would go up due to higher Δh_{abs}
- Impact on the process is that [water] may need to be kept low. Water becomes separate phase > ~9 wt%
- Increasing the hydrophobicity of the solvent chemistry was thought to be one way to handle

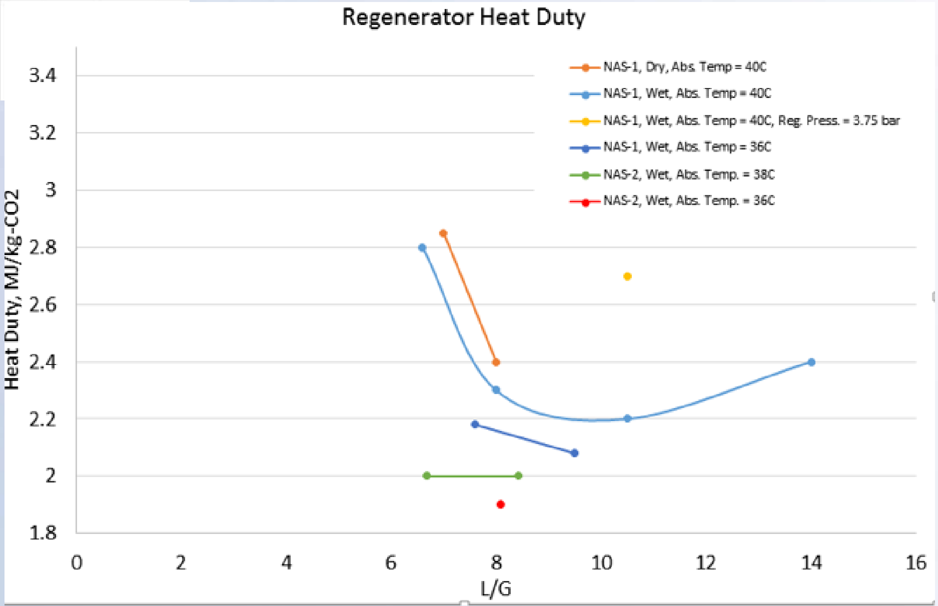
Bench Scale Test Unit Results with Wet Flue Gas



- 100 hr test with wet flue gas
- Feed composition
  - o 15.4% CO_2
  - o 7% H_2O
  - o balance of air
- No water separators
- Water in solvent controlled by absorber temperature profile

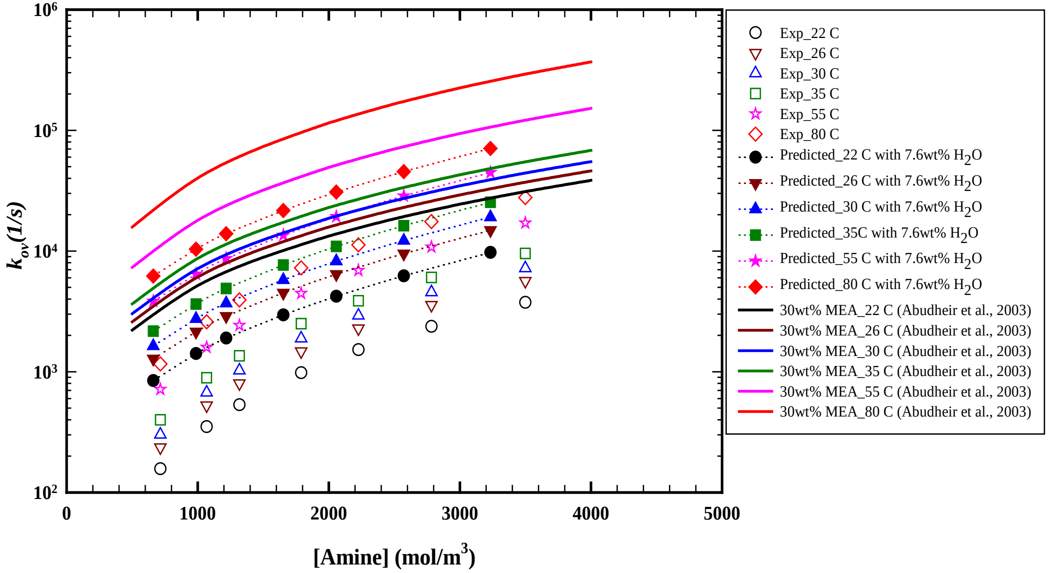
NAS-1
Absorber: 40-36° C
Regenerator: 115 - 95° C
Regenerator Pressure: 2.5-3.75 bar
Interstage Heater Regeneration

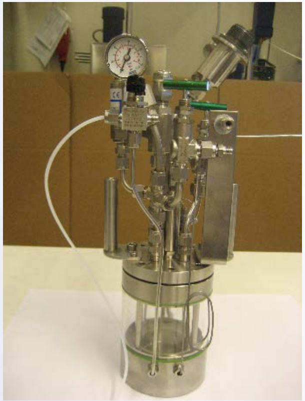
NAS-2
Absorber: 37-40° C
Regenerator: 100-105° C
Regenerator Pressure: 2.5 bar
Interstage Heater Regeneration



Reaction Kinetics

$$3\ \text{amine} + 2\ CO_2 + H_2O \leftrightarrow \text{AmineCO}^- + 2\text{AmineH}^+ + HCO_3^-$$

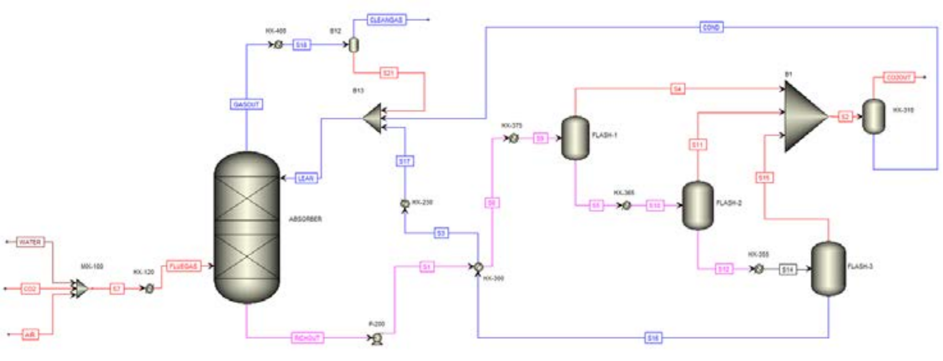


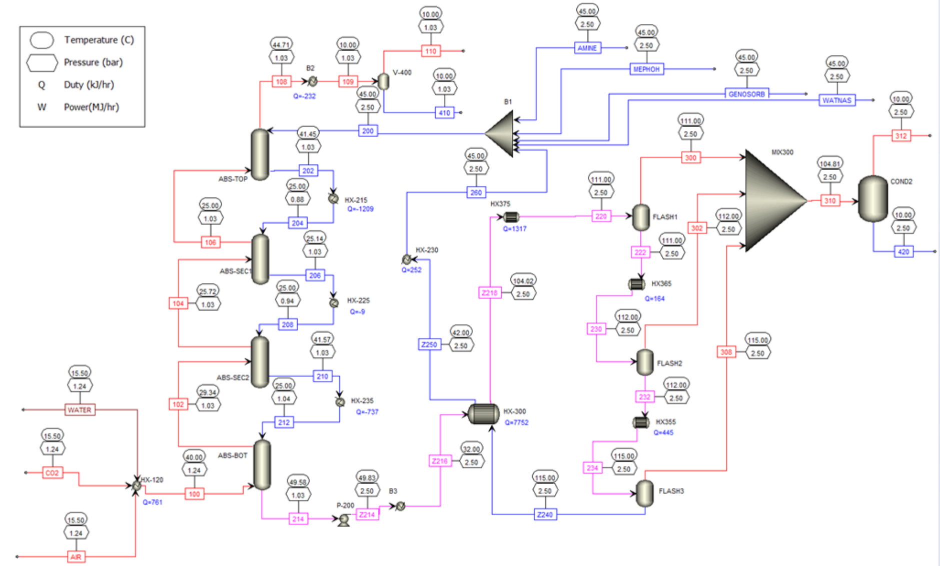


- CPA-102 Calorimeter
- Stirred cell reactor
- Falling pressure drop method
- 260 mL reactor volume
- 22.6 cm^2 interfacial area
- T=298-353K
- P_{CO2}= 4.48-6.29 kPa
- 100 mL solvent volume
- Kierzkowska-Pawlak et al., 2014, Int. J. Greenhouse Gas Control., 24, 106-114

- In the absence of water kinetics are substantially slower than MEA
- With water, kinetics are approximately 2 times slower than MEA
- Ramifications
  - NAS requires higher absorber column to capture 90% CO_2 than 30wt% MEA
  - Process modelling of NAS showed a need for intercoolers to attain equilibrium
  - Use promoter to improve kinetics

Process Modeling





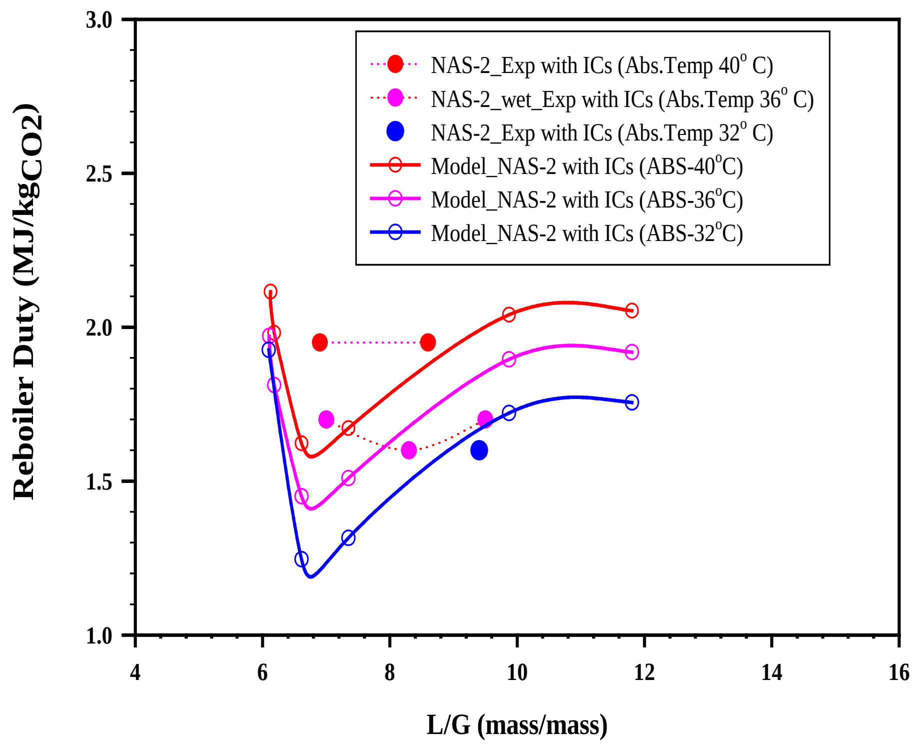
Developed rate-based process model Aspen ENRTL-SR

Thermodynamic and physical properties acquired experimentally:

- Henry's constant for CO_2
- Liquid heat capacity
- Vapor pressures
- Reference state properties
- Heat of vaporization
- Dissociation constants
- VLE
- Density
- Δh_{abs}
- Viscosity
- Surface tension
- Thermal conductivity
- Dielectric constant
- Diffusivity of CO_2

Used process model to direct bench-scale testing after initial runs

Impact of Intercooler Temperatures on Reboiler Duty



- Impact of temperature on absorber bottom
- Modeled 40-32° C
- Lower temperature
- Lower L/G
- Lower reboiler duty
- Guided BsTU experiments at lower absorber temperatures
- Observed lower reboiler duties experimentally
- Will continue to investigate moving forward

<u>Conditions for Experimental Data NAS-2</u>

- Absorber: 37-40° C
- Regenerator: 87-98° C
- Pressure: 2.5 bar
- Interstage Heater Regeneration

Techno-Economic Analysis

	Case 11_2011 No Capture	Case 12_2011 w/ MEA	NAS2-2.5 bar	NAS2-3.6 bar	NAS3-3.6 bar
Power Performance					
Net Plant HHV Efficiency (%)	***39.3%***	***28.4%***	***31.10%***	***32.00%***	***32.90%***
Capital Investment (Total Installed Costs) 1000 $					
Total Plant Cost ($/kW)	2,451	4,391	3,956	3,826	3,674
Operating and Maintenance Costs					
Annual ($/y)	104,594,992	144,512,589	131,245,575	129,556,370	125,614,892
COE Determination					
Total ($/MWh)	***80.94***	***147.33***	***137.41***	***134.05***	***130.76***
ICOE (%)	***0%***	***82%***	***70%***	***66%***	***62%***
CO_2 Capture Summary					
CO_2 Captured (tonne/MWh)		1.00	0.94	0.89	0.85
CO_2 Avoided (tonne/MWh)		0.69	0.71	0.70	0.70
CO_2 Capture Cost ($/tonne)		66.7	59.8	59.9	58.7
CO_2 Capture Cost excl. TS&M ($/tonne)		56.55	49.23	48.64	46.97
CO_2 Avoided Cost ($/tonne)		***96.0***	***80.0***	***74.1***	***73.0***

Summary of BP2 Testing

- With Linde, performed testing of NAS solvents in bench-scale test unit at 75-150 liter solvent scale using simulated flue gas

- Under dry conditions, measured reboiler heat duties as low as 2.4 GJ/tonCO_2 but did not realize duties as low as anticipated

- Under wet conditions, measured reboiler heat duties 1.6-1.9 GJ/tonCO_2 under conditions with regenerator operating at temperature less than 100° C

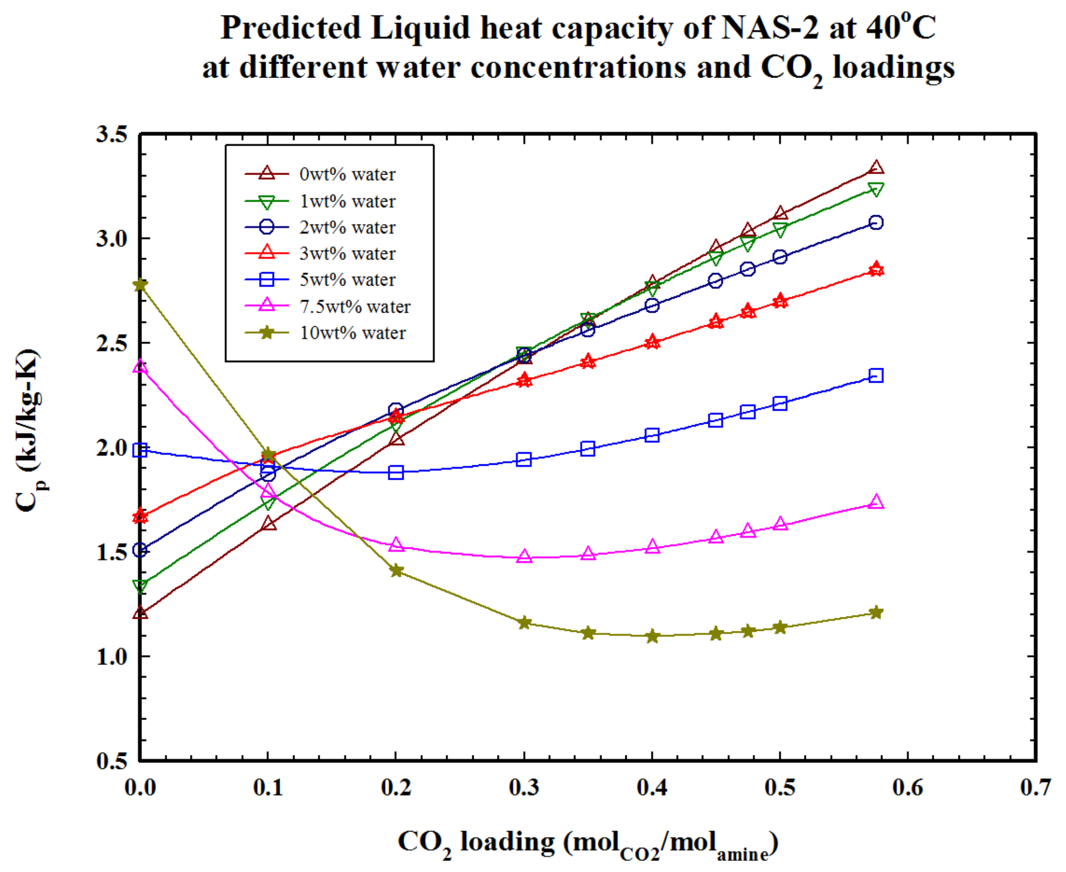
- Measured kinetics of CO_2 absorption and observed the rate constants of the wet solvent to be approximately 2 times slower than 30% aqueous MEA, with the kinetics of the dry solvent being substantially slower

- Developed rate-based ASPEN process model that matches well with experiment and used it to direct experiments

- Performed techno-economic analysis which shows potential of NAS process for lowering cost of CO_2 capture to ~$47/ ton$CO_2$ (excluding TS&M costs)

- Completed long-term (five week) degradation testing at SINTEF on simulated flue gas showing that NAS is stable relative to aqueous MEA and is less corrosive

Impact of water on NAS



State-Point Data Table for NAS-1

	Units	Measured Performance	Projected Performance
Pure Solvent			
Molecular Weight	$g\ mol^{-1}$	139.17[a] 153.6[b]	**< 250**
Normal Boiling Point	°C	243 to 288.45	**181 to 200**
Normal Freezing Point	°C	52.5 to -24	**52.5 to -24**
Vapor Pressure @ 15°C	Bar	0.00001 to 0.003[c]	**< 0.005[b]**
Working Solution			
Concentration	kg/kg	0.316[d]	**0.4 to 0.6**
Specific Gravity (15°C)	kg/L	1.066 to 1.1[c]	**0.9 to 1.2**
Specific Heat Capacity @ STP	kJ/kg K	1.28 to 1.48[d]	**1.2 to 1.5**
Viscosity @ STP	cP	26.2[d]	**< 40**
Surface Tension @ STP	dyn/cm	36.6 to 38.7[c]	**< 40**
Absorption			
Pressure	bar CO_2	0.133	**0.133**
Temperature	°C	35 to 45 (40)	**35 to 45**
Equilibrium Loading	g molCO_2/kg	0.85 to 1.59[c] (1.06)	**0.85 to 1.59**
Heat of Absorption	kJ/kg CO_2	1,590 to 1,931[d]	**1,590 to 1,931**
Solution Viscosity	cP	26.2	**2 to 30**
Desorption			
Pressure	bar CO_2	2 to 7.8 (2.0)	**2 to 7.8**
Temperature	°C	90 to120 (90)	**90 to 120**
Equilibrium Loading	g molCO_2/kg	0.02 to 0.4[c] (0.2)	**0.02 to 0.4**
Heat of Desorption	kJ/kg CO_2	1,250 to 1,591[c] (1,591)	**1,250 to 1,591**

[a] Nitrogenous Base Component

[b] NAS Formulation

[c] Individual components, range lowest to highest

[d] Ranges based on exp. measurements for most promising NASs

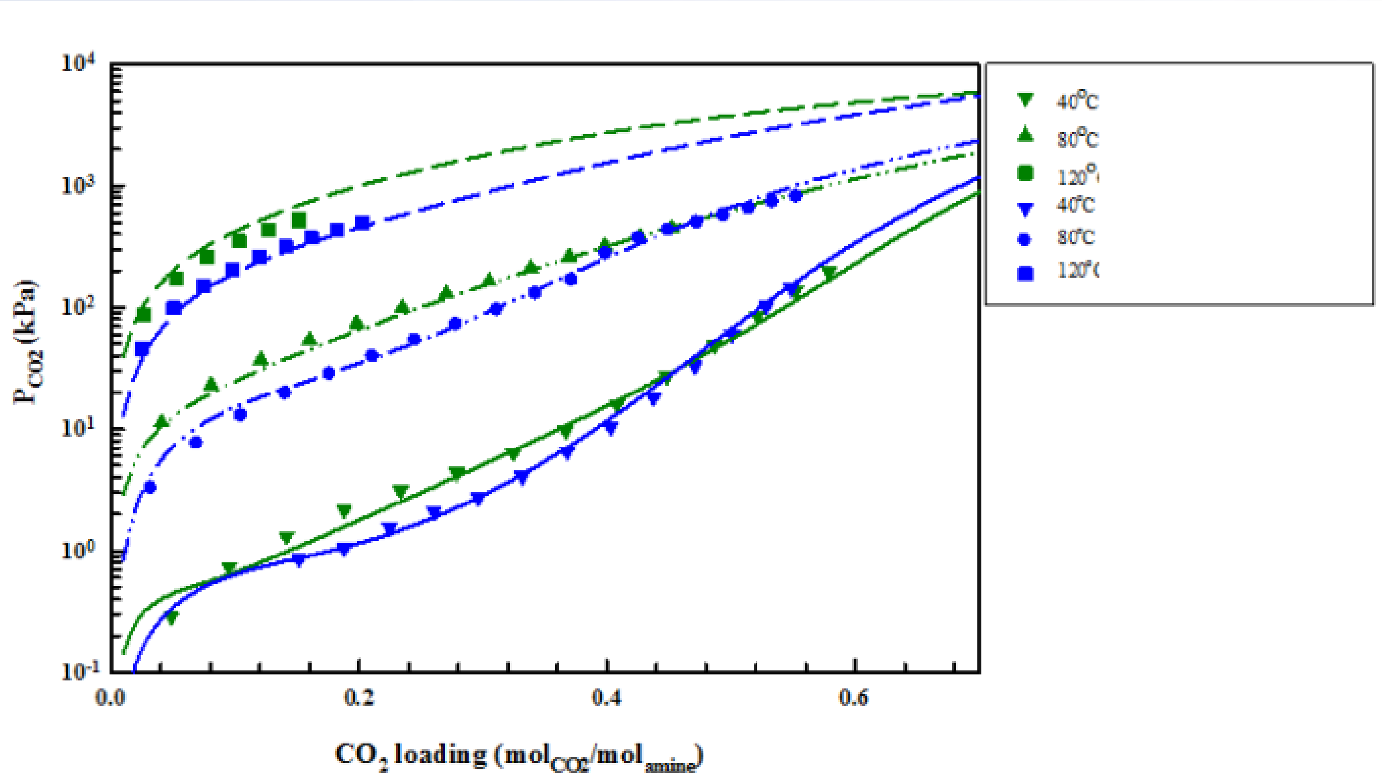
Italicized numbers used in preliminary technical and economic assessment.

Properties of NAS Solvent

Criteria	Target	NAS-2
Vapor Pressure [kPa] @ 40°C	< 1	0.3 (Estimated)
Water Content [wt%]	<10	7.26
Viscosity [cP] CO_2-rich at 40°C	< 40	< 30
Foaming Tendency	Low	Low
Cost [$/kg]	< 50	comparable
Health Rating	≤ 3 (≤MEA)	2
Min. thermal regeneration energy* [kJt/kg CO_2]	<2,000	2,000

*Notz et al. A short-cut method for assessing absorbents for post-combustion carbon dioxide capture. *Int. J. Greenhouse Gas Control* 2011, 5, 3 413-421

Updated VLE Curves from ENRTL-SR



Lab-Scale Gas Absorption System

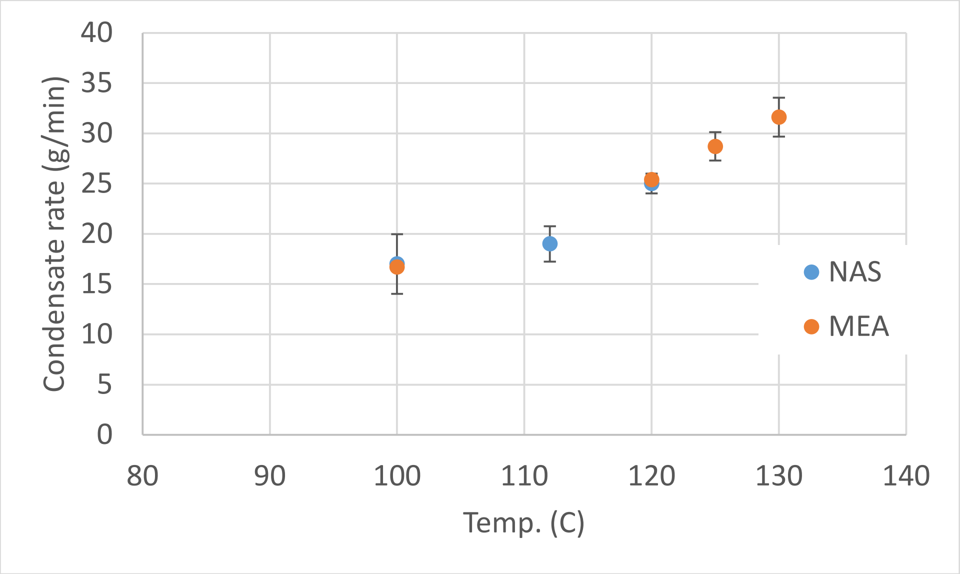
Description

- Simple gas scrubbing system suitable for evaluation of aq. and non-aq. solvents
- 2-10 SLPM of sim. flue gas with relevant blends of CO_2, H_2O, O_2, SO_2, N_2
- Liquid flowrates of 10 to 130 mL/min
- Operates continuously; > 50 days (1,000h) commissioning with MEA-Water
- Total solvent volume: ~400 mL
- Off-line solvent compositional analysis
- On-line gas analysis

Scope of Testing

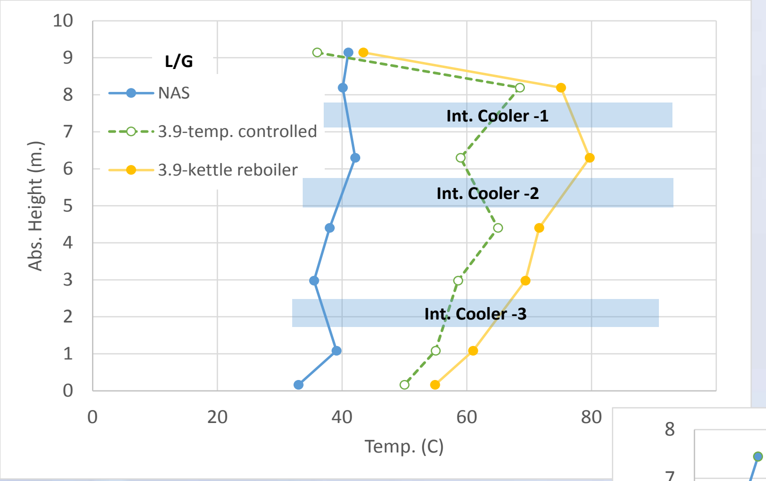
- Demonstrate stability of non-aq. solvents in a representative process arrangement using high-fidelity sim. FG
- Evaluate/demonstrate key process concepts specific to non-aqueous solvent process
- Compare performance of the NAS process and 30 wt% MEA-H_2O
  - Estimate regen. energy [$kJ_t/kg\ CO_2$]
  - Support design of large, bench-scale unit

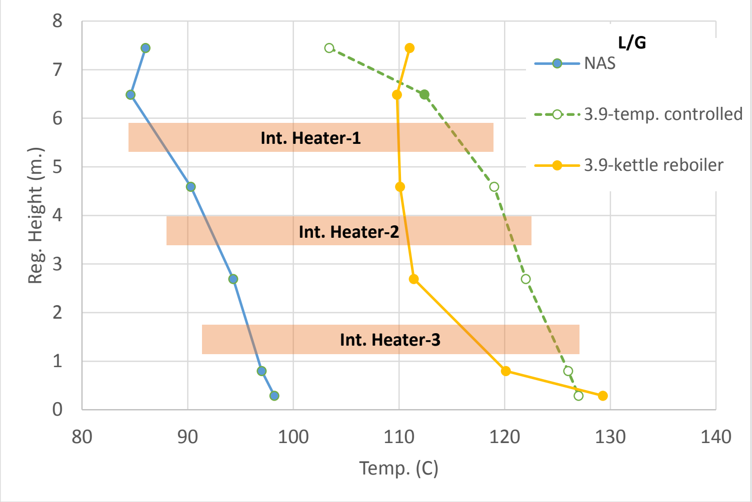
Heat Loss Measurement BsTU



The heat loss determination using MEA/H_2O solution was performed in similar manner as that of NAS where the regenerator was maintained at a uniform temperature of 100, 120, 125, and 130 °C while the lean MEA solution was circulating throughout the system. The heat loss measurement was evaluated for NAS at 100, 112, and 120 °C. The condensate collection during the heat loss determination at different temperature from both NAS and MEA solutions are provided in the figure.

Temperature Profiles of the Absorber and Regenerator





Kinetics Experiment