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

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SINTEF

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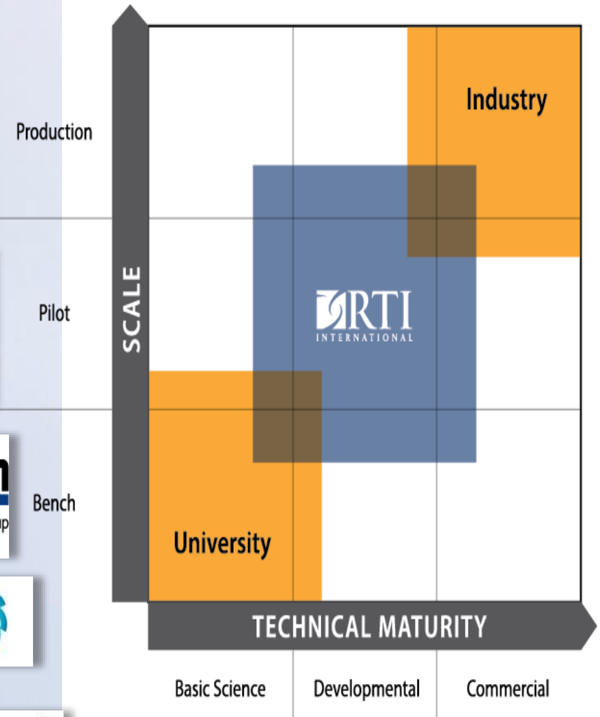
Technology Development with RTI

- RTI develops advanced process technologies in partnership with leaders in energy
- From concept to large scale demonstration
- Full alignment with industry objectives
  - Defined commercialization pathways
  - Flexible intellectual property arrangements
  - Potential leveraging of industrial R&D funding with government provided funding



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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 ≤ 2,100 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

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

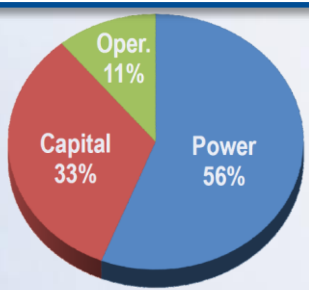
Reboiler Heat Duty — Sensible Heat — Heat of Vaporization — Heat of Absorption

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	1.2	65	0	0.38	0.45	2.36

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



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

Objectives and Challenges for Current Project

Objective: Continue the advancement of the NAS CO_2 Capture Process

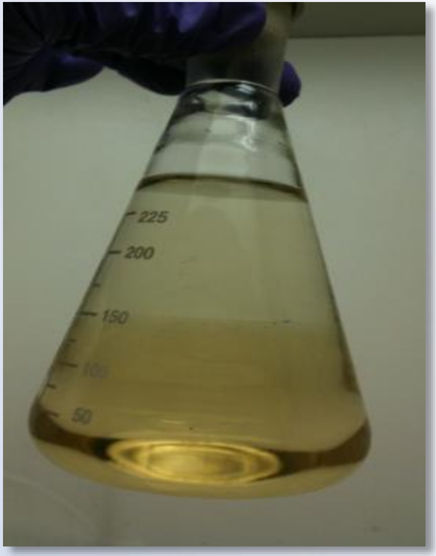
- Address specific challenges facing technical and economic potential
- Bench-scale demonstration of the potential to reduce the energy penalty to <2,100 kJ_t/kg of CO_2 captured

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 03/31/16 (BP2, 12 months)

Cost: $1.51 M BP1, $1.55 M BP2



RTI NAS Solvent

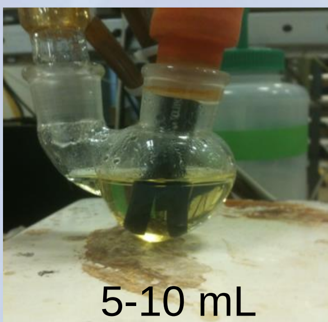
Progressed Solvent Refinements to VLE-ΔH_r Measurement

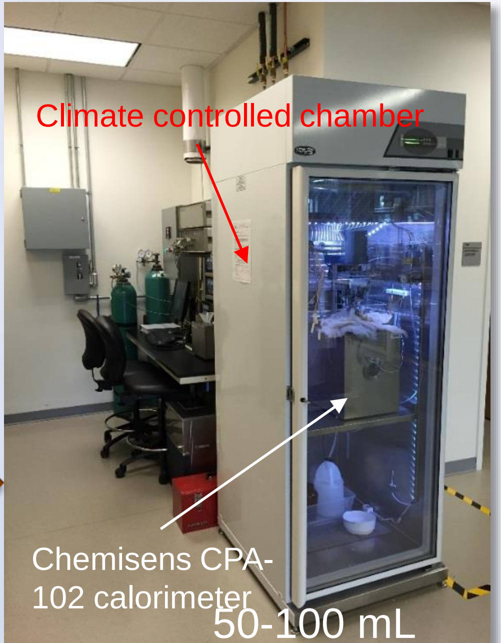
First screened by measuring :

- CO_2 breakthrough curves
- Viscosity
- Water content
- 5-10 mL scale

Promising refinements measured in automated VLE and reaction calorimetry:

- Operating range to 150° C
- Reproducibility
- Minimize experiment time (as much as possible)
- 50-100 mL solvent scale

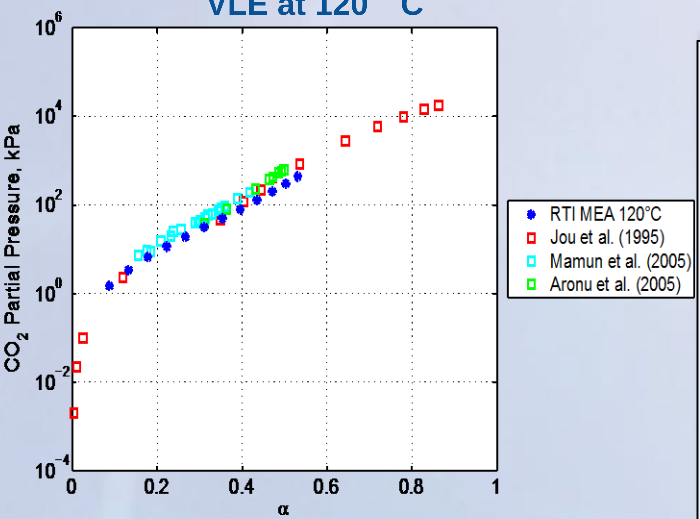




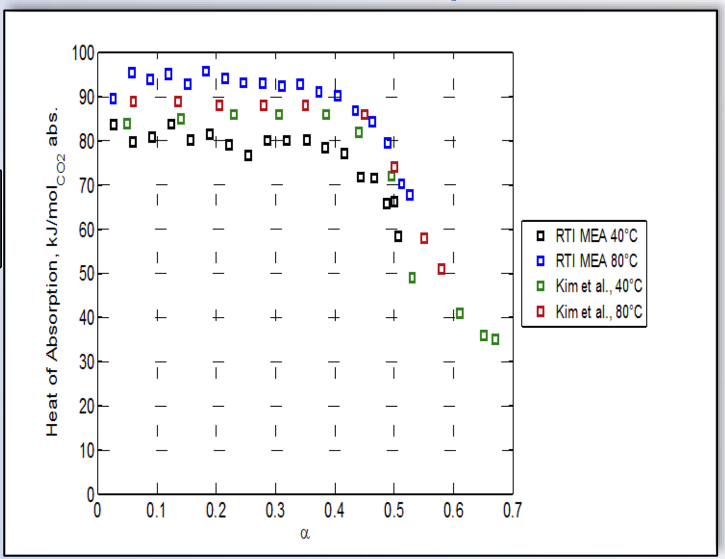
VLE-ΔH_r Validation with 30 wt% MEA-Water

- System and methods capable of generating high-quality data comparable to the highest-quality data reported in academic literature

VLE at 120° C



Heat of Absorption



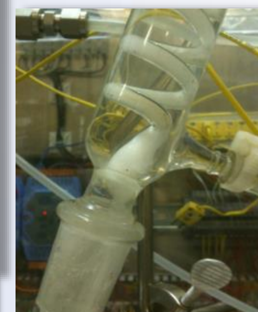
Lab-Scale Testing of Refined Solvents

Operating Conditions

- 0.5 liter solvent volume, ~2.5 SLPM gas flow rate
- Simulated flue gas containing 13.3% CO_2, 7.5% H_2O, 2% O_2, 50 ppm SO_2, and balance N_2
- Commissioning runs with 30 wt% MEA-water
- Evaluated 'best-candidate' NAS formulations
- Provides engineering team with a training tool to understand start-up and shut-down, system dynamics for larger, bench-scale unit and can be a useful troubleshooting tool

0.5 liter solvent volume, ~0.85 kg CO_2/day

Precipitation



Scaling

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

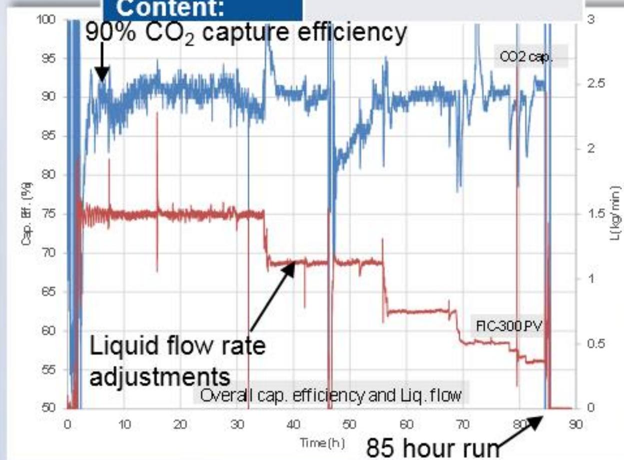
Gas Vel: 0.33-1.5 m/s
L: 15-75 kg/h

Regenerator
3" Sch. 10
SS316 (7.1 m height)
Mellapak 350x

Temp :Up to 150° C

Pressure: Up to 1MPa

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 15 %vol
Water Content:	~0 to 12.3%vol



Baseline testing with aqueous MEA

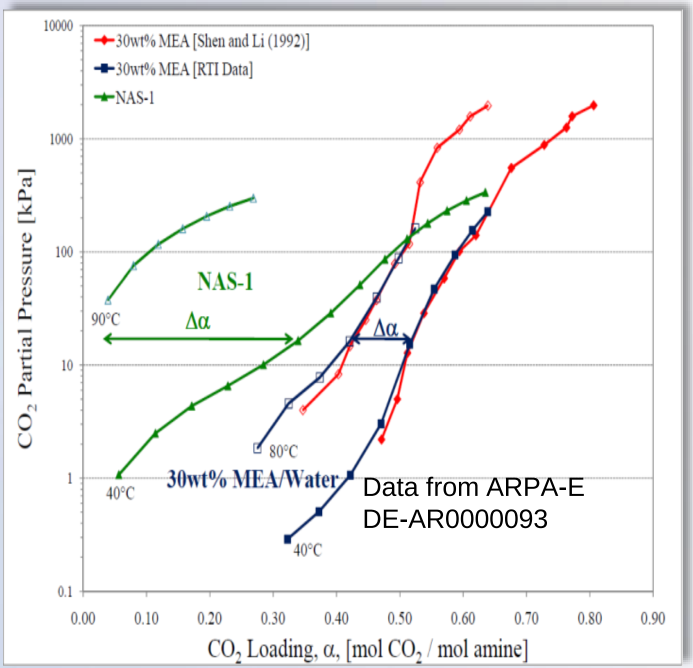
Solvent Refinement to Reduce Make-up costs and Emissions

BP1 Key Challenges

- NAS costs ($/kg) 10- to 100-X that of simple aqueous-amine components
- NAS-1 components have evaporative losses ~ 10X that of 30 wt% MEA-water
- Main volatile component is a diluent with vapor pressure of 1.85 kPa at 40ºC

Key Characteristics of NAS

- Large working capacity at low regeneration temperatures
- Low specific heat capacity
- Reasonable viscosity



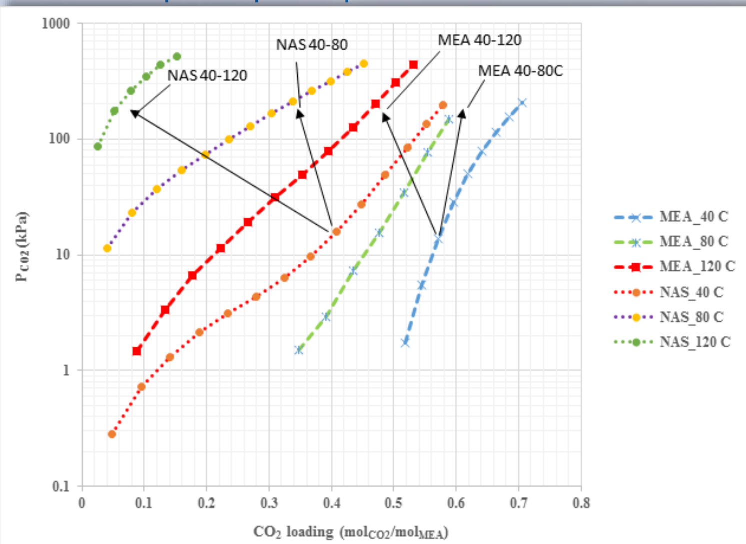
Simple Solution: Replace volatile diluent with a non volatile diluent

Incorporation of a Non-Volatile Hydrophobic Diluent (NAS-2, NAS-3)

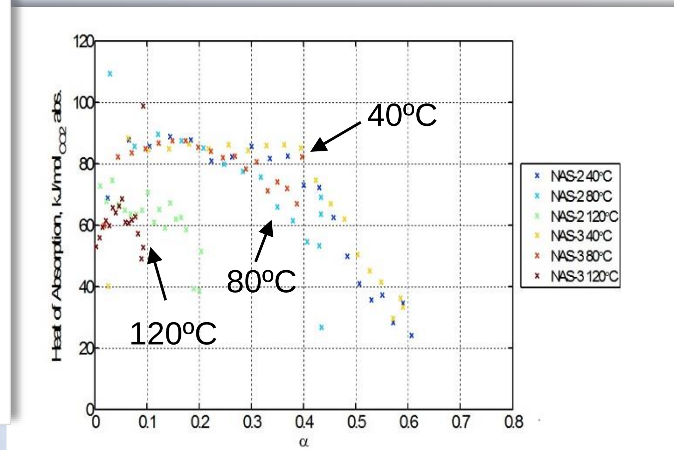
Identified hydrophobic diluent with suitable properties :

- Vapor pressure <0.13 kPa, 25° C
- Low viscosity
- Low cost

Vapor Liquid Equilibria NAS-3



Heats of Absorption NAS-2, NAS-3

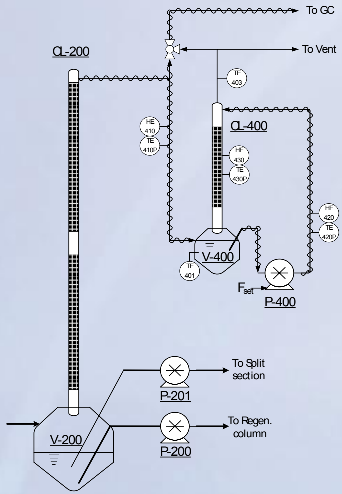


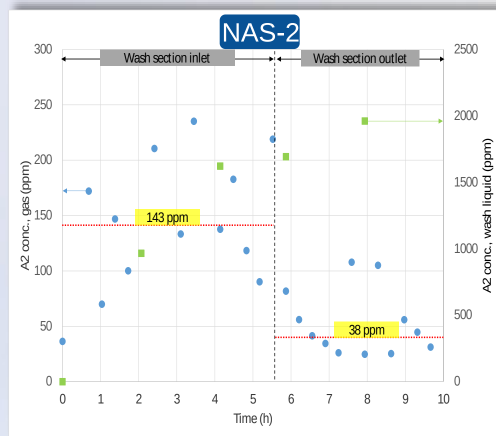
Formulated diluent with hydrophobic amines

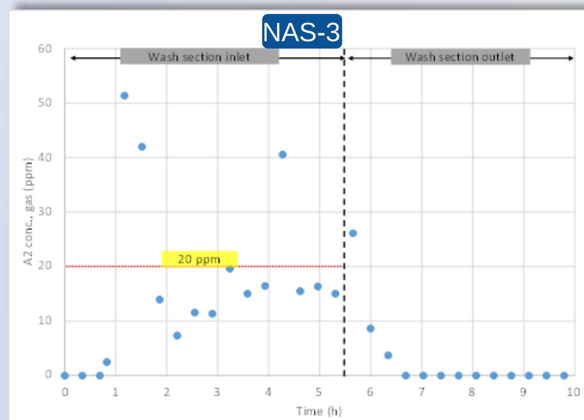
- Low heats of absorption
- No precipitates
- Low viscosities
- High CO_2 capacity
- Cost is <$50/kg

Patent Applications 13/820,027 and 14/382,108

Assessment of Emissions Using Absorber Wash Section



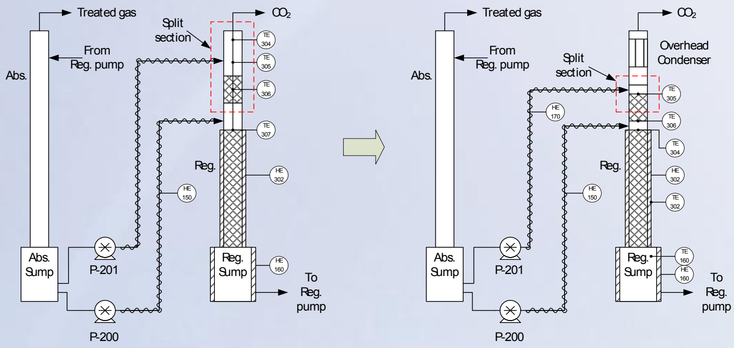


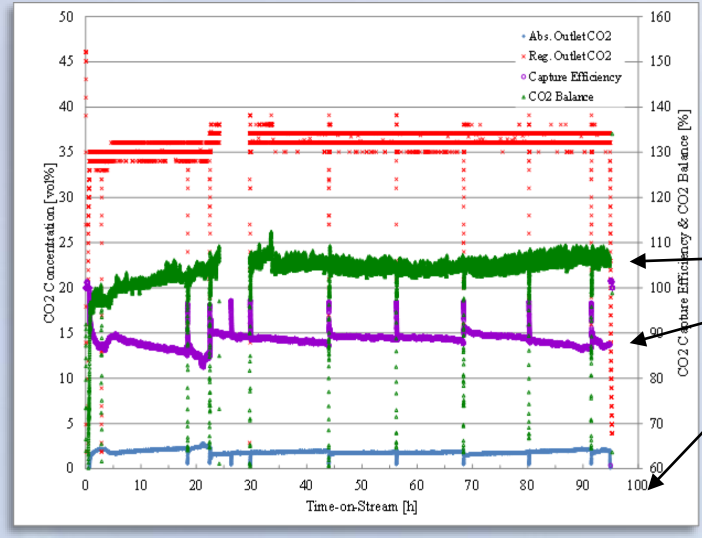


- Ran experiments to demonstrate wash section
- Top experiment performed on NAS-2
- Bottom experiment performed on NAS-3
- Observed higher emissions for NAS-2
- Doubled the length of the wash section
- Observed emissions of NAS-3 solvent lower and well below 10 ppm (target criteria)

Through appropriate solvent formulation and design of the wash section emissions are well below target

Long Term Lab-Scale Evaluation (NAS-2)





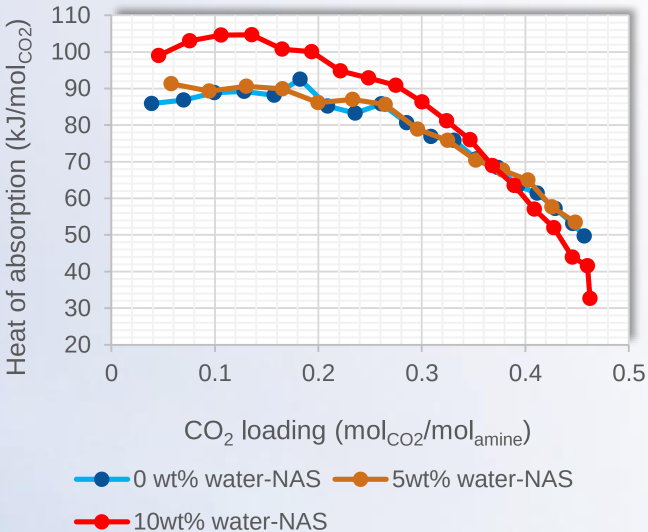
- Rich-split section overhead condenser integrated into design
- CO_2 balance
- Capture efficiency (~90%)
- Long-term, stable operation demonstrated (~100 hrs)
- Achieved water balance without issue

Impact of Water (NAS-2, NAS-3)

Properties of NAS Solvent

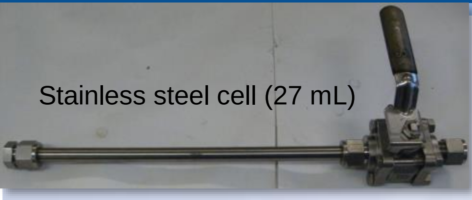
Criteria	Target	NAS-2
Vapor Pressure [kPa] @ 40°C	< 1	0.3 (Estimated)
Water Content [wt%]	<10	9.26
Viscosity [cP] CO_2-rich at 40°C	< 40	< 30
Foaming Tendency	Low	Low
Cost [$/kg]	< 50	< 50
Health Rating	≤ 3 (≤MEA)	2
Min. thermal regeneration energy* [kJt/kg CO_2]	<2,100	2,000

*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



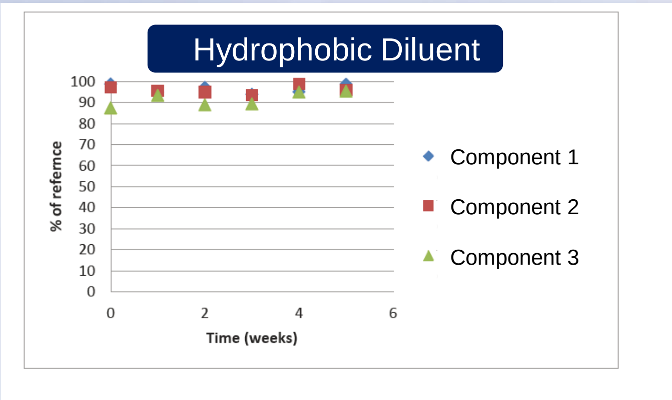
- Heat of absorption of dry NAS vs. “wet” NAS
- Observed increase in heat of absorption when NAS was fully saturated with water
- Impact on the process is that water may need to be kept ≤ 5wt%
- Improving the hydrophobicity of the solvent chemistry would be another way to handle this issue

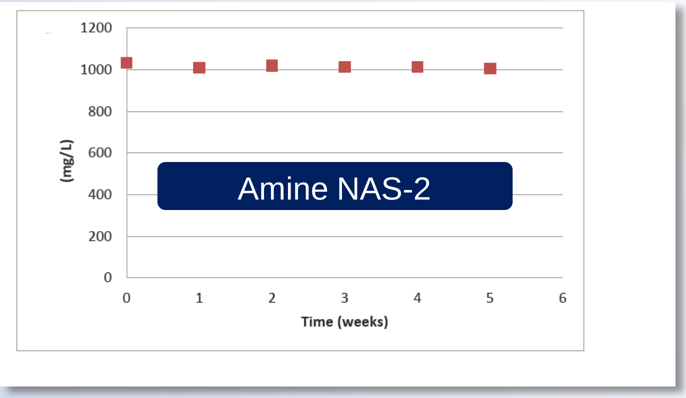
Thermal Degradation Studies



- Five-week thermal degradation studies
- Study conducted at 110° C on sealed, CO_2 loaded sample (15 ml)
- Studied three NAS components and three NAS formulations
- 100% MEA also tested

Results





- Single components of diluent are thermally stable
- NAS-2 and NAS-3 amines are thermally stable
- All changes are within sampling and analysis uncertainties
- Typical carbamate polymerization products are not formed
- Oxazolidinone formation not observed
- Corrosion results promising (Fe, Ni, Cr)

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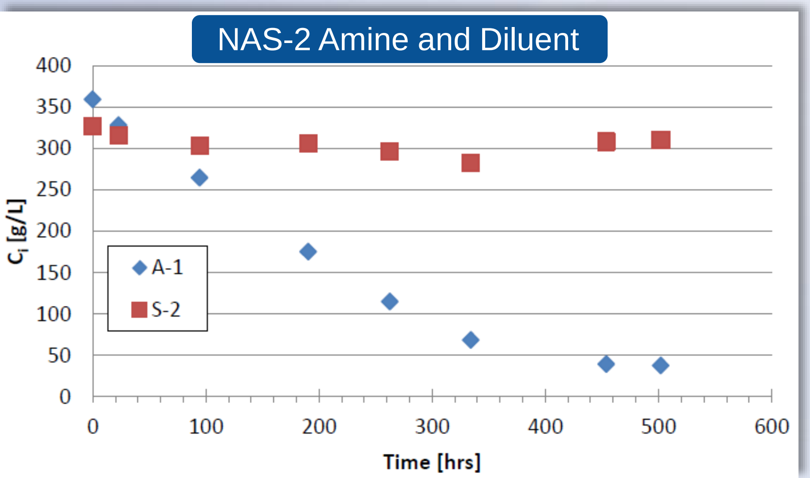
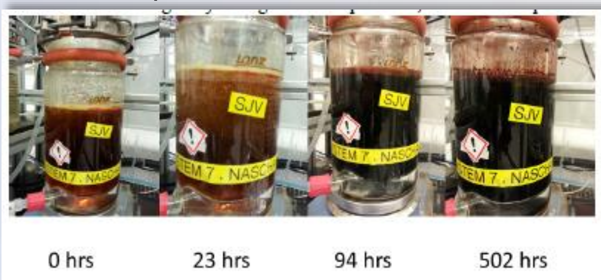
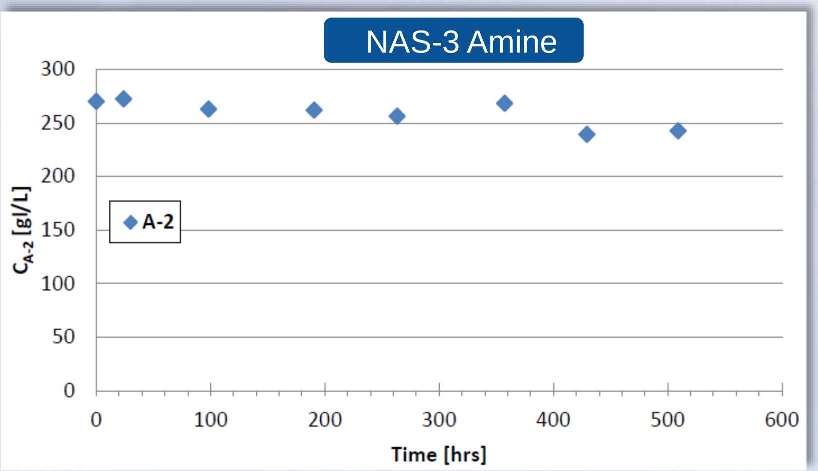
Oxidative Degradation Testing



Accelerated degradation conditions

- Open batch reactor
- Gas Composition = air + 2vol% CO_2
- Temp = 55° C





- NAS-2 amine oxidative degradation high
- Will require an oxidation inhibitor
- Hydrophobic diluent stable
- NAS-3 amine oxidative degradation low
- NAS-3 formulation: main component does not show oxidative degradation

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Summary of BP1 Scale-Up and Next Steps

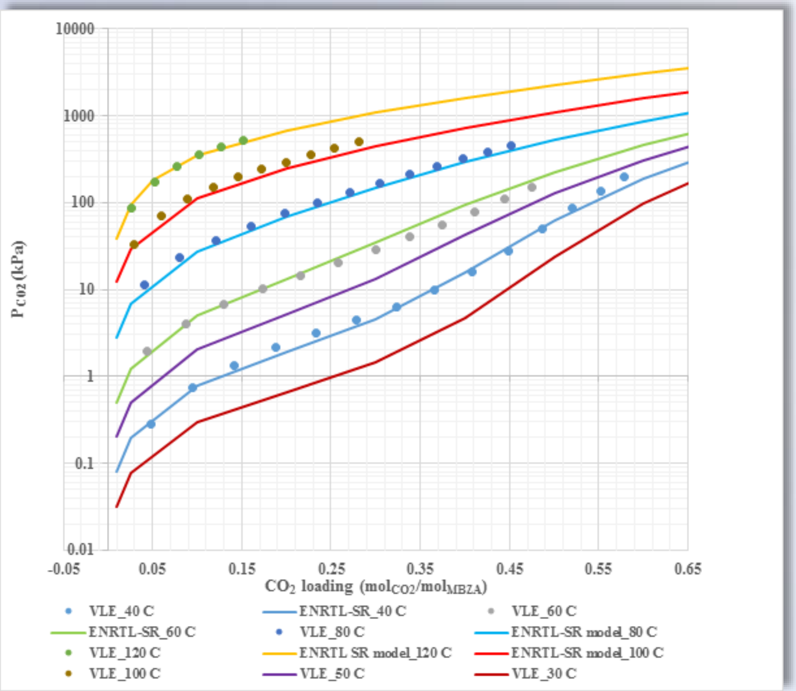
- Refined several NAS solvent formulations to maintain promising thermodynamic and physical properties discovered in previous ARPA-E project (viscosity, heat of absorption, working capacity)
- Replaced volatile formulation components with diluents with low vapor pressure (<0.3 kPa at 40° C)
- Conducted long-term, continuous, lab-scale testing on simulated flue gas to validate performance characteristics and avoid process surprises
- Performed thermal and oxidative degradation studies and found one amine component to be sensitive to oxidative degradation under accelerated conditions
- Determined experimental properties for ASPEN equilibrium thermodynamic ENRTL-SR model (not discussed)
- With Linde, currently evaluating NAS performance in bench-scale test unit, bench-marking against 30wt% aqueous monoethanolamine
- Ongoing long-term degradation testing at SINTEF using solvent degradation rig

State-Point Data Table for NAS-3

	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	ºC	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	ºC	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.

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