Non-Aqueous Solvents for Post-Combustion CO_2 Capture

RTI International

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BASF

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July 11, 2012

Project Overview

Project Objective

- Develop non-aqueous solvent and process for CO_2 capture that substantially reduces the parasitic energy load and corresponding ICOE for post-combustion CO_2 capture
- Transition process from TRL-3 to TRL- 5

Project Details

Project Number: DE-AR0000093

Funding: Total: $2,750,000

- ARPA-E: $2,200,000
- BASF: $500,000
- RTI: $50,000

Performance Period: July 2010 → June 2013

Project Team

arpa·e CO_2 IMPACCT Program

RTI INTERNATIONAL

- Inventor of novel, non-aqueous CO_2 solvent chemistry
- Novel solvent synthesis and formulation, solvent screening and evaluation, and process design and simulation efforts

BASF The Chemical Company

- Global leader in gas treatment solutions
- Extensive experience in the design, engineering, and servicing of acid-gas removal systems
- Guide solvent evaluation and process design to focus efforts on solving technical challenges to commercialization

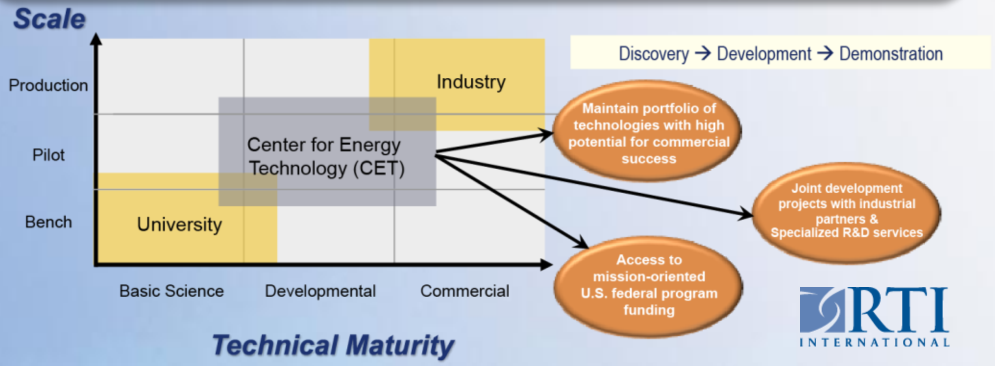
RTI's Center for Energy Technology

RTI's Johnson Science and Engineering Building
Home of RTI's Center for Energy Technology

Objective: Development of new energy technologies from laboratory bench to full-scale commercialization

Program Areas

- Advanced Gasification
- Syngas Conversion and Clean Fuels
- CO_2 Capture and Conversion
- Biomass Conversion and Biofuels
- Water Treatment
- Shale Gas



Scale

Production
Pilot
Bench

Industry
Center for Energy Technology (CET)
University

Basic Science
Developmental
Commercial

Technical Maturity

Discovery → Development → Demonstration

Maintain portfolio of technologies with high potential for commercial success

Joint development projects with industrial partners & Specialized R&D services

Access to mission-oriented U.S. federal program funding

BASF – The Chemical Company

BASF

- The world's leading chemical company
- Sales 2011: €73,497 million
- Income from operations (EBIT) 2011: €8,586 million
- Employees at year-end 2011: 111,141

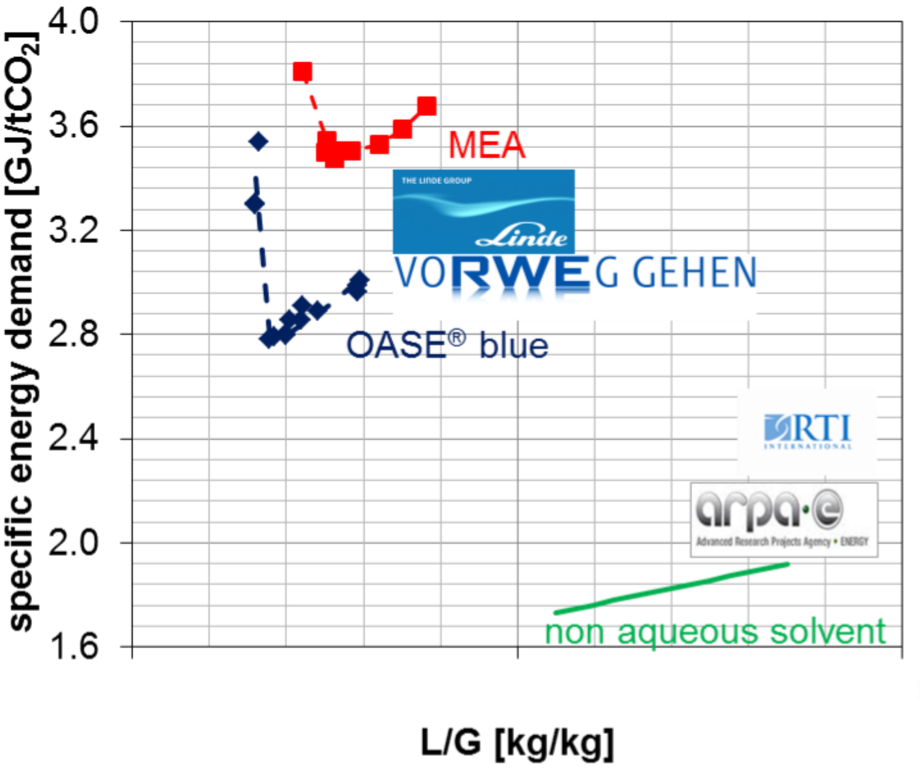
Gas Treatment

- Leading provider of gas treatment solutions
- Customer focused solution provider
- +300 industry references
- Innovation driven business unit
- Gas treating excellence

BASF
The Chemical Company

Post-Combustion CO_2 Capture Process

Three Generations of Solvents



MEA: well established technology

OASE® blue: ready for commercial scale

Non aqueous solvent: lab phase

BASF
The Chemical Company

R&D Opportunity

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

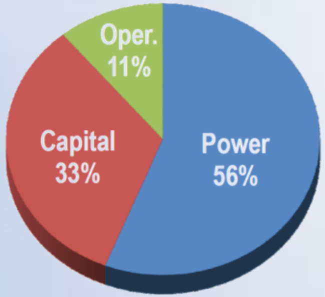
Heat of Absorption

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	⬇	⬇	⬇	⬆	⬆	⬇

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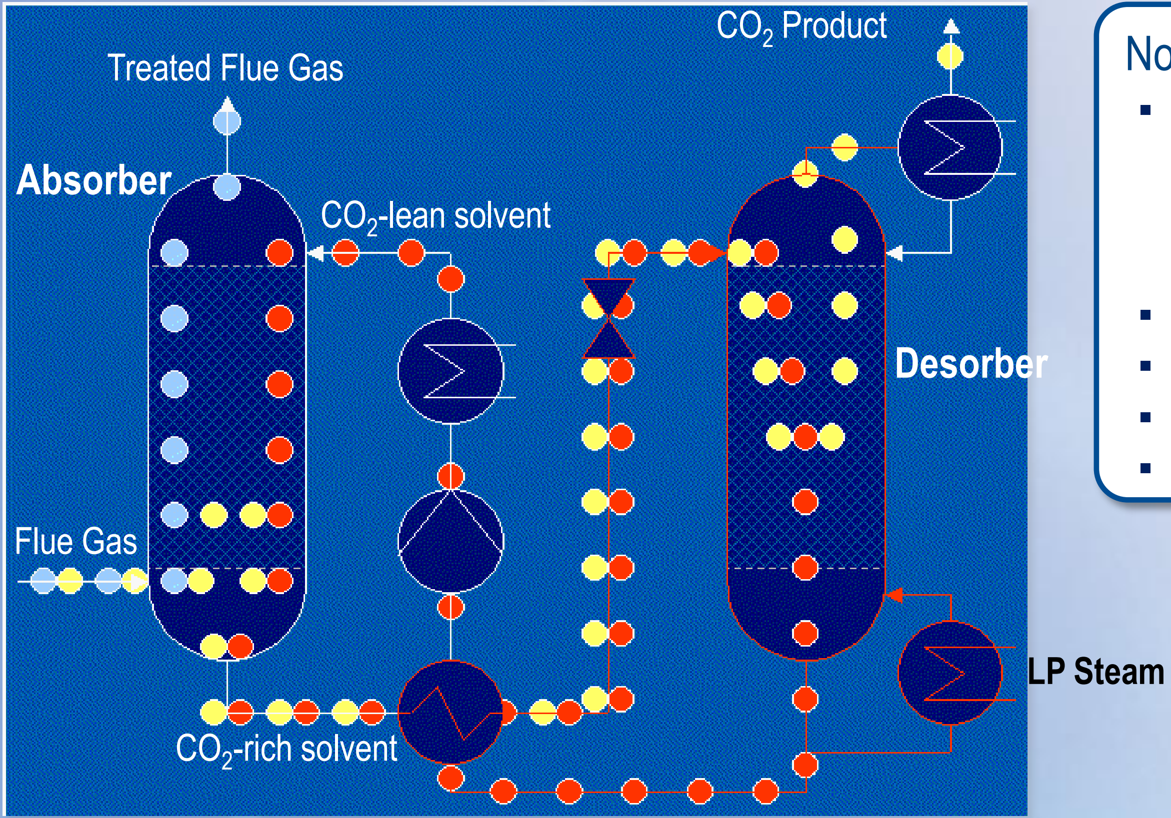
[1] Rochelle, G. T. Amine Scrubbing for CO_2 Capture. *Science* **2009**, 325, 1652-1654.

Non-Aqueous Solvents and Envisioned Process

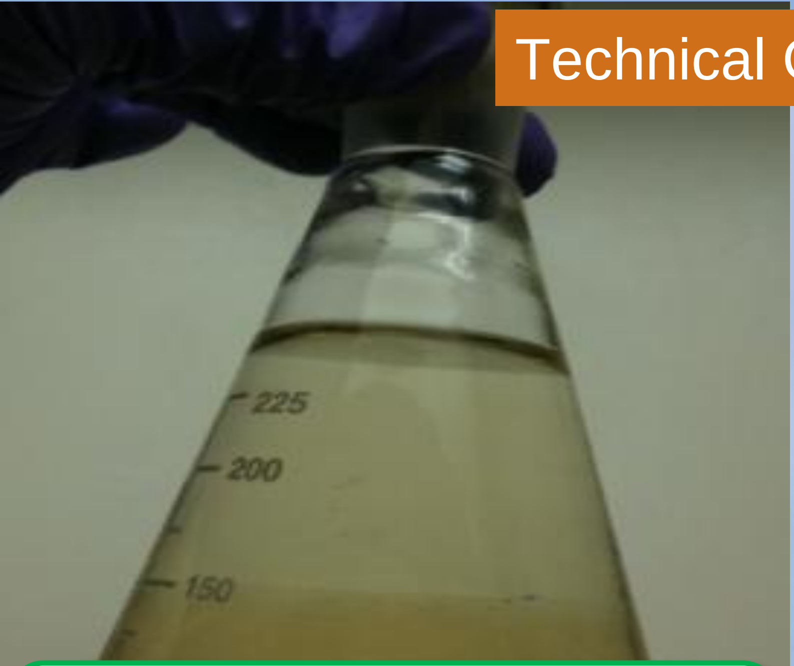


Non-aqueous solvent systems

- Favorable thermodynamics
  - Low heat of absorption
  - High working capacity
  - Low regeneration temperature
- Low specific heat capacity
- Low heat of vaporization
- Tunable vapor pressure
- Low water solubility

○	Flue Gas
●	CO_2
●	**Non-Aqueous Solvent**

Technical Challenges for Non-Aqueous Solvents



- Undesirable reactions with water
  Competitive reaction with water can lead to more stable bicarbonates
- Accumulation of water from flue gas in solvent
  Water can be stripped from the flue gas and accumulate in the capture process
- Solids formation in rich solvent
  Formation of insoluble salts or gels at high CO_2 loadings
- Viscosity of solvent
  Affects rate of CO_2 capture and column size
- Foaming
  Affects column performance
- Solvent cost and availability
  Exotic components can be expensive and may not be readily available for large-scale applications
- Emissions in process water and treated flue gas
  Solvents must not be hazardous

Development plan is focused to

- identify promising solvent formulations that reduce reboiler heat duty and directly address these technical challenges
- demonstrate superior performance
- rapidly transition from the lab to the field

Technology Development Plan – Year 1 Efforts

	Previous Work			Current Project		Future Development			
Yr	2009-10			2010-13		2014-15		2016-18	2019+
TRL	1	2	3	4	5	6	7	8	9

Proof of Concept/Feasibility

Laboratory Validation

- Comprehensive solvent screening to identify promising solvent systems
- Process modeling to evaluate novel process configurations and integration strategies
- Preliminary technical and economic assessment to compare cost and performance to conventional solvent systems

Year 1 Major Milestones and Targets

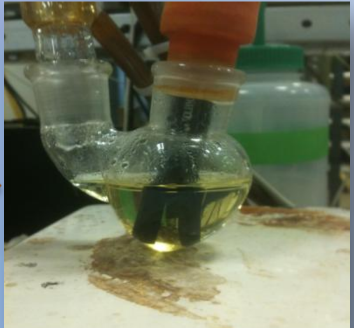
- Identify at least 1 promising solvent system meeting all performance criteria for bench-scale testing in Y2 & Y3
- Preliminary estimates of parasitic power load and COE completed.
  - Reboiler Duty: < 2.5 GJ/tonne CO_2
  - % Increase in COE < 75%

Process for Identification of Promising Solvent Formulations

A. Propose solvent formulations meeting internal requirements
B. Screen formulations for CO_2 loading and regeneration temperature
C. Determine impact of water and water solubility
D. Measure thermodynamic properties- VLE & ΔHR
E. Measure physical properties of lean and rich solutions – viscosity and foaming
F. Evaluate long-term stability using high-fidelity FG including H_2O, O_2, and SO_2

Formulation conception

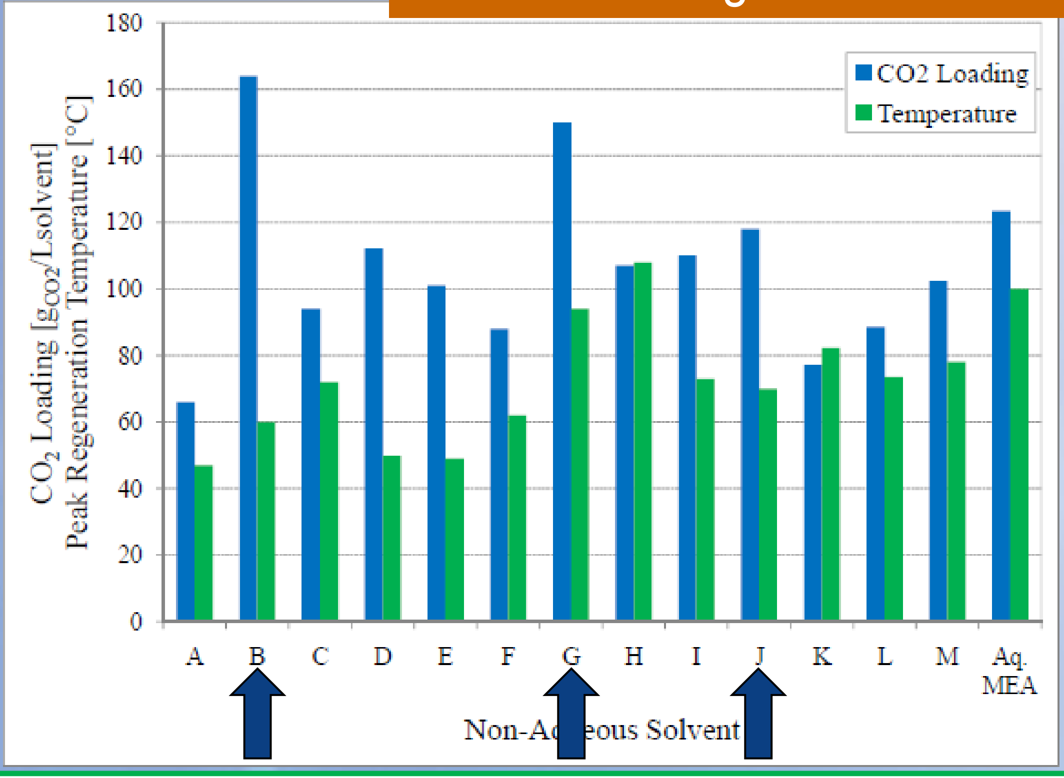
Initial screening



Screening with water

Long-term testing & measurement of physical and thermodynamic properties

Initial Screening of Candidate Systems



- Screened a broad array of non-aqueous solvent families
- Low regeneration temperatures
  45 to 110°C
- High CO_2 loading capacities
  60 to 163 g CO_2 / $L_{solvent}$

Identified promising candidates with higher loadings and lower regeneration temperatures than conventional aqueous-amine solvents

Screening with Water

Critical Issues

Precipitation during absorption

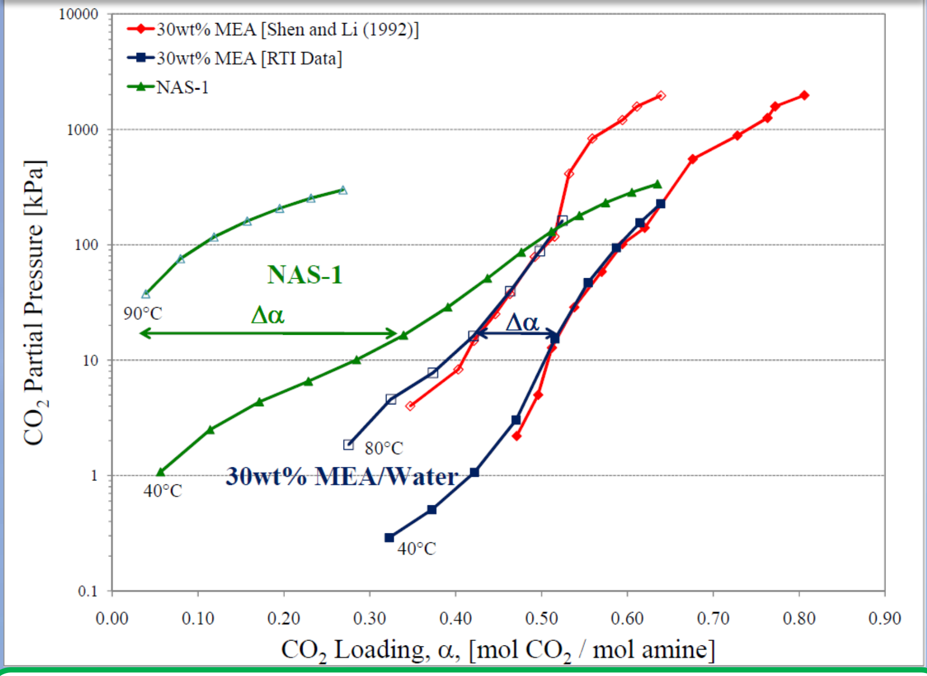
Scaling in the overhead during regeneration

Formation of a second liquid phase

- Eliminated numerous solvent formulation due to critical issues related to water
- Narrowed promising candidate solvent systems that maintain desired performance in the presence of water

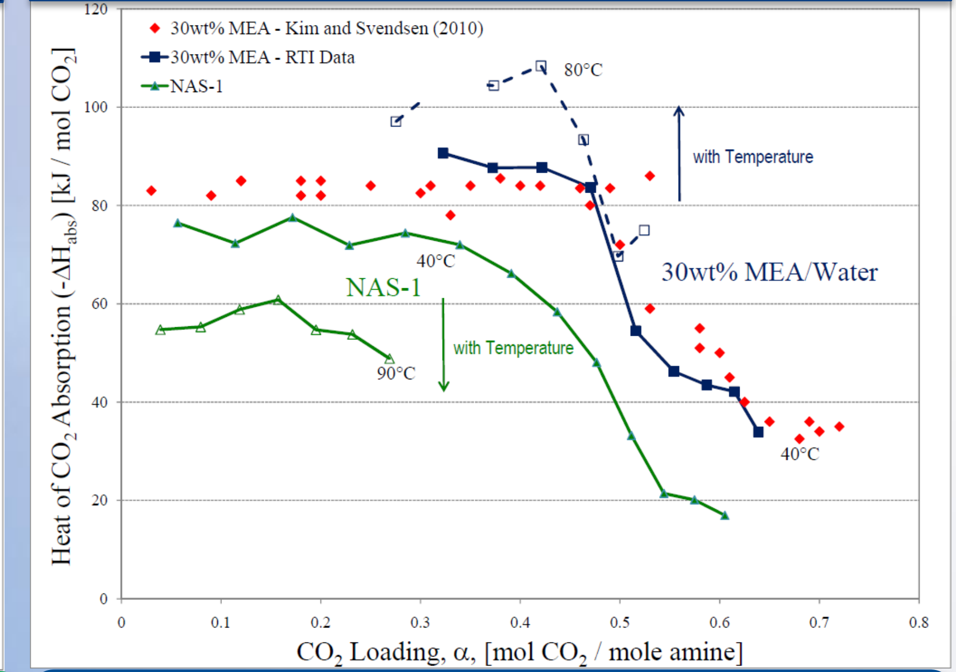
Measurement of Thermodynamic Properties

CO_2 Isotherms



- NASs achieve larger dynamic capacities (Δα) with smaller ΔTs
- CO_2 pressure of > 2bar can be achieved around 90 C

Heat of Absorption



- Heat of absorption ranging from 55 to 75 kJ/mol CO_2
- Specific heat capacity of 1.2 to 1.5 kJ/kg K

Measurement of Physical Properties - Viscosity

- Viscosity measured using Brookfield DVI-Plus viscometer
- Viscosity measured for CO_2-lean and CO_2-rich solvents at absorption (40°C) and regeneration (80°C) temperatures

Measured Viscosity

Sample Name	Viscosity [cP]	Temp [C]
NAS-1, CO_2-Lean	4.5	40
	1.6	80
NAS-1, CO_2-Rich	20.7	40
NAS-2, CO_2-Lean	7.2	40
	2.5	80
NAS-2, CO_2-Rich	27.1	40

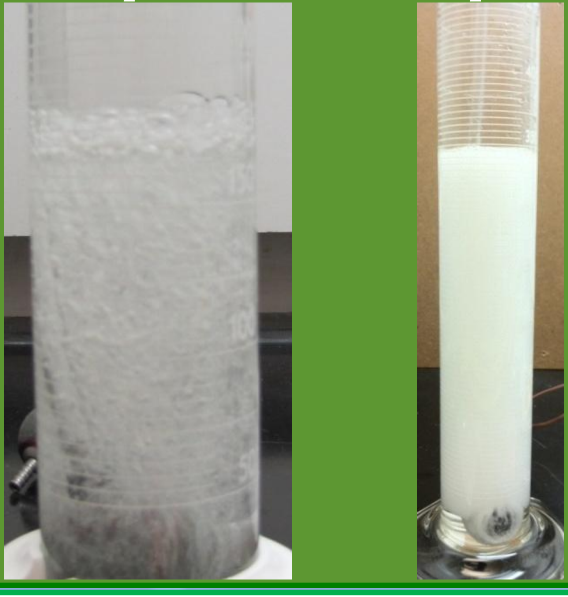
- 30 wt% MEA is reported to be 1.7 cP (lean) and 2.7 cP (rich) at 40°C[1]
- Non-aqueous solvents have very reasonable viscosities and can utilize conventional gas absorption equipment

[1] Amundsen, T. G. CO_2 Absorption in Alkaline . MSc. Thesis. Telemark University College 2008.

Measurement of Physical Properties – Foaming

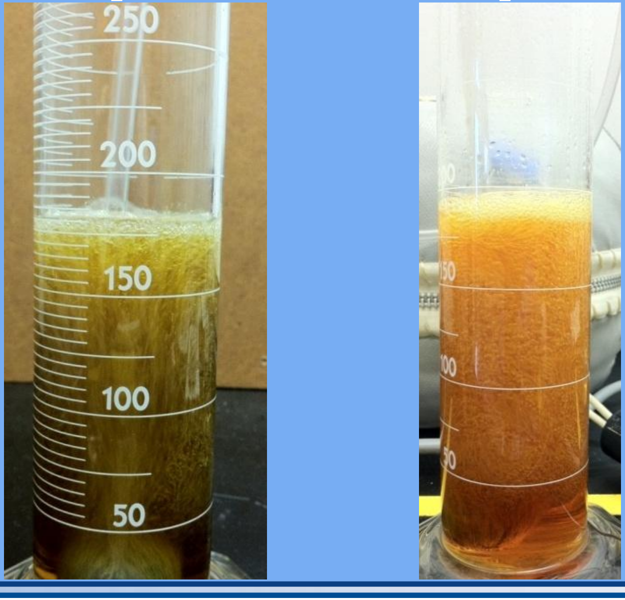
30 wt% MEA / Water

CO_2-Lean CO_2-Rich



NAS-2

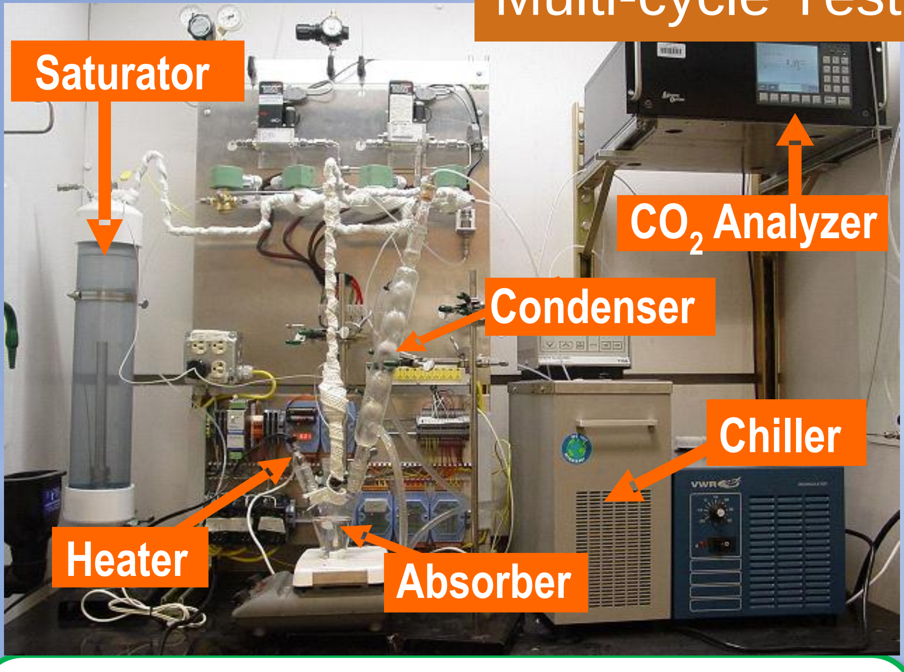
CO_2-Lean CO_2-Rich

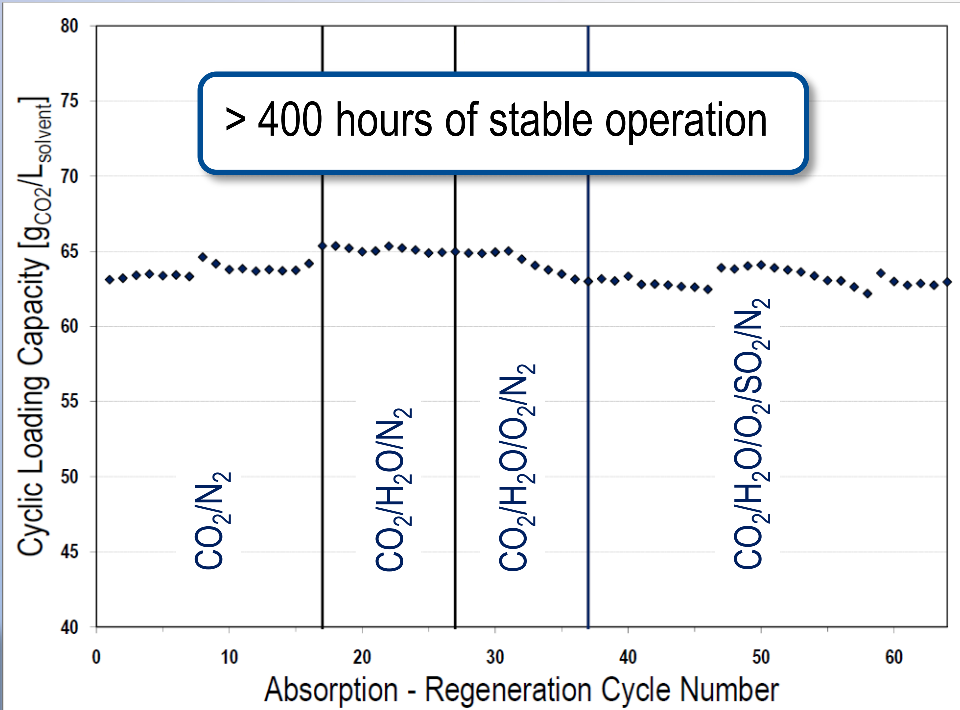


- Foaming issues observed without addition of anti-foaming agents
- Failed test by expanding > 3x to overflow cylinder

- No foaming issues observed for non-aqueous solvents
- Very little retention of gas in solvent

Multi-cycle Testing with FG Contaminants



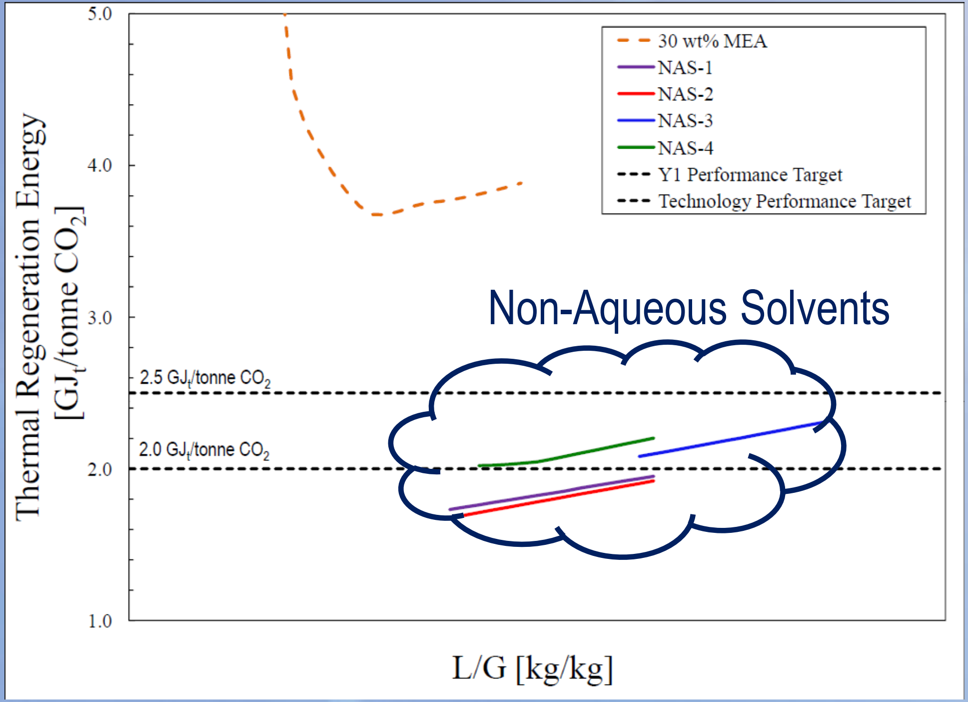


> 400 hours of stable operation

Absorption:
Temperature: 30°C
Gas Composition:
14%CO_2, 4%O_2, 50 ppm SO_2, N_2
Water Content: fully saturated

Regeneration:
Temperature: Ramp to 75°C
Gas Composition: N_2 Purge
Water Content: fully saturated

Estimate of Reboiler Heat Duty using Short-cut Method[a]



Basis:

- Solvent parameters
  - Measured thermodynamic data for NASs and MEA /water
- Process parameters
  - Flue Gas Composition (mole fraction)
    - N_2: 69.61; O_2: 3.35; H_2O: 13.04; CO_2: 14.00
  - Percent CO_2 captured: 90%
  - Pressure
    - Absorber: 1013 mbar; Desorber: 2000 mbar
  - Temperature
    - Absorber: 40 °C; Desorber: 120 °C (MEA); 90°C (NAS)
    - Crossover exchanger approach temperature: 10 °C

- Several candidates have been identified that have potential to achieve regeneration energies < 2.0 GJ$_t$ / tonne CO_2
- Promising candidates to be evaluated in the bench-scale unit in Years 2 & 3

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[a] 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

Preliminary Technical & Economic Assessment

Power Performance Assessment

- Basis: Case 12 – Supercritical PC Power Plant with CO2 Capture. DOE/NETL-2007/1281.
- Process model of a supercritical PC power plant was developed to estimate parasitic power load and net energy penalty (Aspen Plus)

CO_2 Capture Process	Gross Power [kWe]	Aux. Power [kWe]	Net Power [kWe]	Net Efficiency [%]	Efficiency Point Loss
No Capture	827,647	42,947	784,700	39.1	-
Fluor Econamine FG+	663,445	117,450	545,995	27.2	11.9
NAS-2	775,913	96,923	678,991	33.9	5.2

- NAS CO_2 capture process has potential to reduce parasitic power load by ~ 50% compared to MEA-based process
- Primarily due to lower quantity and quality of steam required for solvent regeneration
- Potential for significant reduction in increase in cost of electricity

Preliminary Technical and Economic Assessment

Economic Assessment

- Basis: Case 12 – Supercritical PC Power Plant with CO_2 Capture. DOE/NETL-2007/1281.
- Assumption: NAS CO_2 capture process has the same capital and operating cost as the Econamine FG+ process

	Case 11 No Capture	Case 12 w/ MEA	Case 12 w/ NAS CO_2 Capture Process
Net Plant Efficiency (%)	39.1	27.2	33.9
Power Plant Cost ($x1000)	866,391	1,109,866	1,109,866
Total Plant Cost ($/kW)	1,574	2,870	2,308
LCOE (mills/kWh)	63.36	115.33	93.58
ICOE (%)	0	82.0	47.7
CO_2 Avoided Cost ($/tonne)		74.8	54.1

- NAS CO_2 Capture Process has potential to achieve < 50% ICOE and < $50/tonne CO_2
- Further reductions are possible with simplified process configuration

Year 1 Major Milestones and Targets

- Identify at least 1 promising solvent system meeting all performance criteria for bench-scale testing in Y2 & Y3
- Preliminary estimates of parasitic power load and COE completed.
  - Reboiler Duty: < 2.5 GJ/tonne CO_2
  - % Increase in COE < 75%

All Y1 milestones and performance targets achieved

Technology Development Plan – Current Efforts

	Previous Work			Current Project		Future Development			
Yr	2009-10			2010-13		2014-15		2016-18	2019+
TRL	1	2	3	4	5	6	7	8	9

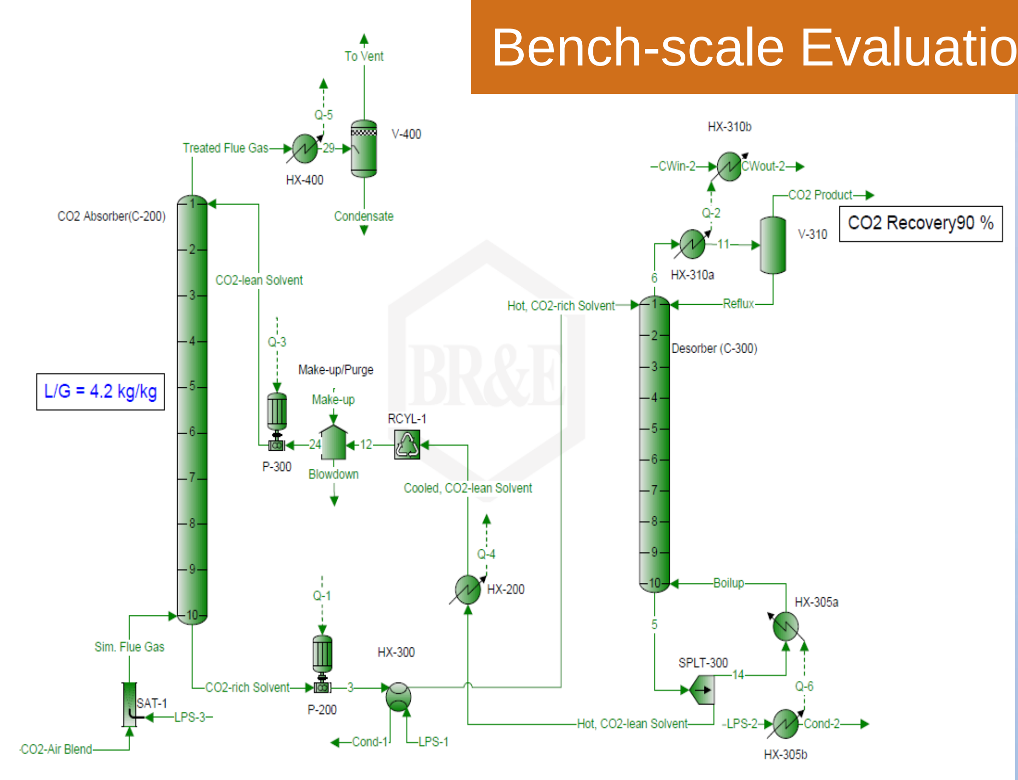
Year 2 & 3 Major Milestones and Targets

- Bench-scale unit built, commissioned, characterized, and baselined with 30 wt% MEA / water
- Long-term testing (~1,000 h) of promising non-aqueous solvents demonstrating >90% CO_2 capture and reduced thermal regeneration energy requirement
- Collect critical process modeling and scale-up information
- Technical and economic assessments indicating:
    - Reboiler Duty: ≤ 2.0 GJ/tonne CO_2
    - % Increase in COE < 50%

Relevant Environment Validation

- Bench-scale testing to assess solvent performance
- Continued process modeling to evaluate novel process configurations and integration strategies
- Updated, comprehensive technical and economic assessment to compare cost and performance to conventional solvent systems

Bench-scale Evaluation of Non-Aqueous Solvent Process



Objective– Assess performance of most-promising NASs in a representation process configuration using high-fidelity flue gas

- Demonstrate >90% CO_2 capture and high CO_2 product purity at an optimal L/G ratio as determined from process modeling
- Compare performance of NASs with that of the SOTA system
- Collect experimental data indicating a ‘significant’ reduction in energy consumption compared to SOTA
- Long-term (1,000 hours) stability testing
- Collect key process information to support simulation and scale-up efforts

Status

- System design completed and procurement and construction underway
- EDC: Installed at RTI by September 30, 2012

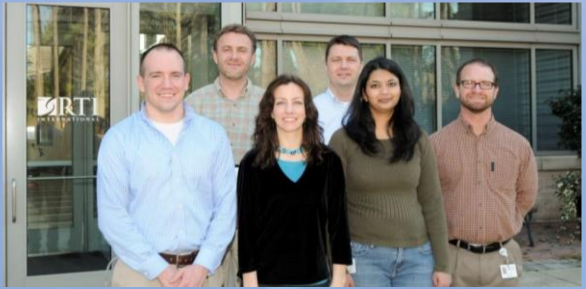
Next Development Phase – Mini-Plant/Slipstream Testing

ARPA-E Portfolio → NETL Portfolio

	Previous Work			Current Project		Future Development			
Yr	2009-10			2010-13		2014-15		2016-18	2019+
TRL	1	2	3	4	5	6	7	8	9

Mini Plant Testing at Power Plant

Acknowledgments



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