Aminosilicone Solvents for Low Cost CO_2 Capture

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GE Global Research
GE Energy
University of Pittsburgh

DOE Contract: DE-NT0005310

NETL CO_2 Capture Technology R&D Meeting
September 13, 2010

GE Global Research

World R&D Headquarters: Niskayuna, NY

First US industrial lab

Founding principle … improve businesses through technology

One of the world's most diverse industrial labs

Partnering with governments, industry, and academia

Program Objectives

Project Team

GE Global Research

- *Materials discovery by high throughput experimentation*
- *Development and synthesis of oligomeric materials*

GE Energy

- *Modeling, and design of integrated energy systems*
- *Economic Analysis*

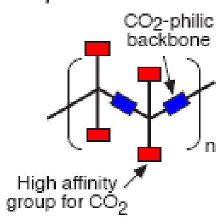
University of Pittsburgh

- *Development of CO_2 soluble materials*
- *Molecular modeling*

Novel High-Capacity Oligomers for Low-Cost CO_2 Capture, 2-Year, \$3.0 M

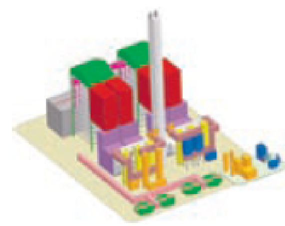
Program Objective: Develop novel oligomeric solvent and process for post-combustion capture of CO_2 from coal-fired power plants with 90% capture efficiency, and less than 20% increase in cost of electricity.

Molecular Modeling, High-Throughput Experimentation



Lab-Scale Synthesis and Testing

System Integration and Optimization



Technical Approach

- Solvent molecular design: CO_2-philic oligomeric backbone modified with high affinity groups for CO_2
- Material development: high throughput experimentation, and molecular modeling
- Process optimization: process model
- System Integration: PC plant – carbon capture system model optimization.

- Develop a novel, CO_2 capture solvent with:
- 90% Carbon capture efficiency
- 25% Increase in capacity vs MEA
- Less than 35% increase in Cost of Energy Services (COE)

- Post-combustion capture of CO_2 from coal-fired power plants

Program Scope

Identify novel solvents and process

Methods

- Molecular modeling to identify candidate solvents
- Synthetic chemistry to prepare solvents in the lab
- High throughput screening for relevant properties
- System modeling integrated with power plant model
- Cost of energy services analysis

Phase 1

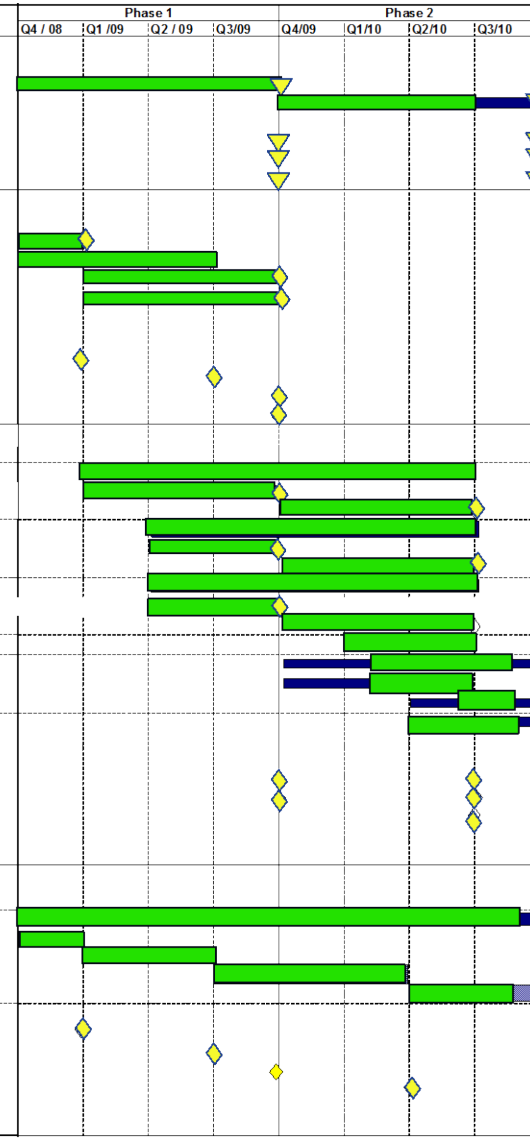
- System model development
- Screening and selection of solvent classes
- Synthetic strategy development
- Development of Gen 1 solvents

Phase 2

- Synthesis & Test Gen 2 solvents
- Bench scale test most promising solvents
- Model refinement
- Degradation testing
- Predict overall solvent and plant performance

Schedule

	Participants
Task 1 Project Management and Planning	GE GRC / GE Energy
Milestones	
Comprehensive topical reports delivered at the completion of each budget period.	
Presentation of technical papers at the DOE/NETL annual contractor's review meeting	
Presentation of detailed briefings to the project officer at least once per year.	
Task 2 Screening and selection of solvent classes for CO2 capture	
2.1 Proposed solvent classes and alternative options	GE GRC / U. Pitt
2.2 Selection of solvent classes (polymeric backbones, and functional groups) by molecular modeling	GE GRC / U. Pitt
2.3 Bench scale, multi-property determination of the commercially available solvents from the classes indentified in 2.1 and 2.2	GE GRC
2.4 Synthetic strategy development for classes of solvent and structure optimization (MW, functional groups, endgroups)	GE GRC
Milestones:	
Physical property targets for the solvent identified.	
Thermodynamic properties for the selected solvents predicted	
A group of solvents with a theorethical capacity CO2 at least 25 % greater than aqueus MEA identified	
A strategy for synthesizing the solvent(s) identified.	
Task 3 CO2 capture solvent synthesis, optimization and property testing	
3.1 Method development and high throughput synthesis of solvent libraries within the selected classes	GE GRC
3.1.1 Gen 1 Libraries	
3.1.2 Gen 2 Libraries	
3.2 High throughput evaluation of selected property within the synthesized solvent libraries	GE GRC
3.2.1 Gen 1 Libraries	
3.2.2 Gen 2 Libraries	
3.3 Multi-property modeling of lead candidates identified in 3.2 (vapor pressure, thermal stability, CO2 adsorption, etc)	GE GRC
3.3.1 Gen 1 Libraries	
3.3.2 Gen 2 Libraries	
3.4 Multi-property determination, and lead validation for the candidates selected from 3.2 and 3.3	GE GRC / U. Pitt
3.5 Bench scale lead solvent performance evaluation (complete adsorption/desorption cycle demonstration)	GE GRC
3.5.1 Gen 1 lead lab demo	
3.5.2 Gen 2 lead demo	
3.6 Degradation testing / Enviromental testing	GE GRC
Milestones:	
Libraries of promising CO2 capture solvents created (Gen 1, and Gen 2)	
Lead candidates indentified based on HT property evaluation, and multi-property modeling	
Physical properties of the synthesized lead solvent(s) measured	
Bench test of one or more lead solvents that are predicted at the commercial scale to have the potential to reach 20% increase in COE	
Lifetime prediction of the lead solvent(s)	
Task 4 Process modeling and cost of energy services	
4.1 Absorption & Stripping Cycles and Plant Simulation	GE Energy
4.1 Calibrated Plant Model	
4.2 Parametric Solvent and Plant integration study with class of materials	
4.3 Model "GEN 1" solvents in plant models	
4.4 Optimize plant around "GEN 2" Solvents	
Milestones:	
Detailed Power Plant Model	
Detailed CO2 capture model for parametric studies	
COE less than 40% increase in COE	
COE evaluated for "GEN 1" solvents	
COE Evaluated for "GEN 2" solvent	



All tasks on track to meet scheduled completion dates

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Milestones

Milestone Description	Planned Completion Date	Actual Completion Date
Phase I		
Physical property targets for the solvent identified.	12/31/08	12/31/08
Detailed power plant model complete.	12/31/08	12/31/08
Thermodynamic properties for the selected solvents predicted.	6/30/09	6/30/09
Parametric studies using detailed CO_2 capture model complete	6/30/09	6/30/09
Libraries of promising CO_2 capture solvents (GEN 1) identified	9/30/09	9/30/09
Lead candidates (GEN 1) identified based on HT property evaluation and multi-property modeling	9/30/09	9/30/09
Strategy for synthesizing the solvent(s) identified	9/30/09	9/30/09
A group of solvents that have been demonstrated to have a CO_2 capacity of at least 25% greater than aqueous monoethanolamine (MEA), and are predicted to achieve 90% CO_2 capture efficiency and less than a 50% increase in COE (with the potential to achieve less than a 35% increase in COE with further optimization) identified	9/30/09 Go/No go	9/30/09
Phase II		
COE evaluated for GEN 1 solvents	3/31/10	3/31/10
Libraries of promising CO_2 capture solvents (GEN 2) identified	6/30/10	6/30/10
Lead candidates (GEN 2) identified based on HT property evaluation and multi-property modeling	6/30/10	6/30/10
Physical properties of the synthesized lead solvent(s) measured	6/30/10	6/30/10
Bench test of one or more lead solvents completed	9/30/10	On target
Lifetime prediction of lead solvent(s) completed	9/30/10	On target
COE evaluated for GEN 2 solvent	9/30/10	On target

Milestones achieved on schedule

Budget

	BP1			BP2			Total		
	Gov't Funding	Cost Share	Total	Gov't Funding	Cost Share	Total	Gov't Funding	Cost Share	Total
GE Global Research	$982,676	$317,600	$1,300,276	$745,436	$236,302	$981,738	$1,728,112	$553,902	$2,282,014
GE Energy	$241,948	$0	$241,948	$253,102	$0	$253,102	$495,050	$0	$495,050
Univ. of Pittsburgh	$174,553	$32,194	$206,747	$75,447	$32,194	$107,641	$250,000	$64,388	$314,388
Total	$1,399,177	$349,794	$1,748,971	$1,073,985	$268,496	$1,342,481	$2,473,162	$618,290	$3,091,452

$3.1MM program with 20% cost share from participants

Baseline Reporting Quarter	Year 1								Year 2							
	Q1		Q2		Q3		Q4		Q1		Q2		Q3		Q4	
	10/1/08 - 12/31/08		1/1/09 - 3/31/09		4/1/09 - 6/30/09		7/1/09 - 9/30/09		10/1/09 - 12/31/09		1/1/10 - 3/31/10		4/1/10 - 6/30/10		7/1/10 - 9/30/10	
	Q1	Total	Q2	Total	Q3	Total	Q4	Total	Q1	Total	Q2	Total	Q3	Total	Q4	Total
Baseline Cost Plan																
Federal Share	238,305	238,305	379,584	617,889	387,179	1,005,068	394,109	1,399,177	266,938	1,666,115	263,722	1,929,837	269,199	2,199,036	274,126	2,473,162
Non-Federal Share	59,576	59,576	94,896	154,472	96,795	251,267	98,527	349,794	66,735	416,529	65,930	482,459	67,300	549,759	68,531	618,290
Total Planned	297,881	297,881	474,480	772,361	483,974	1,256,335	492,636	1,748,971	333,673	2,082,644	329,652	2,412,296	336,499	2,748,795	342,657	3,091,452
Actual Incurred Cost																
Federal Share	194,157	194,157	437,262	631,419	367,960	999,379	298,869	1,298,248	201,354	1,499,602	163,842	1,663,444	526,978	2,190,422		
Non-Federal Share	48,539	48,539	109,316	157,855	91,990	249,845	67,217	317,062	50,338	367,400	40,961	408,362	131,745	540,107		
Total Incurred Costs	242,696	242,696	546,578	789,274	459,950	1,249,224	336,087	1,615,310	251,692	1,867,002	204,803	2,071,805	658,723	2,730,529		
Variance																
Federal Share	(44,148)	(44,148)	57,678	13,530	(19,219)	(5,689)	(95,240)	(100,929)	(65,584)	(166,513)	(99,880)	(266,393)	257,779	(8,614)		
Non-Federal Share	(11,037)	(11,037)	14,422	3,383	(4,805)	(1,422)	(31,358)	(32,732)	(16,397)	(49,129)	(24,969)	(74,097)	64,445	(9,652)		
Total Variance	(55,185)	(55,185)	72,098	16,913	(24,024)	(7,111)	(156,549)	(133,661)	(81,891)	(215,642)	(124,849)	(340,491)	322,224	(18,266)		

Within 1% of budget after Q7

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Technology Fundamentals

Relating Chemistry to COE

Chemical Parameters

Thermal stability

High CO_2 loading

High desorption pressure

Low reaction energy

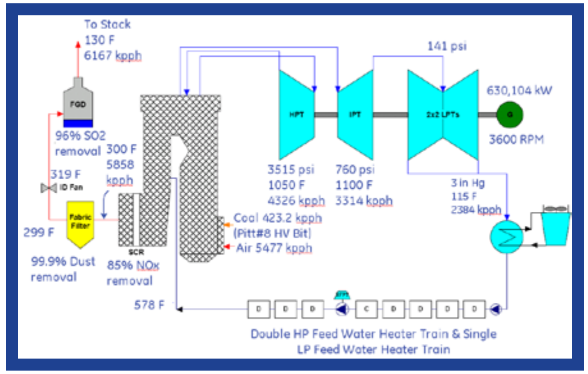
Low volatility

High reaction rate

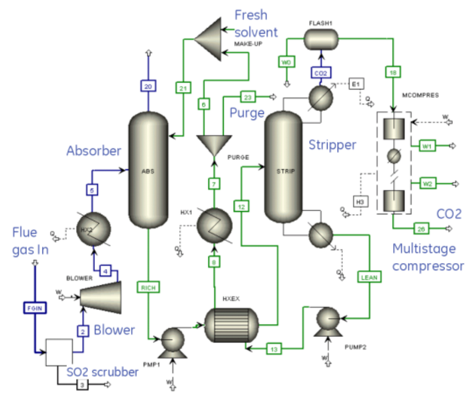
Low cost

Plant & Process Models

A detailed calibrated coal power plant model complete in Thermoflow & THB

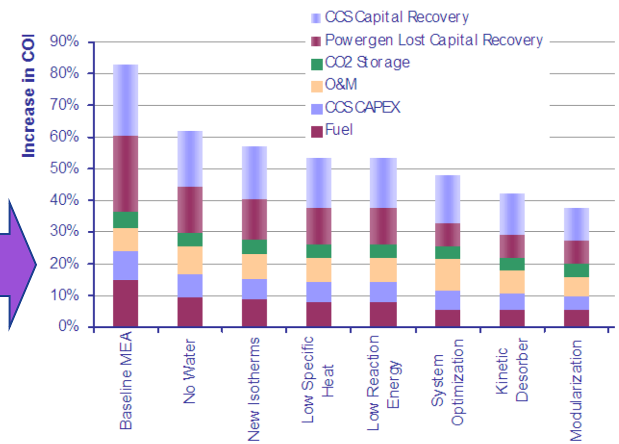


Non-Aqueous chemistry requires new process designs in Aspen Plus



Cost of Electricity

Cost of Electricity Model Complete, calibrated to DOE references



Cost of Electricity components define critical chemical characteristics

Solvent properties have a significant influence on COE

Dynamic interplay between modeling and experimental results

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Novel Solvent

Advantages

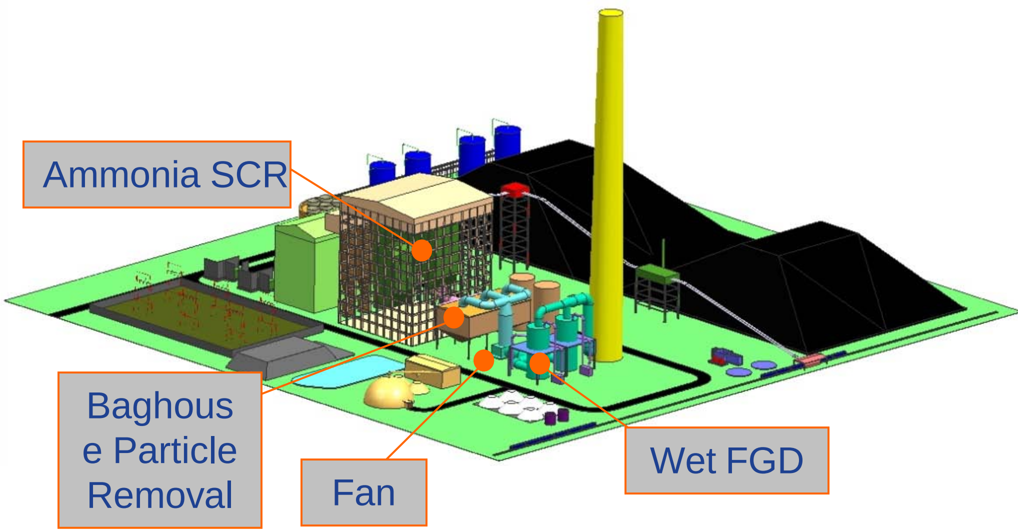
- Higher CO_2 loading – decreased volume, lower CAPEX
- Lower volatility – less make-up needed, lower cost
- Greater thermal stability – decreased decomposition, lower cost
- High desorption pressure – less compression energy needed, cost savings
- Low reaction energy – less heat (energy) needed to regenerate solvent
- Fast reaction kinetics – smaller absorber unit, decreased CAPEX

Potential Challenges

- Large footprint – no space
- Viscosity too high
- Slow CO_2 desorption kinetics
- Process too costly
- Optimal CO_2 loading not achieved

Project Status - Plant Model

Plant Overview



630 MW Gross Super critical coal fired plant

South Eastern U.S.
- Ambient 95 F, Wet Bulb 80 F
- Relative Humidity 53%

Super Critical Steam Turbines
- HP 3515 psia, 1050 F
- IP 760 psia & 1100 F
- LP 141 psia

Generator 13.8 kV, Transmission 765 kV

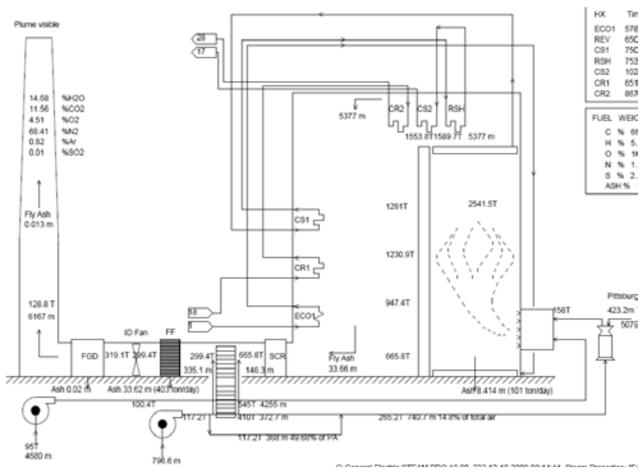
Excess Air - 20%

Pittsburgh No. 8
- Eastern Bituminous Coal
- HHV – 12,450 Btu/lb
- 9.94% Ash
- 6% moisture
- 2.89% Sulfur

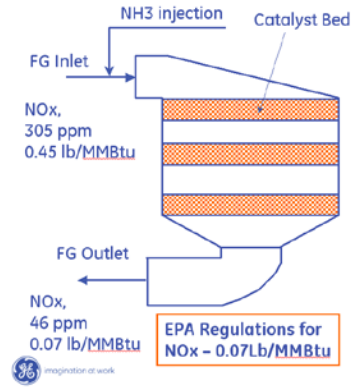
Emission Regulations
- NOx – 0.07 lb/MMBTU
- SOx – 0.182 lb/MMBTU
- PM – 0.035 lb/MMBTU

Detailed Process Models

Boiler



SCR

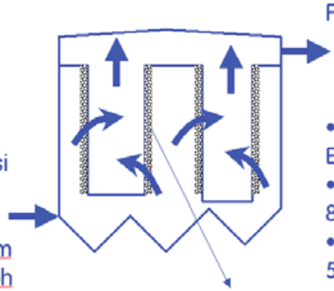


Vol, Mcfm	2.53
Mass*, kpph	5410
Temp, F	666
Pressure, psia	14.6
Number of reactors	3
Gas Velocity	16
NOx reduction	85%
Pressure Drop, in H2O	7
NOx removed, kpph	2.03
NH3 consumed, kpph	0.75
NH3 Slip, kpph	0.009
Power, kW	213

*5626 kpph for Santee Cooper Pee Dee, ~615 MW Gross

Baghouse

- Flue Gas Inlet
- PM – 6.4 lb/MMBtu
- Pressure – 14.14 psi
- Temp – 300 F
- Mass – 5899 kpph
- Volume – 1.93 mcfm
- Fly Ash – 33.81 kpph



PM – 0.006 lb/MMBtu
Fly Ash – 0.03 kpph

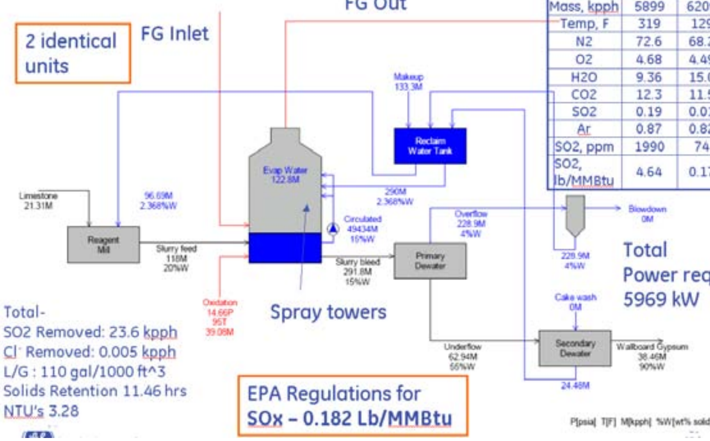
- Dust Collection Efficiency 99.9%
- Power Consumption 832 kW
- W x D x H = 296 ft x 54 ft x 70 ft

Fly Ash removed – 33.78 kpph

- Type – Pulse-jet
- Material – Fiberglass
- Number of Casings – 4
- Total Cloth Area – 0.58 M ft^2

EPA Regulations for PM 0.035 Lb/MMBtu. Further Particles removed by FGD

FGD



	FG In	FG Out
Mass, kpph	5899	6209
Temp, F	319	129
N2	72.6	68.2
O2	4.68	4.49
H2O	9.36	15.0
CO2	12.3	11.5
SO2	0.19	0.01
Ar	0.87	0.82
SO2, ppm	1990	74
SO2, lb/MMBtu	4.64	0.17

Total-
SO2 Removed: 23.6 kpph
Cl⁻ Removed: 0.005 kpph
L/G : 110 gal/1000 ft^3
Solids Retention 11.46 hrs
NTU's 3.28

EPA Regulations for SOx – 0.182 Lb/MMBtu

Thermoflow process models calibrated with external references

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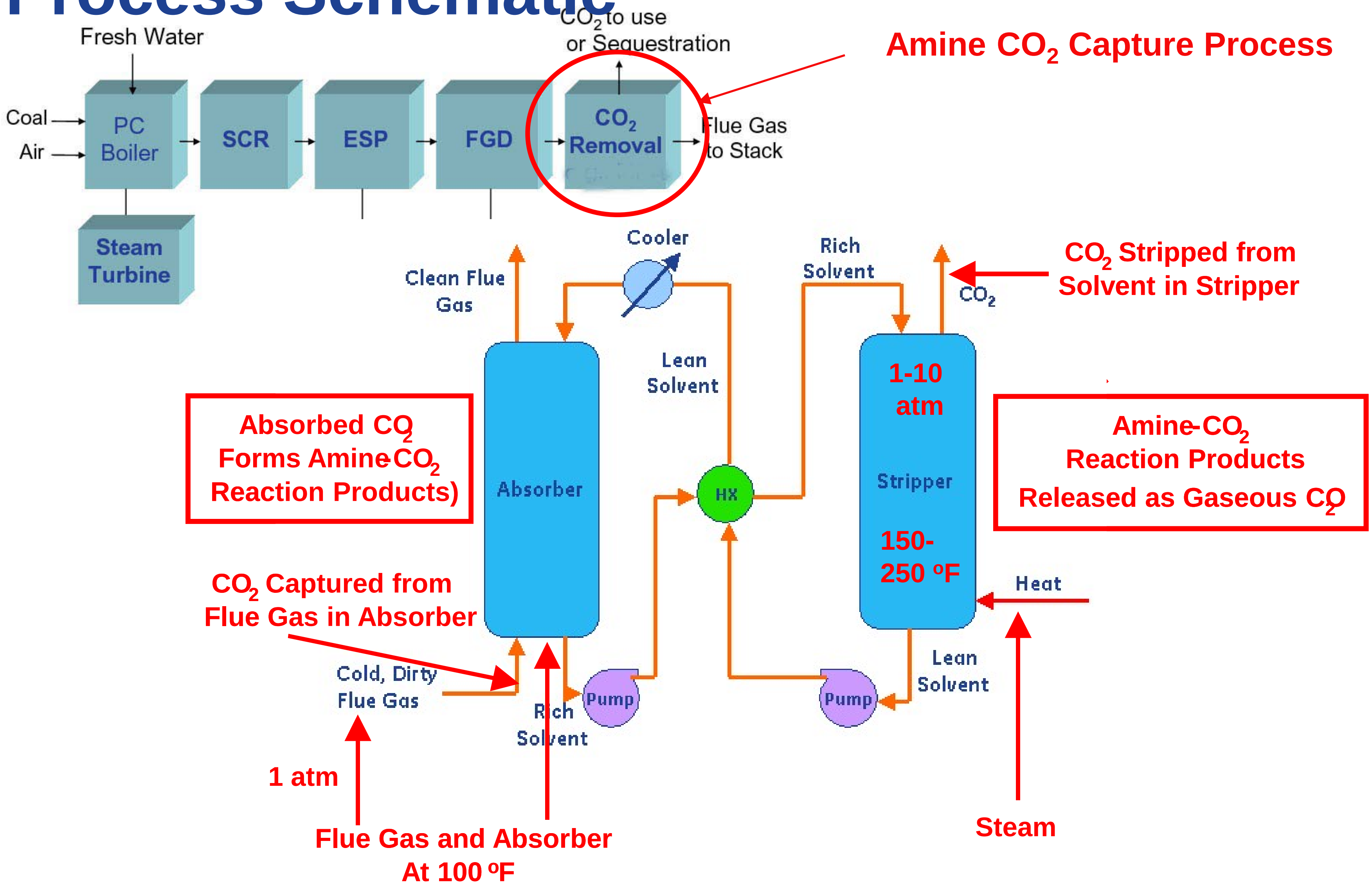
Power

Details	DOE Report	% of Gross	Current Model	% of Gross
Gross Power, kW	**586,980**	**100.00%**	630,107	100.00%
Coal Handling, kW	2,590	0.44%	3,411	0.54%
Ash Handling, kW	2,070	0.35%	841	0.13%
Primary Air Fans, kW	1,220	0.21%	1,406	0.22%
Forced Draft Fans, kW	2,550	0.43%	1,996	0.32%
Induced Draft Fans, kW	9,160	1.56%	9,574	1.52%
SCR, kW	300	0.05%	212	0.03%
Baghouse, kW	100	0.02%	806	0.13%
FGD Pumps & Agitators, kW	6,620	1.13%	5,934	0.94%
Condensate Pumps, kW	780	0.13%	1,015	0.16%
Circulating Water Pumps, kW	4,170	0.71%	5,265	0.84%
Cooling Tower Fans, kW	2,370	0.40%	2,265	0.36%
Misc. BOP, kW	5,270	0.90%	8,820	1.40%
Total Auxiliaries, kW	37,280	6.35%	41,545	6.59%
Net Power, kW	**549,700**	**93.65%**	**588,562**	**93.41%**
Net Efficiency (HHV) %	**39.50**		**38.11**	
Net Heat Rate (HHV), Btu/kWhr	8,646		8,953	
Type of Coal	IL#6 HV Bit		Pitt#8, East HV Bit	
Ash in Coal, wt%	9.7		9.9	
Moisture in Coal	11.1		6	
Sulfur in Coal	2.51		2.89	

Plant model captures key auxiliary energy flows affected by carbon capture

Process Schematic



CO_2 Loading Limited by Amine Chemical Equilibrium

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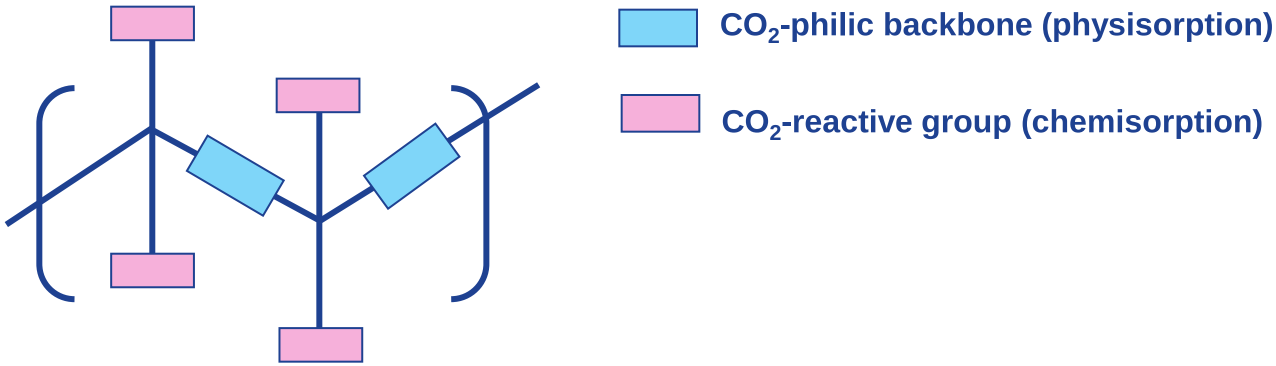
Project Status - Solvent

Concept



- Backbone or core that is CO_2-philic
- Reactive functional groups that chemically combine with CO_2
- Down-select to aminosilicones
  - Possessed desirable physical/chemical properties
  - Clear IP space
  - Variety of core architectures available
  - Prior experience

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Synthesis and HTS

- 27 and 48 well reactors
- Temperature controlled
- Multiple gas input capabilities
- Coupled to robot for sample weighing

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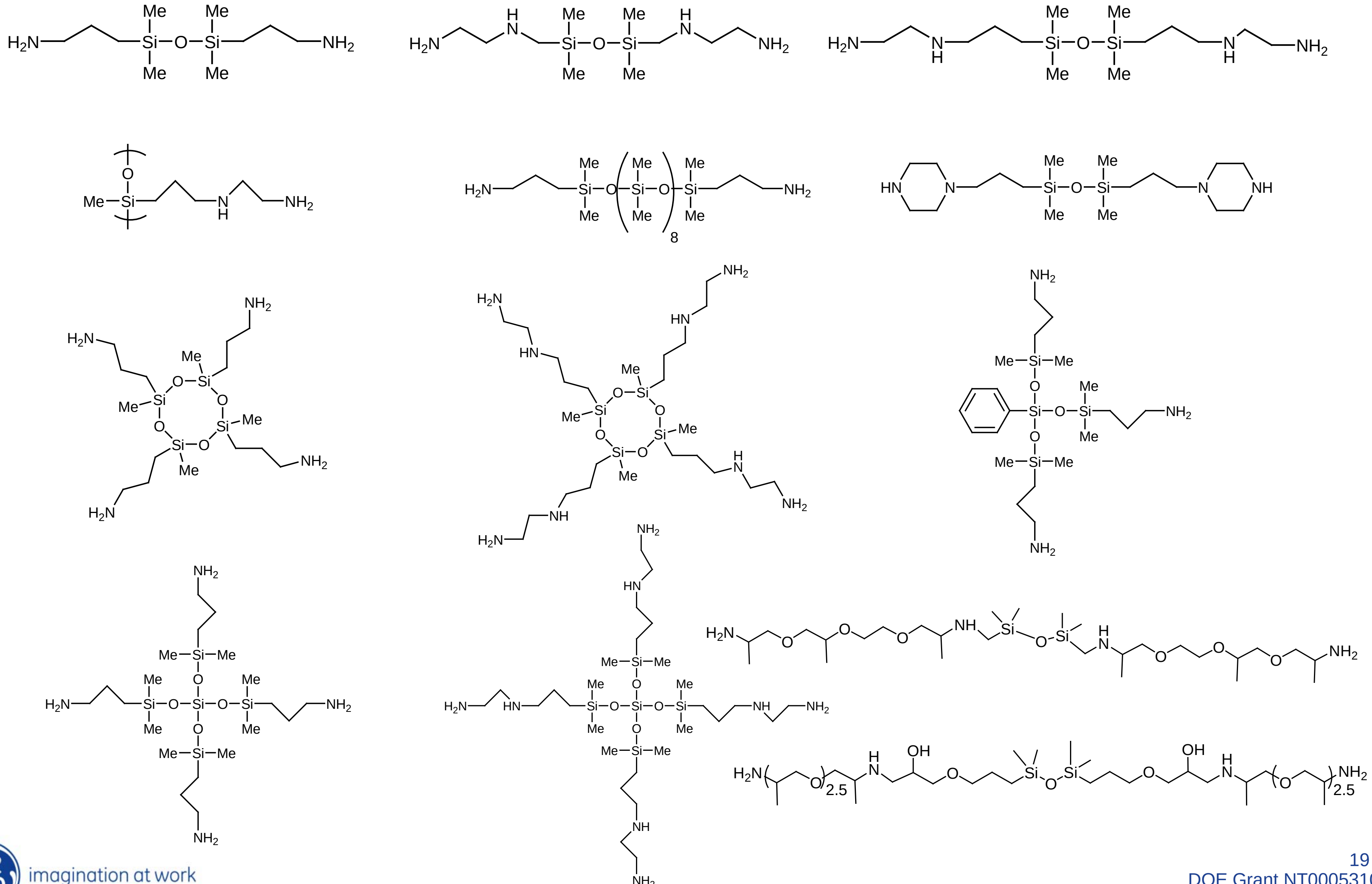
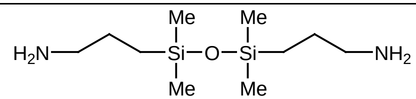
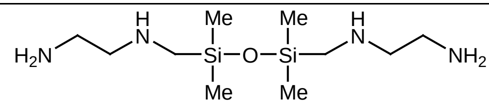
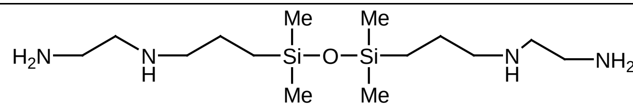
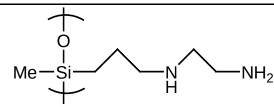
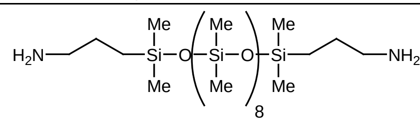
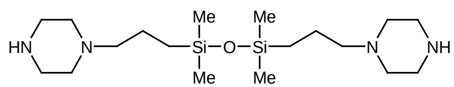
Materials for HTS

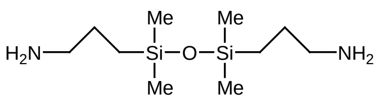
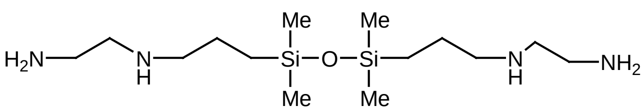
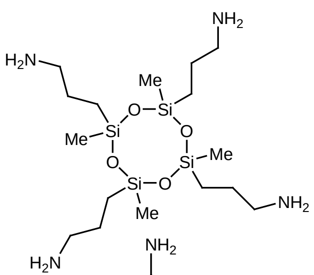
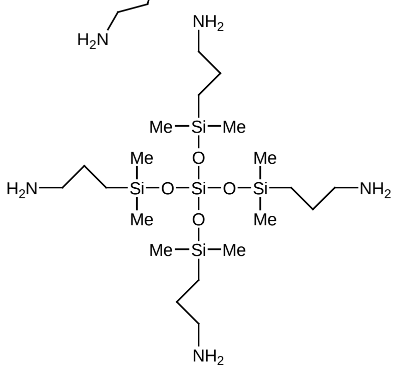


High Throughput Screening (HTS)

Cmpd	Structure	CO_2 Wt Gain (%)	Theoretical CO_2 Wt gain (%)	% of Theory
1		16.5	17.7	94
2		15.3	31.6	48
3		10.9	26.3	41
4		8.5	27.5	31
5		4.6	5.5	84
6		3.8	11.4	33

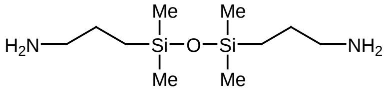
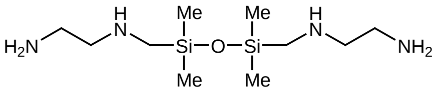
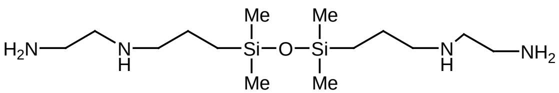
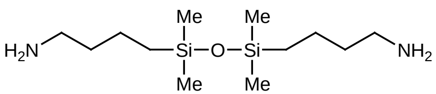
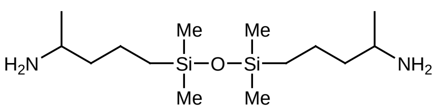
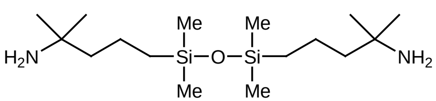
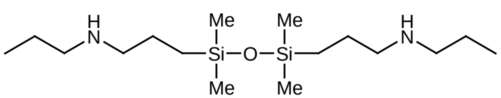
- Tested as neat materials
- Compare to 10.2% wt gain for MEA benchmark
- Calculate based on 2:1 amine:CO_2 stoichiometry

Advantage of Co-Solvent

Amine	50% TEG	% Wt Gain (of Theory)	% Wt Gain	State
 GAP-0	no	94	16.5	S
	yes	114	10.1	L
	no	64	16.7	S
	yes	90	11.8	L
	no	30	5.6	S
	yes	108	10.1	L
	no	87	13.8	S
	yes	116	9.0	L
MEA	30% water	94	10.2	L

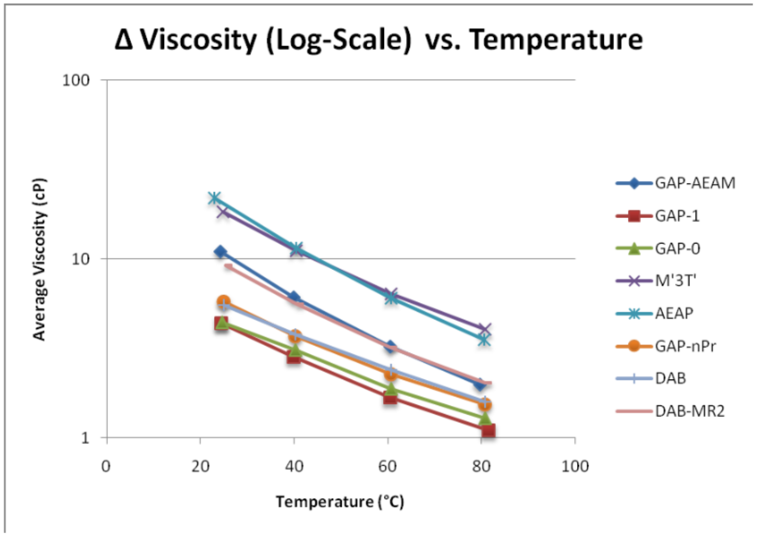
- Decreased viscosity, better reactivity
- Chemical and physical absorption

Optimizing Amino Siloxane

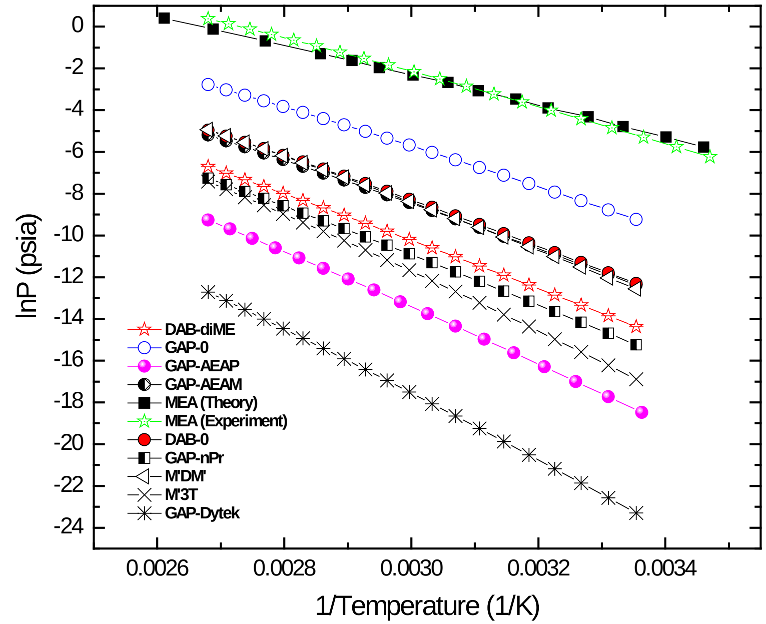
Solvent	CO_2 Wt Gain	% of Theory	ΔH_{rxn}(J/g)
	10.2	115	1596
	15.9	101	1168
	11.8	90	948
	8.6	108	1303
	8.2	116	1223
	5.4	84	1105
	5.6	60	1838

- Unhindered primary amines are best for capture; hindered amine reduces ΔH_{rxn}

Physical Properties



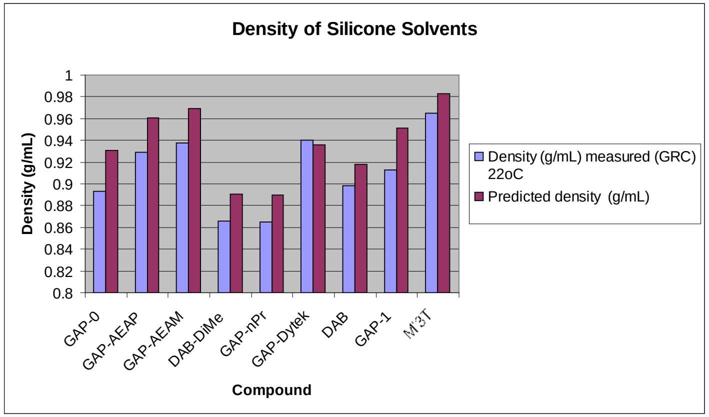
Viscosity



Vapor pressure

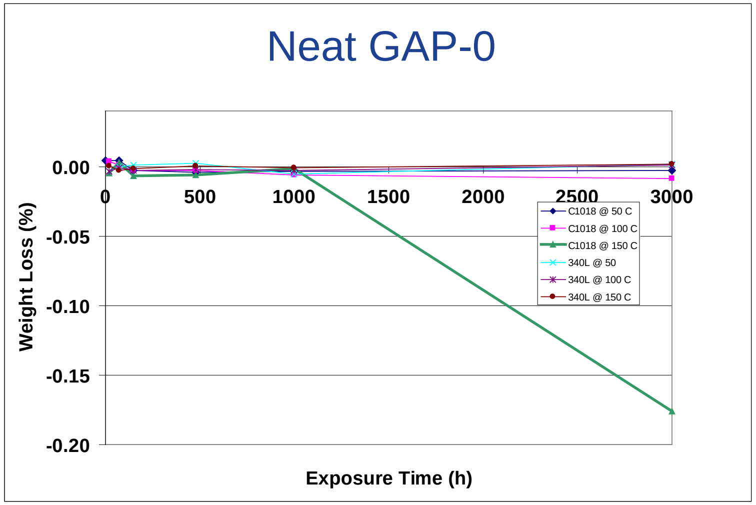
	Experimental (J/g)	Predicted (J/g)
MEA	1647 +/- 104	1550
1-amino-2-propanol (β)	1484 +/- 124	1464
2-amino-1-propanol (α)	1223 +/- 110	1265

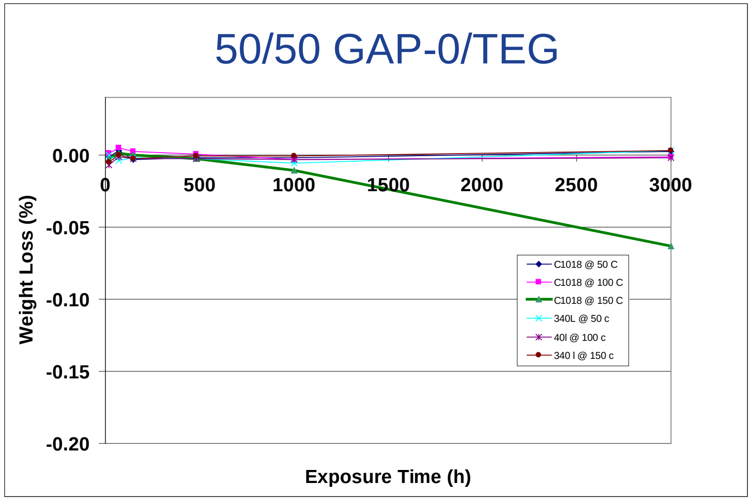
ΔH reaction

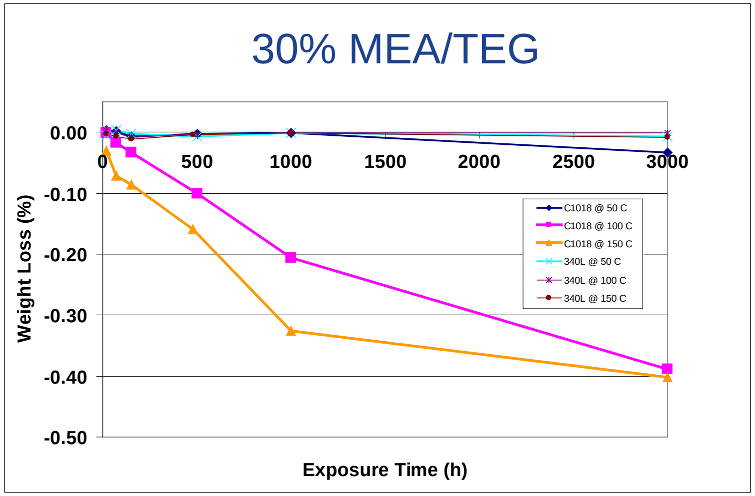


Density

Corrosion Studies



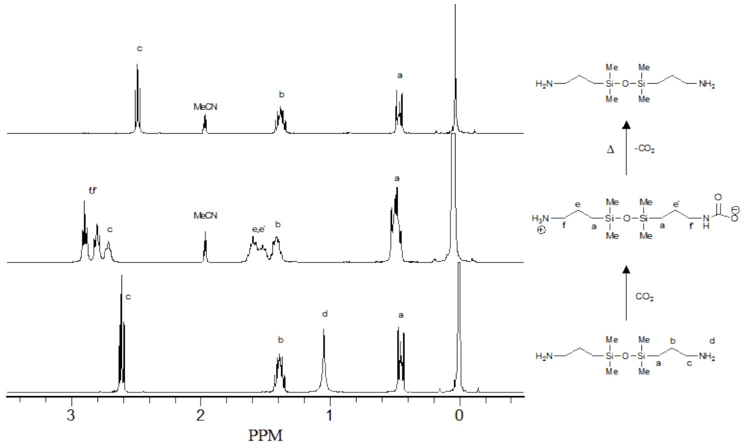




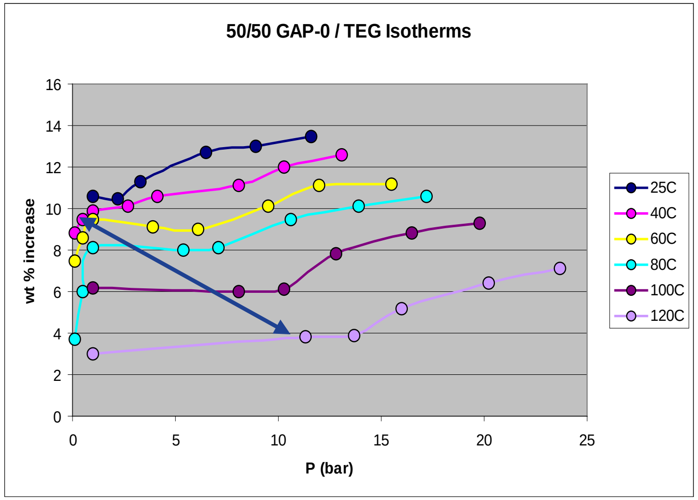
- SS coupons stable in all solvent systems
- Carbon steel stable in neat GAP-0 to 1000 h
- Weight loss/corrosion seen with carbon steel in GAP-0/TEG and large effect with 30% MEA/TEG

imagination at work

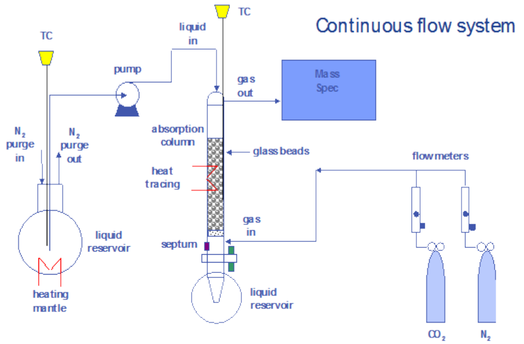
Properties

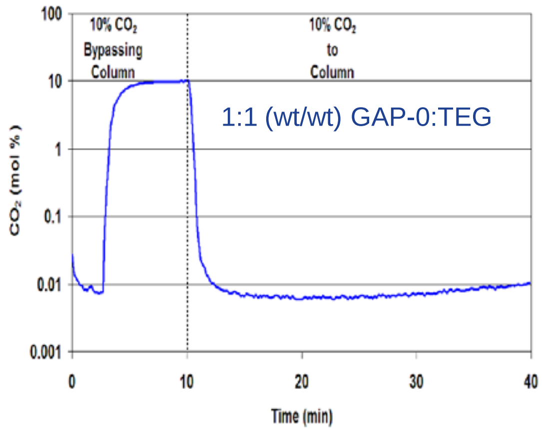


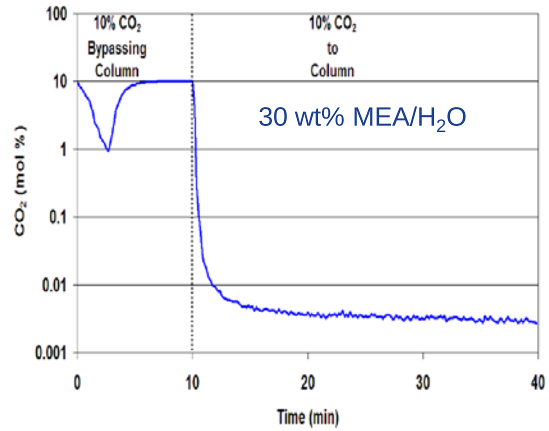
Thermal reversibility



Isotherms



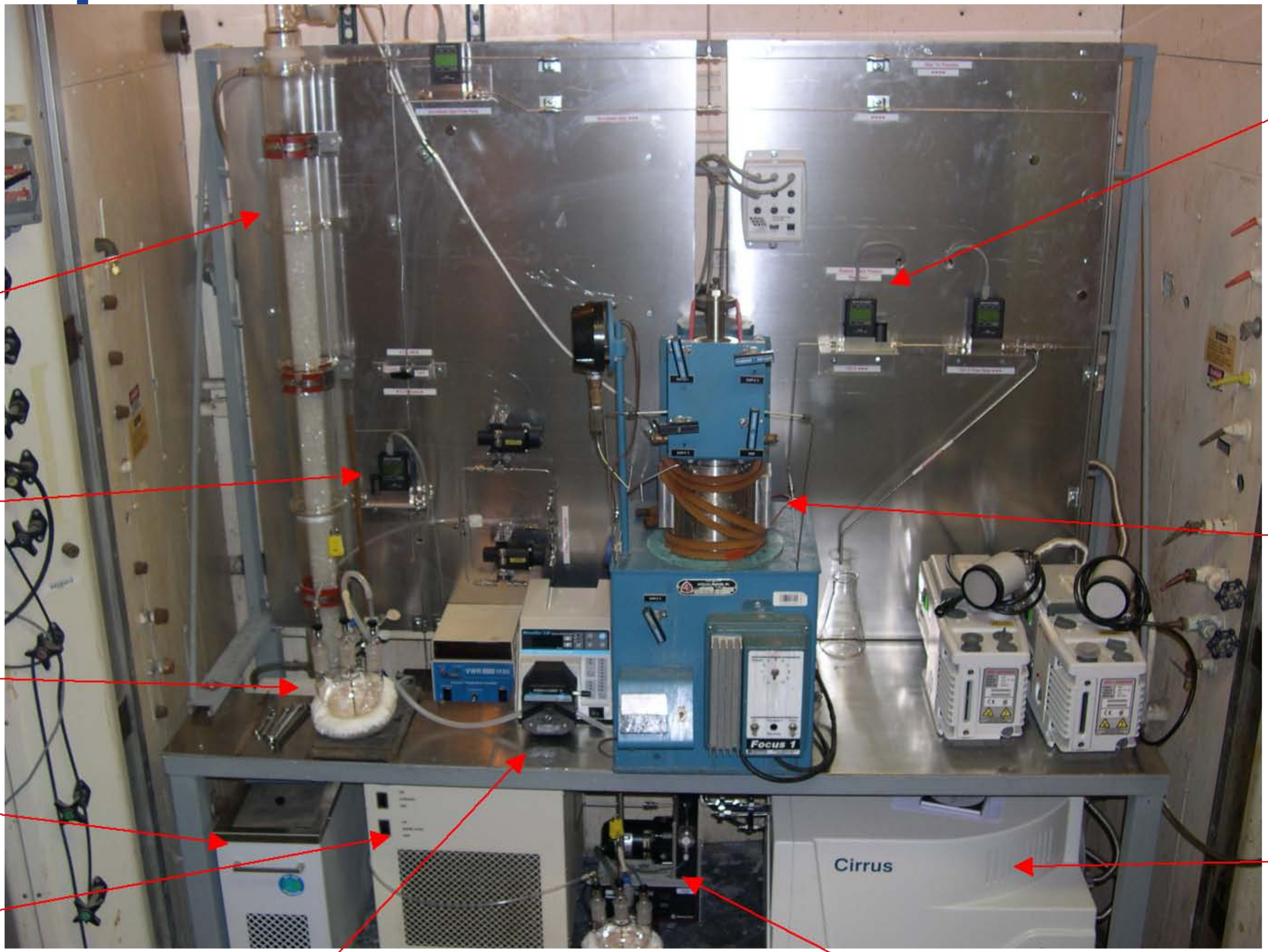




Continuous absorption

imagination at work

Scale-up



- Continuous absorption/desorption lab scale unit

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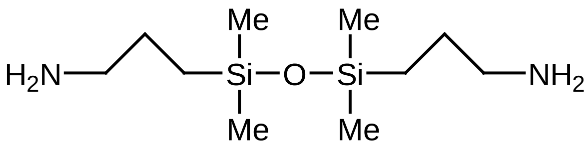
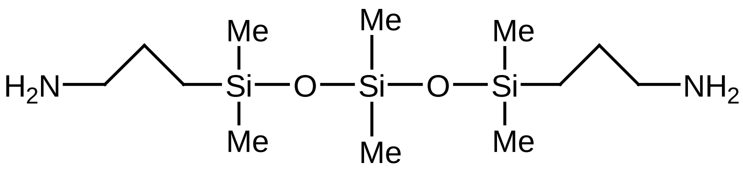
Continuous Absorption/Desorption



GAP-0

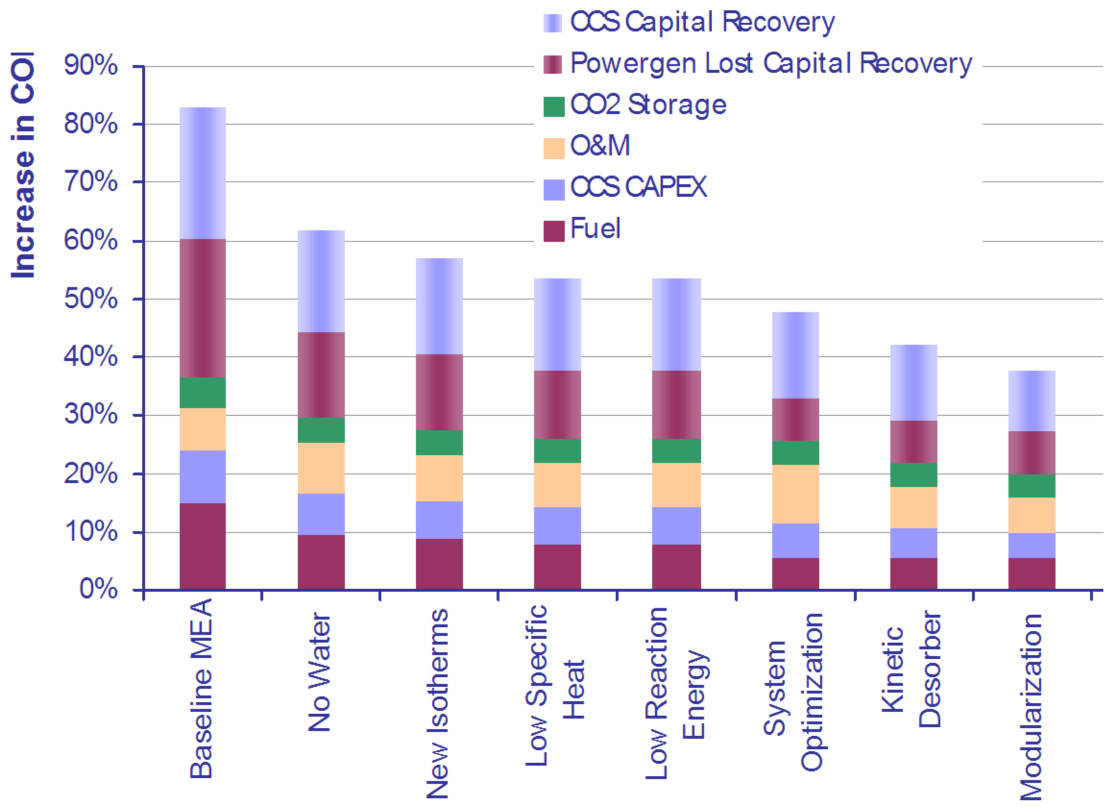


GAP-1

- Eliminated precipitation in system
- Retain ~10% CO_2 absorption at 40 ^oC
- Regeneration of solvent on desorption
- Isotherms nearly identical to GAP-0
- Currently seeing ~3% dynamic loading at operating conditions
- Looking at higher desorption temperatures

imagination at work

COE Waterfall



- Calculations based on isotherm data
- Modeling in progress for continuous data
- Large advantage maintained with anhydrous system
- Decreased capture capacity and lower pressure will impact COE

Summary

- Designed novel CO_2 capture solvent system
- Developed accurate process and COE models
- Prepared and screened aminosilicones
- Modeled and measured physical properties of solvents
- Confirmed continuous CO_2 absorption capability of solvent
- Demonstrated continuous absorption and desorption of CO_2
- Regeneration of solvent demonstrated
- Found that corrosivity of new solvent $\leq$ MEA after 4 months
- Minimal thermal degradation after 2 months @ 120 ^oC
- Calculating COE of GEN 2 solvent from continuous data

Next Steps

- Explore higher desorption temperatures
- Determine effects of water and flue gas contaminants
- Examine variations in flow rates and absorption temperatures
- Build larger scale system
- Obtain scale-up information
- Gather process design data
- Continue to document results

Documentation

- Patent Applications
  - US 2010/0158777
  - US 2010/0154639
  - Dockets 242793, 238253, 238260
- Publications
  - Fuel Preprints, **2010**, 282.
  - ChemSusChem **2010**, *3*, 919.
  - J. Phys. Chem. A. (submitted)
  - J. Phys. Chem. A. (in preparation)
  - J. Org. Chem. (in preparation)
- Presentations
  - 239th ACS National Meeting, March 2010
  - 43rd Silicon Symposium, May 2010
  - AIChE National Meeting, November 2010
  - Pacifichem 2010, December 2010

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