Pilot-Scale Silicone Process for Low-Cost CO_2 Capture

GE Global Research

DOE Award: DE-FE0026498

Final Report
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Acknowledgments:
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Agenda

- **Program Overview..** Feasibility study for 10 MW_e demo
- **GE Aminosilicone..** Water lean CO_2 Capture Solvent
- **Solvent Manufacturing..** Wacker qualified
- **Host Evaluation..** Criteria to run water-lean solvent
- **Techno-economic Analysis..** 20 % Cost-out vs. MEA
- **Technology GAP Analysis..** Solvent management & Gen 2 Solvent

Overview

Large Scale Pilot Test of Aminosilicone Solvent for CO_2 Capture: Phase 1

Technology Demonstration Planning

Project Objective: *Develop project definition and preliminary design for 10+MWe pilot scale testing of the Aminosilicone CO_2 capture solvent technology.*

2008–2010
Lab

Design and Optimize Process

2010–2013
Bench Scale

Establish Scalability and Commercial Value

2014–2015
Small Pilot

0.5 MWe Demonstration

2015–
Large Pilot

10 MWe Demonstration

Technical Approach

- Host site evaluation
- Solvent acquisition
- Process model & equipment design
- Environmental health and safety

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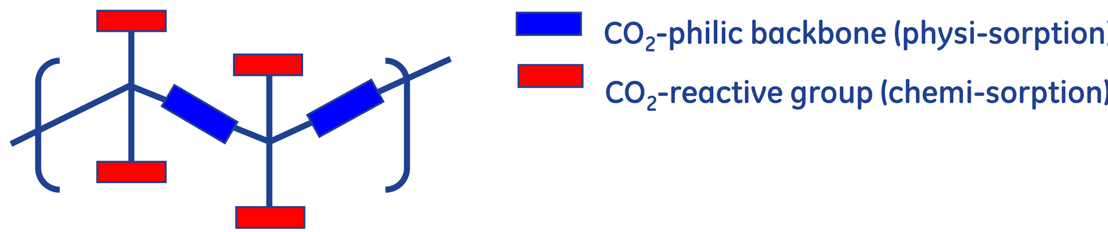
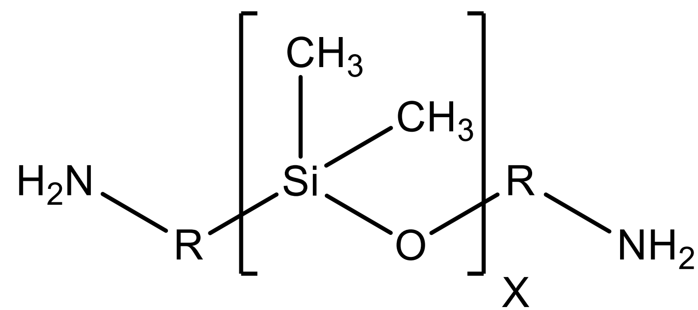
New Solvent System.. Amino-Silicone

Desired Solvent Properties for cost effective CO_2 capture:

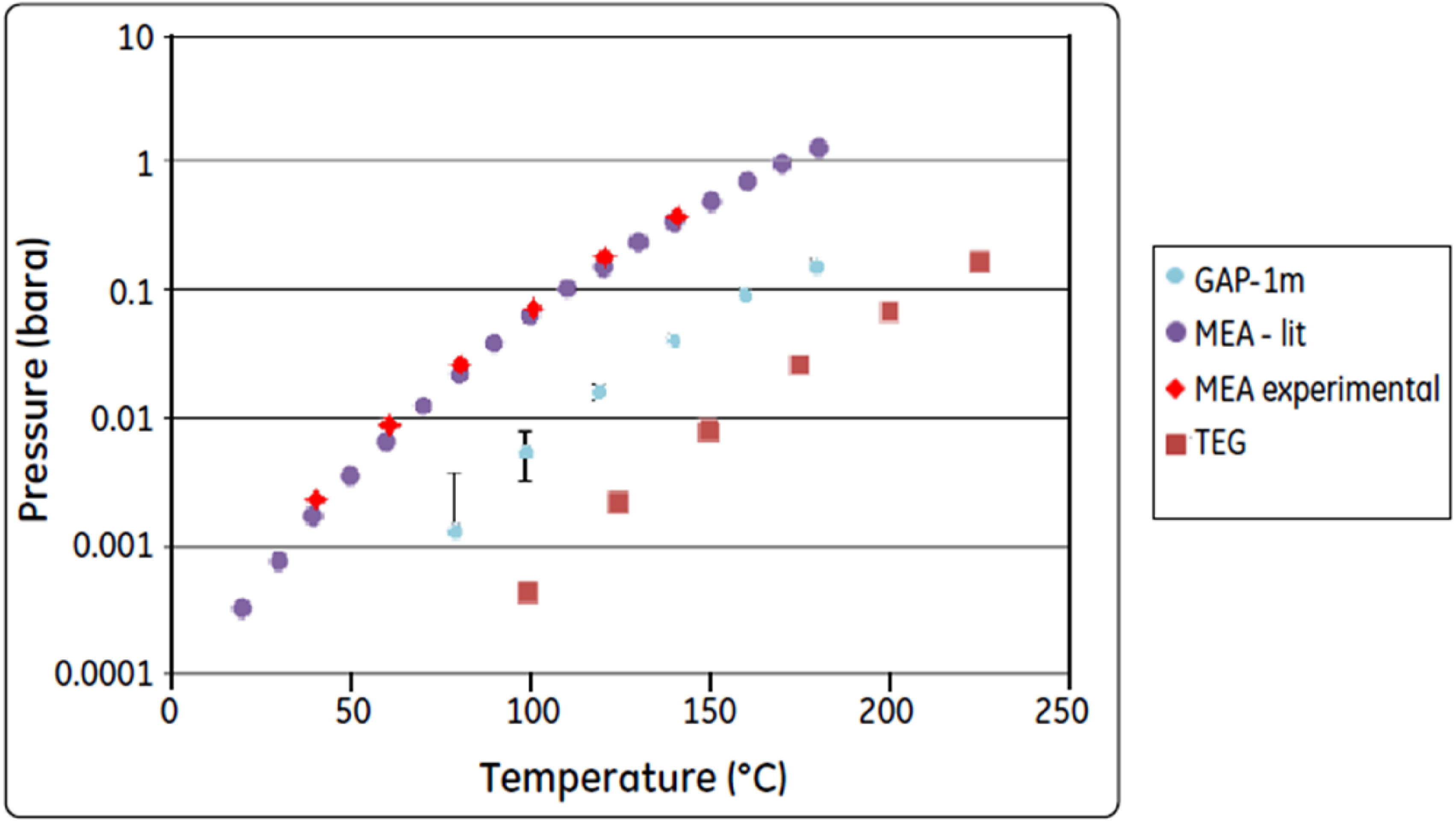
- Low/no water
- Liquid carbamate salt
- Thermal stability
- High CO_2 loading
- High desorption pressure
- Low volatility
- High reaction rates



Aminosiloxanes



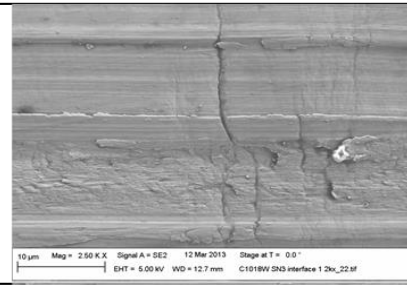
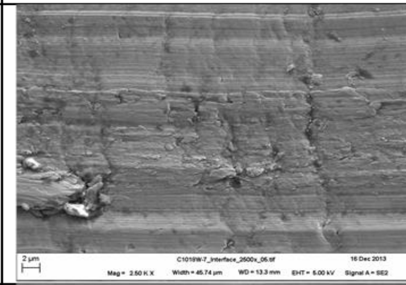
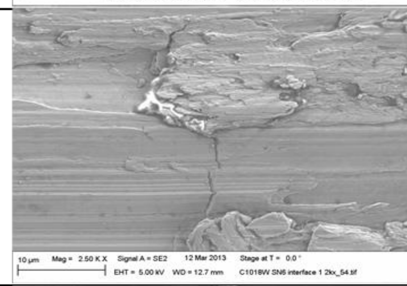
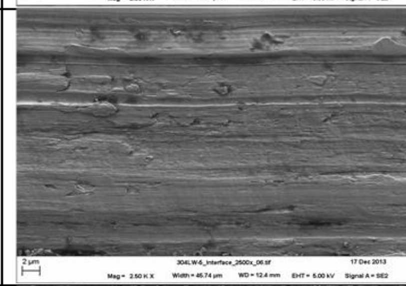
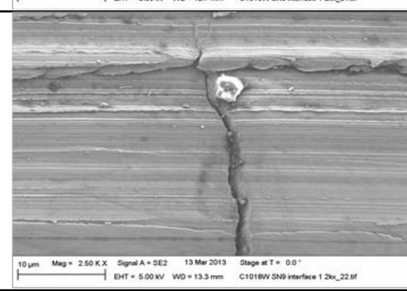
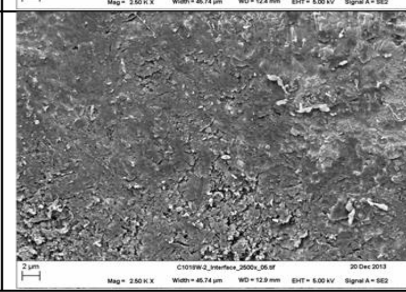
Amino-Silicone.. Volatility



Low Volatility.. Simplified Desorption Process

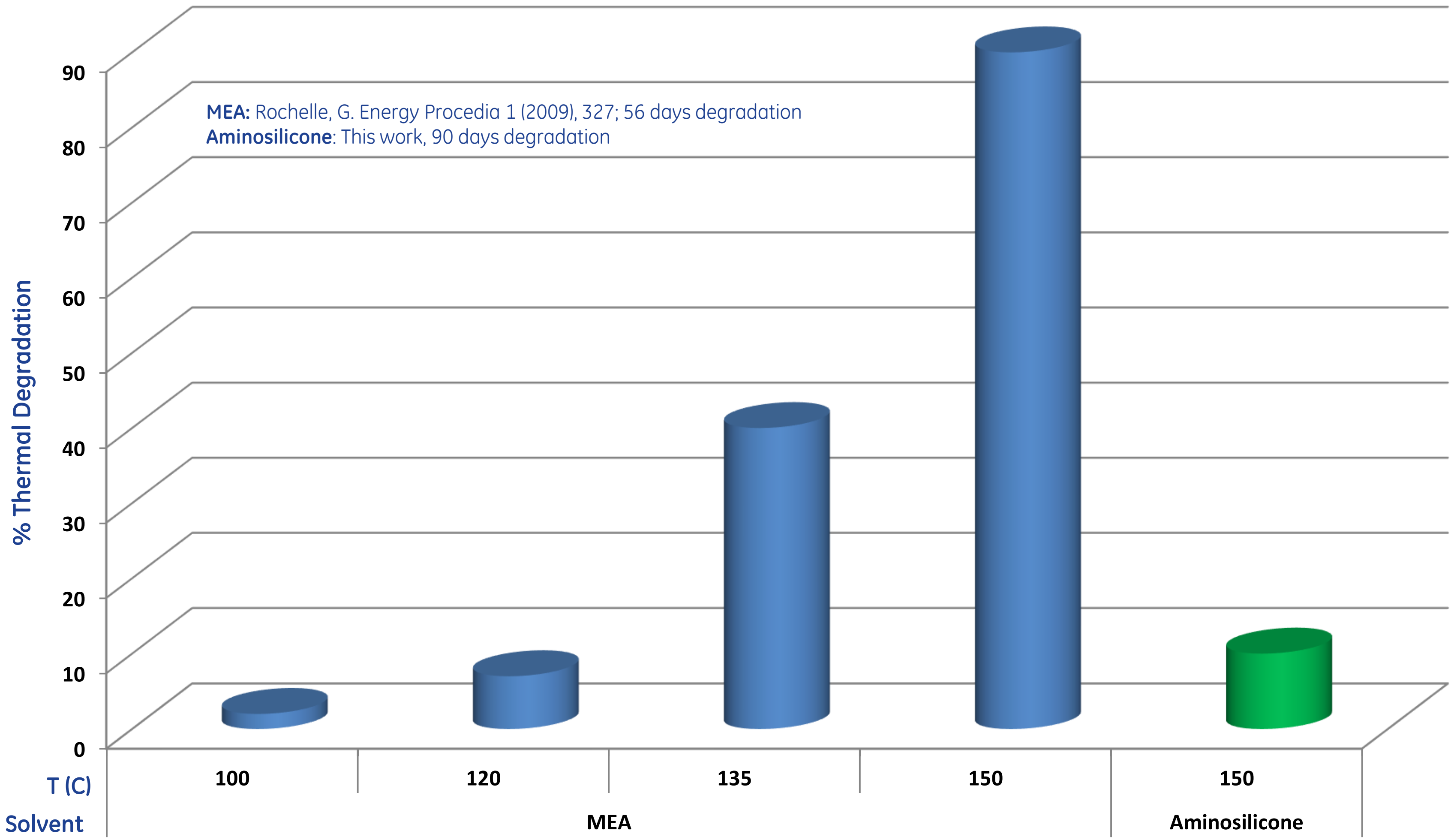
Reduced Solvent Loss

Amino-Silicone.. Corrosion

Location / Metal Type	Conditions	Unexposed samples (interface images)	Exposed samples (interface images)	Corrosion Rate (µm/yr)
Lean Storage / C1018	~380 hours at ~34 °C and ~6138 hours at ~25 °C			1.27
Absorber Sump / C1018	~389 hours at ~52 °C and ~6138 hours at ~25 °C			0.47
Desorber / C1018	~388hours at ~145 °C and ~6138 hours at ~25 °C			2188

Reduced Corrosion.. Corrosion Inhibitor not Required

Amino-Silicone (Lean).. Thermal Stability



Improved thermal stability for **Lean** Solvent..

Amino-Silicone (Rich).. Thermal Stability

$$\underset{\text{Lean Solvent}}{R\text{-}NH_2} + CO_{2\,(g)} \rightleftharpoons \underset{\text{Rich Solvent}}{R - NH - COOH}$$

$$R - NH - COOH \xrightarrow{+\,R\text{-}NH_2} \underset{\text{Urea}}{R - NH - CO - NH - R} \quad \left(\xleftarrow{+\,H_2O}\right)$$

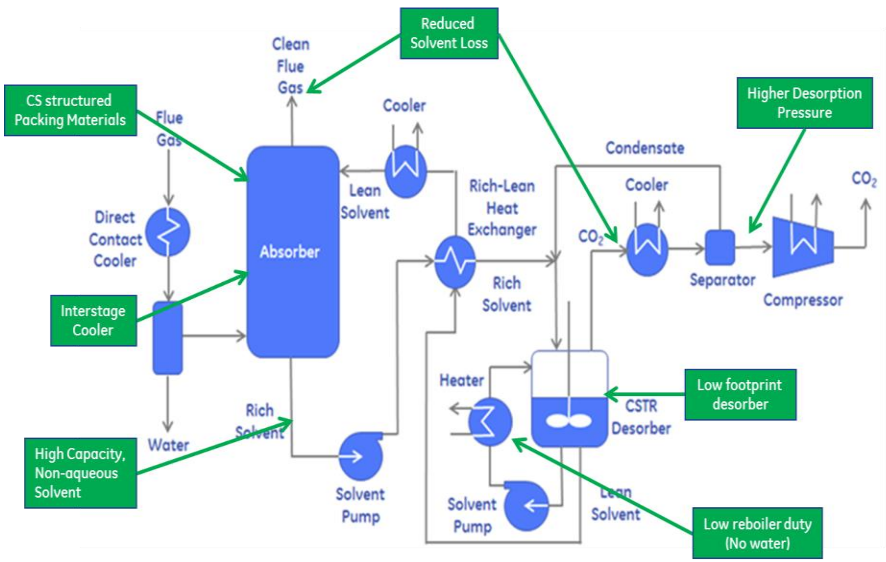
$$\text{Degradation Rate} \sim T \cdot \frac{1}{H_2O} \cdot Rich$$

Thermal stability for **Rich** Solvent ..

Lower T & Controlled Water Addition

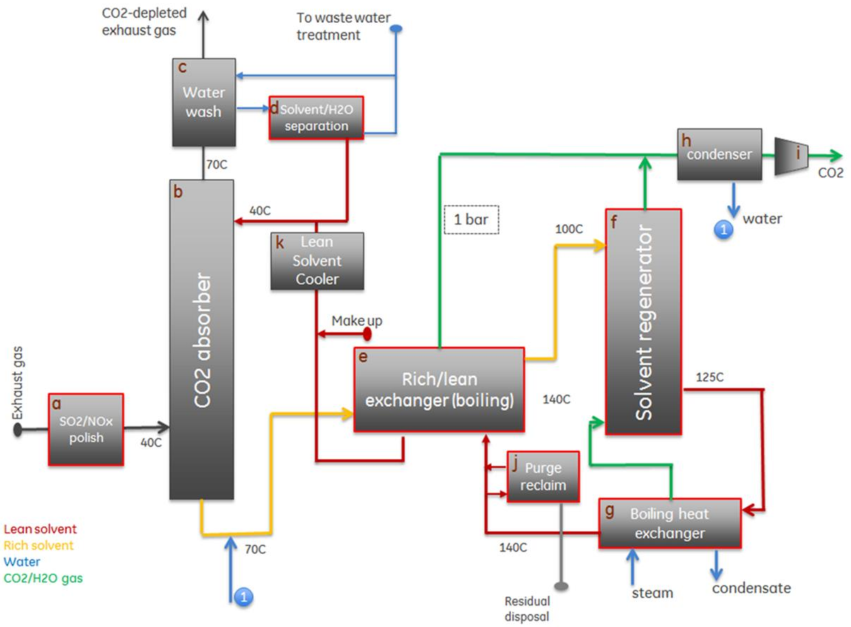
Desorption Options.. CSTR vs. SSC

CSTR Desorber



- ✓ Lower CAPEX and footprint
- ✓ Single Stage Desorption
- \- H_2O < 5 wt.%

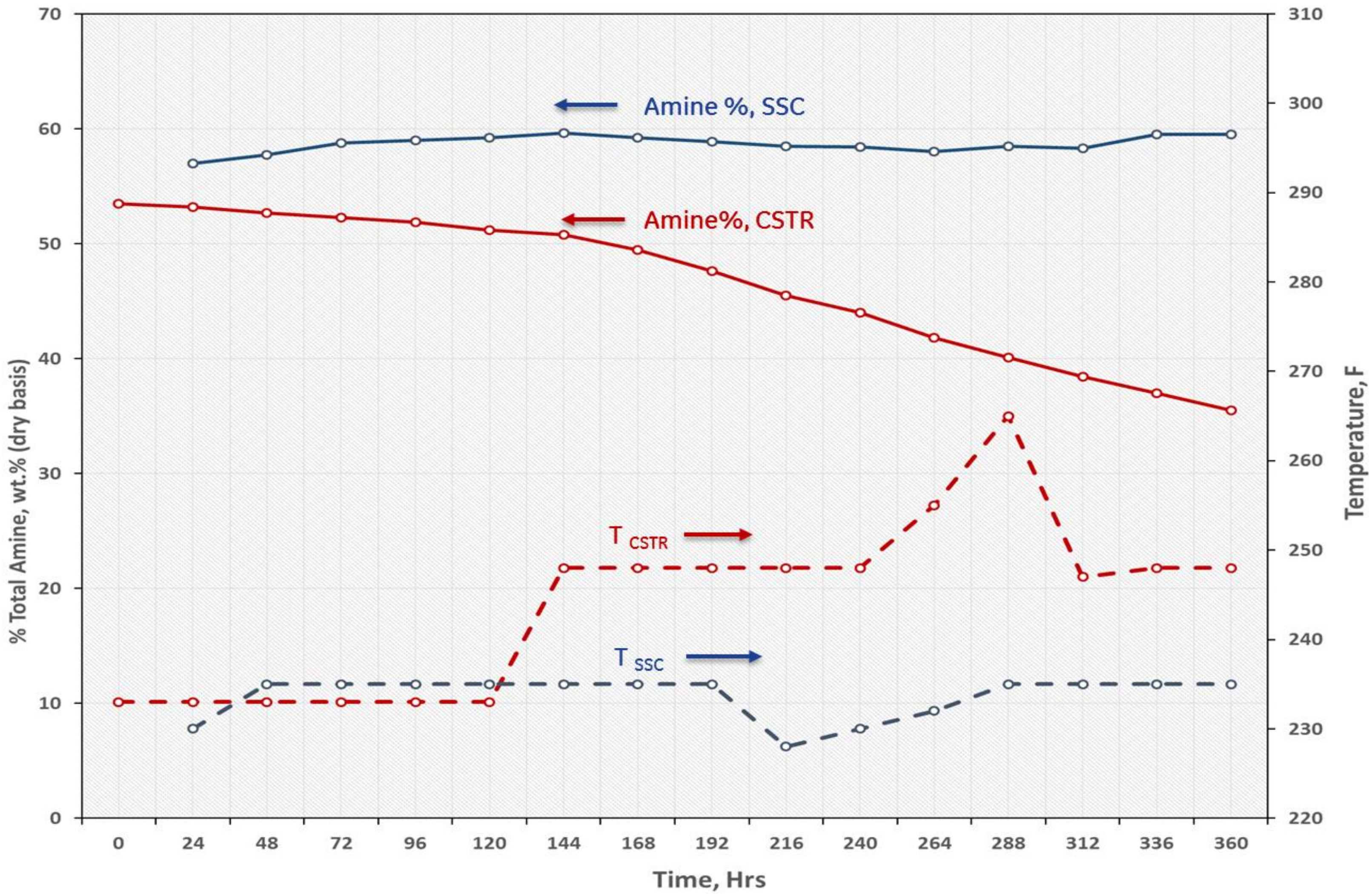
Steam Stripper Column (SSC)



- ✓ Multi-stage desorption
- ✓ Lower desorption temperature

Amine Degradation.. CSTR vs. Steam Stripping

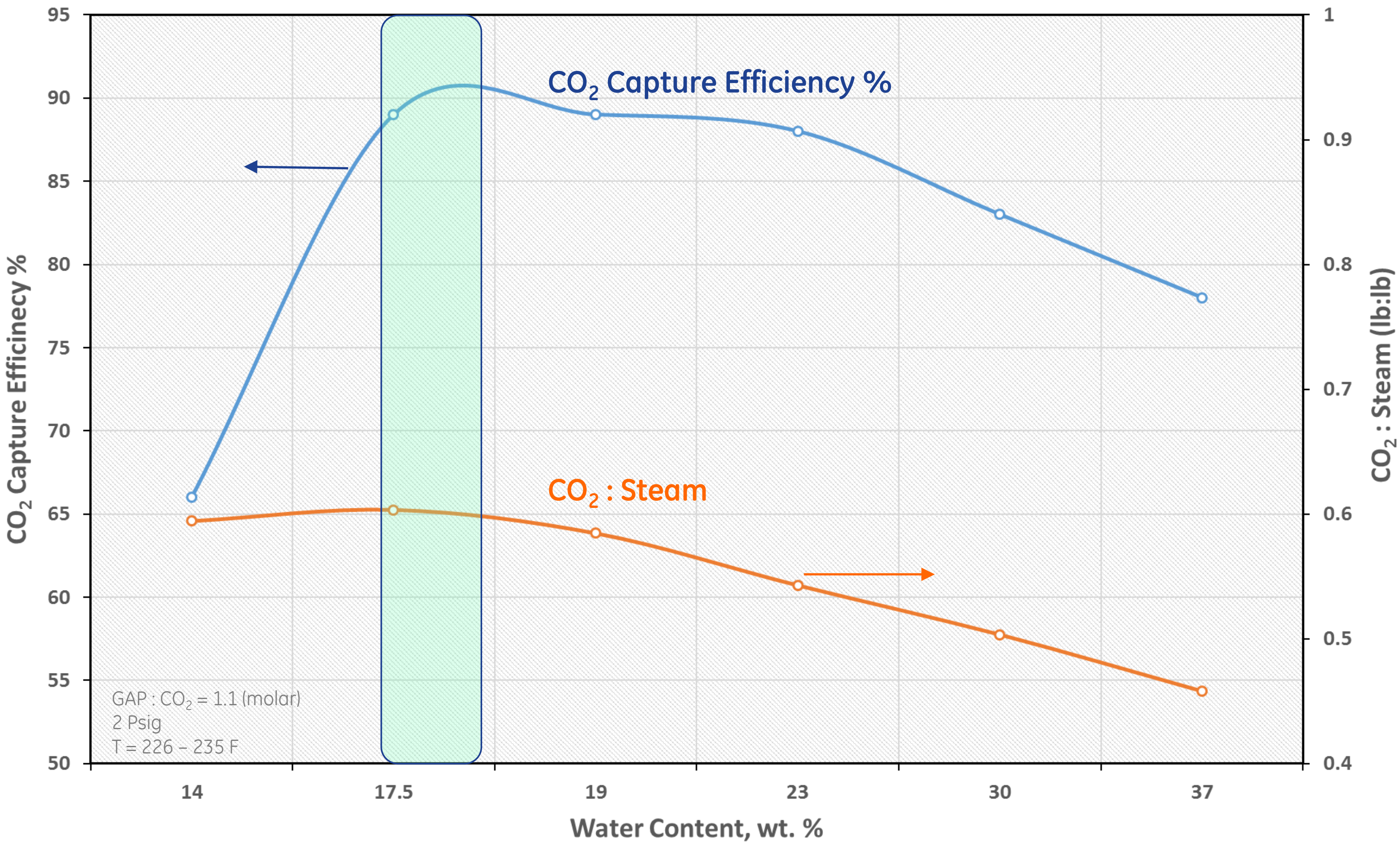
NCCC (0.5 MW)



Amine degradation: SSC << CSTR

0.5 MW NCCC.. Steam Duty = f (H_2O)

NCCC (0.5 MW)



Capture Efficiency & CO_2: Steam optimum at 18 wt. % H_2O

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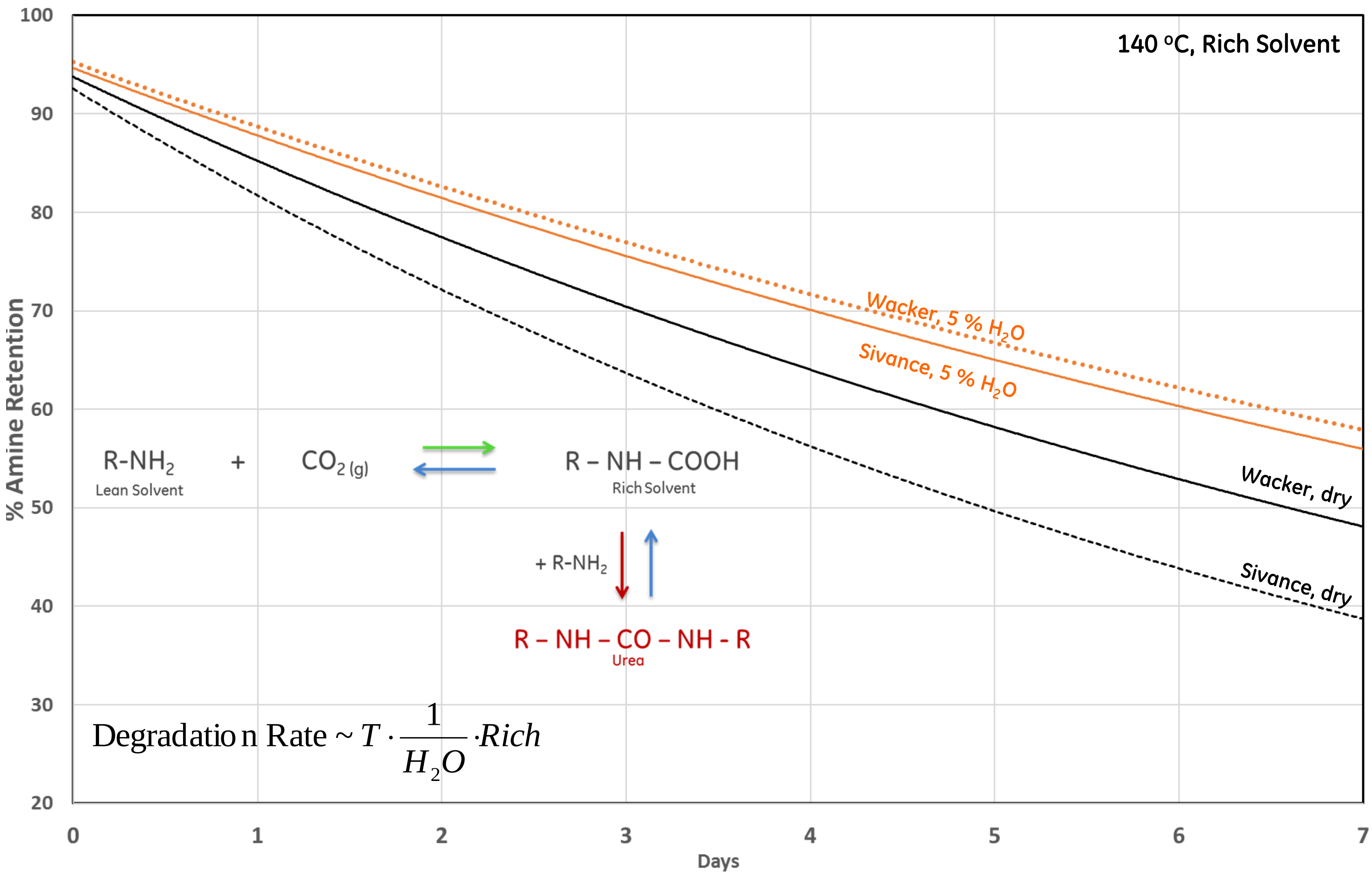
Solvent Evaluation Protocol.. Wacker vs. Sivance*

- **Accelerated Thermal Degradation..** Lab evaluation
- **Oxidation stability..** Lab & 2 KW_e evaluation
- **CO_2 Capture Efficiency..** 2KW_e evaluation
- **Hydrothermal stability..** Steam stripper glass column

*Sivance - Solvent Manufacturer for NCCC

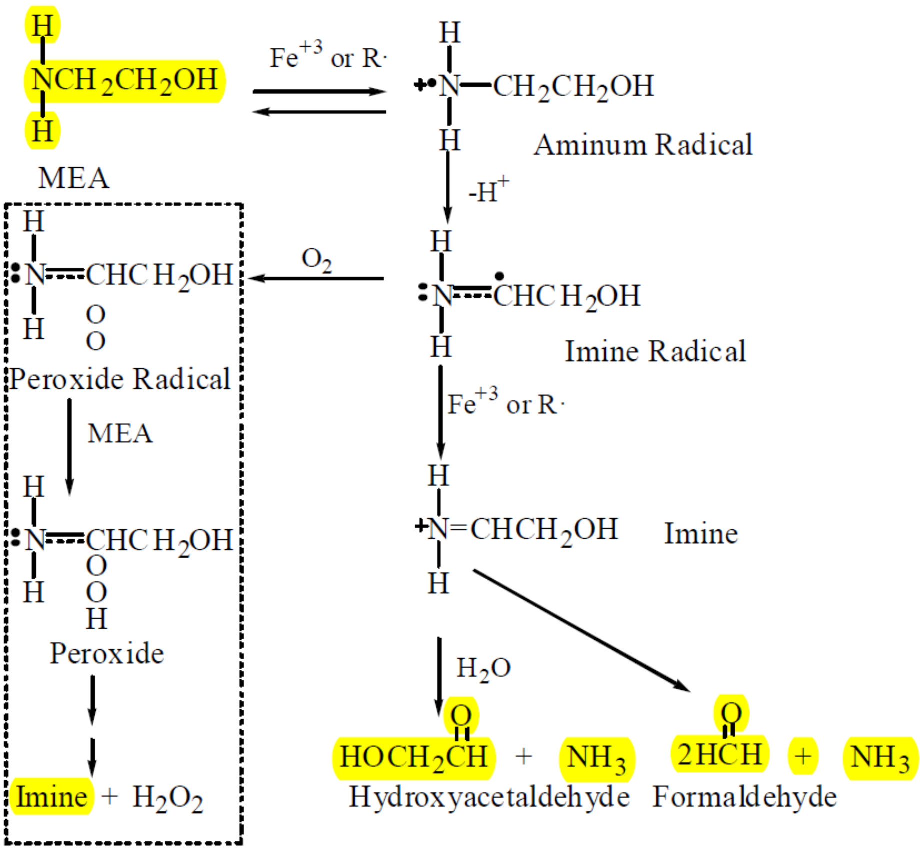
Thermal Degradation.. Lab evaluation



$$\text{Degradation Rate} \sim T \cdot \frac{1}{H_2O} \cdot Rich$$

✓ **Accelerated Thermal Degradation**: Wacker ~ Sivance

Oxidation.. Ammonia Generation

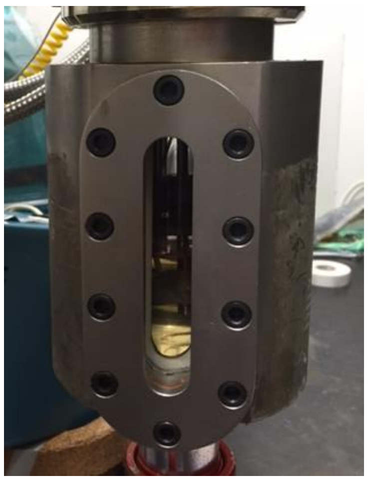


Rochelle, 2010

- Formation of ammonia is an quantifier for thermo-oxidation
- Iron is a catalyst

Oxidation (lab).. Experimental Set-up

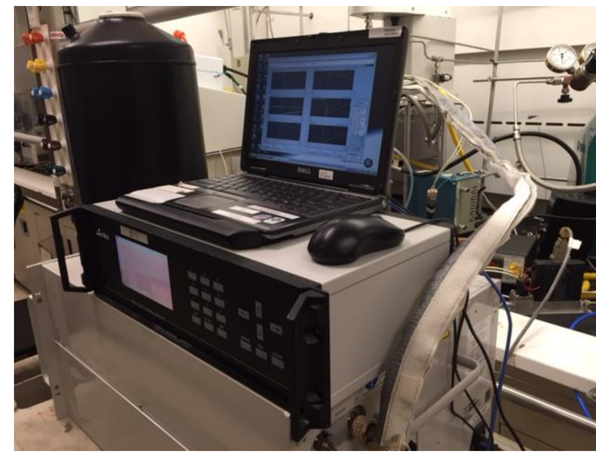
Parr Reactor



- 400 mL windowed Parr reactor
- Mechanical agitation
- 200 mL 60 wt. % GAP-1 / 40 wt. % TEG
- Gases were bubbled through the GAP-1 / TEG solution via dip-tube
- Temperature controlled via internal coil

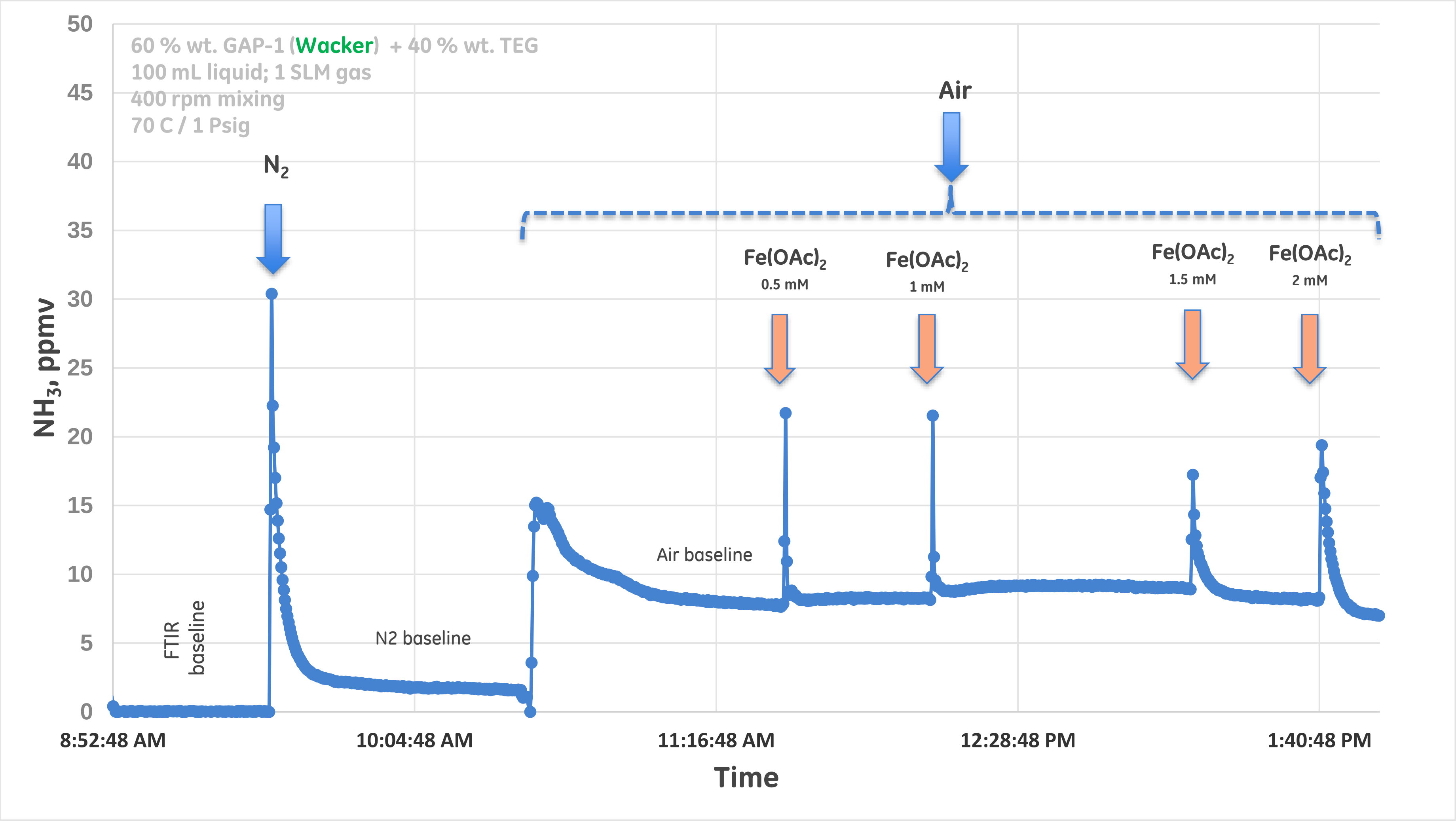
FTIR and Gas Delivery system

- Heated transfer line at 190 C



- FTIR (MKS): analysis of acetadeldehyde, formaldehyde ammonia, propylene
- Gas Delivery System: N2 and air via MKS MFC

Oxidation (lab).. Fe^{2+} doping



Oxidation (lab).. Sivance vs. Wacker

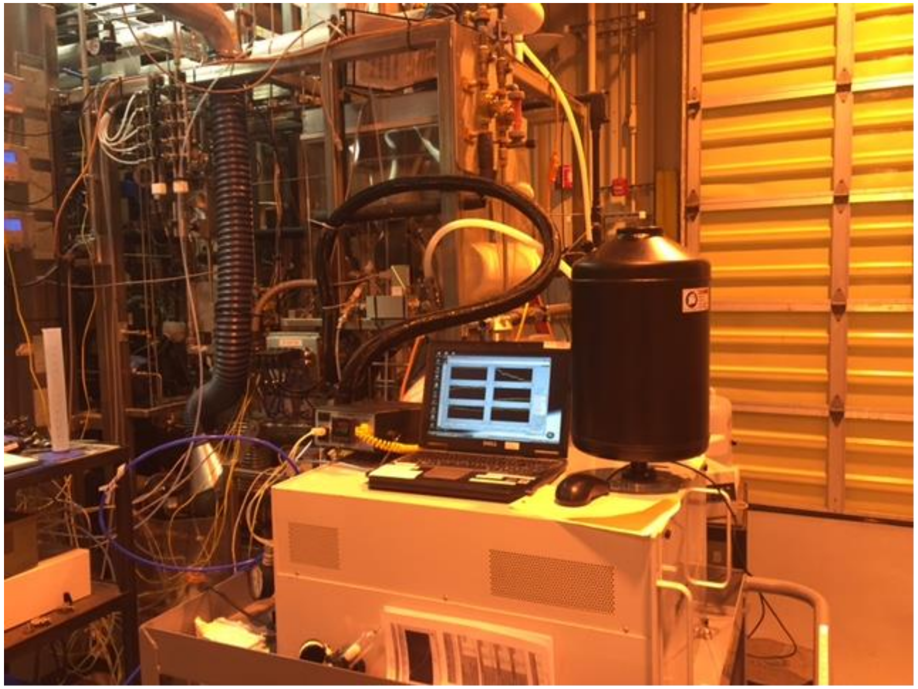
60 % wt. GAP-1 + 40 % wt. TEG
100 mL liquid; 1 SLM gas
400 rpm mixing
70 C / 1 Psig

	Sivance			Wacker		
	NH3, ppmv		NH3, mol/min*10^4	NH3 ppmv		NH3 mol/min * 10^4
	Average	Max	Average	Average	Max	Average
Baseline, FTIR	0	0	0	0	0	0
N2, initial	3	1005	0.1	1	30	0.04
Air	130	212	5.8	8	15	0.4
Air & Fe2+ (2.5 mM)	140	203	6.2	8	20	0.4

✓ **Rate of oxidation (lab)**: Wacker = 1/10 Sivance

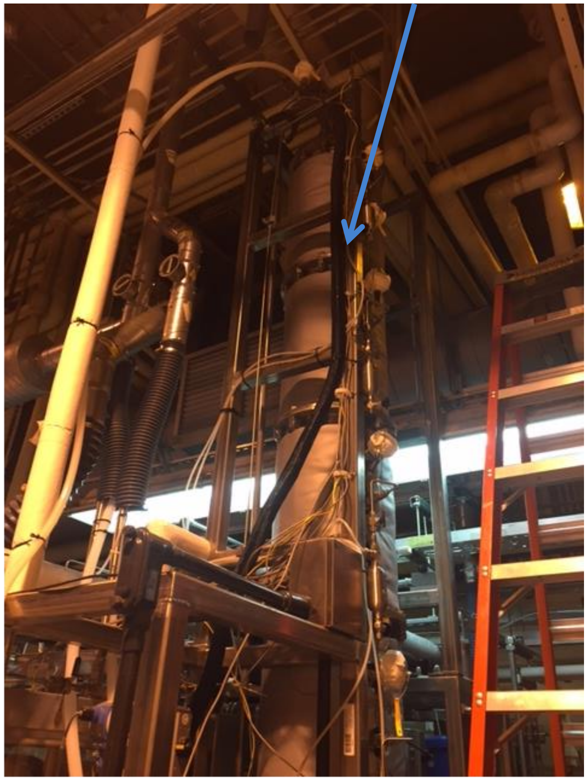
Oxidation (2kW skid).. Experimental Set-up

MKS FTIR installed on the skid



- Analysis: ammonia, acetaldehyde, propylene, formaldehyde

Heated FTIR Line –
Top of the absorber



- Heated transfer line at 190 C

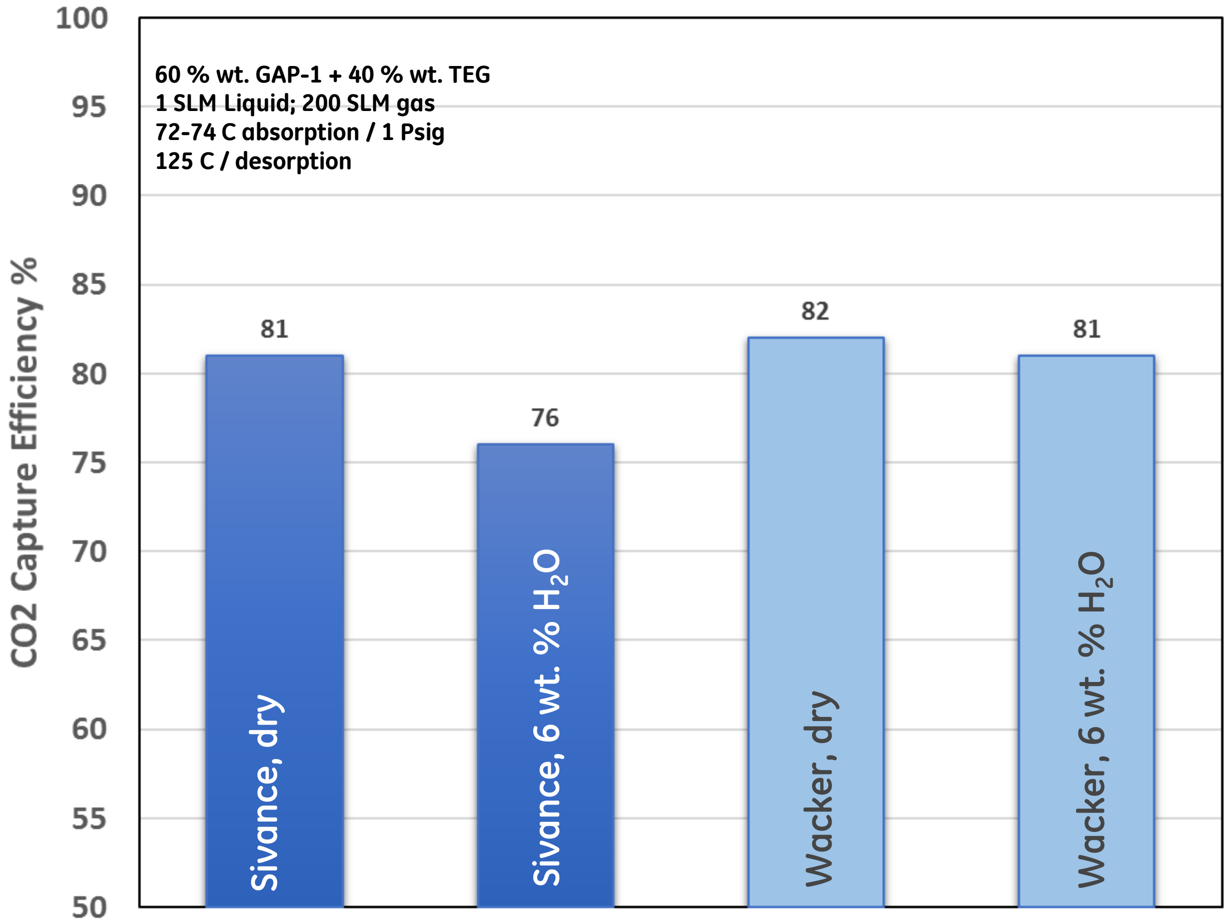
Oxidation (2kW Skid).. Sivance vs. Wacker

60 % wt. GAP-1 + 40 % wt. TEG
1 SLM Liquid; 200 SLM gas
72-74 C absorption / 1 Psig
125 C / desorption

	Sivance		Wacker	
	NH3, ppmv		NH3 ppmv	
	Dry	Wet	Dry	Wet
Baseline, FTIR	0	0	0	0
5 % O2, 12 % CO2	60	59	7	6
20 % O2, 3 % CO2	NA	NA	NA	4

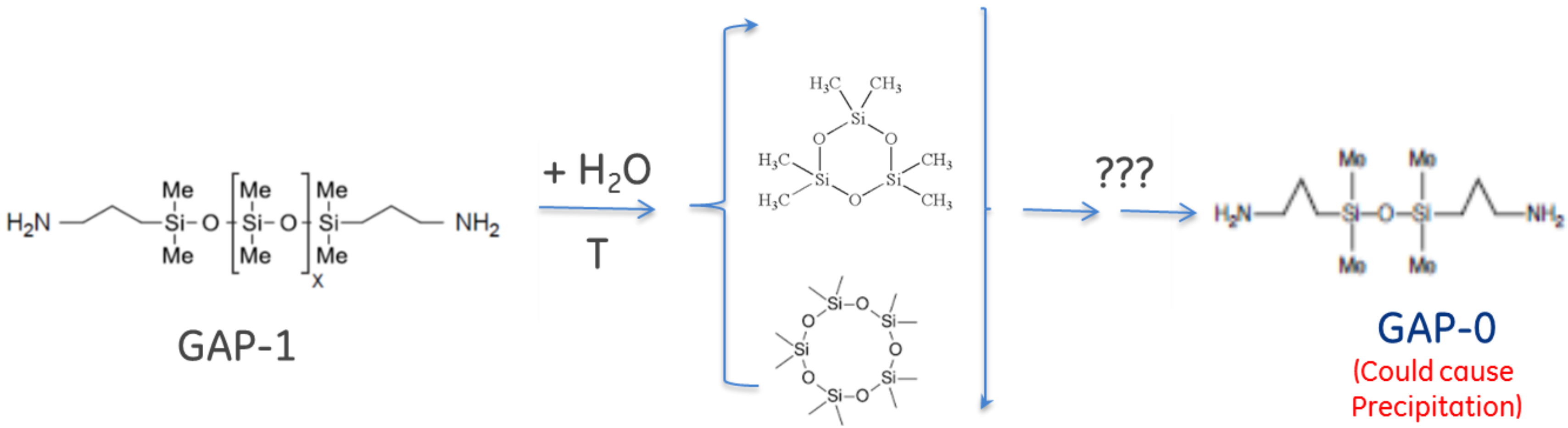
- ✓ **Rate of oxidation (2 kW_e):** Wacker = 1/10 (Sivance)
- ✓ **Wacker GAP-1_m:** not sensitive to elevated O_2 % (< 20%)

CO_2 Capture (2kW Skid).. Sivance vs. Wacker



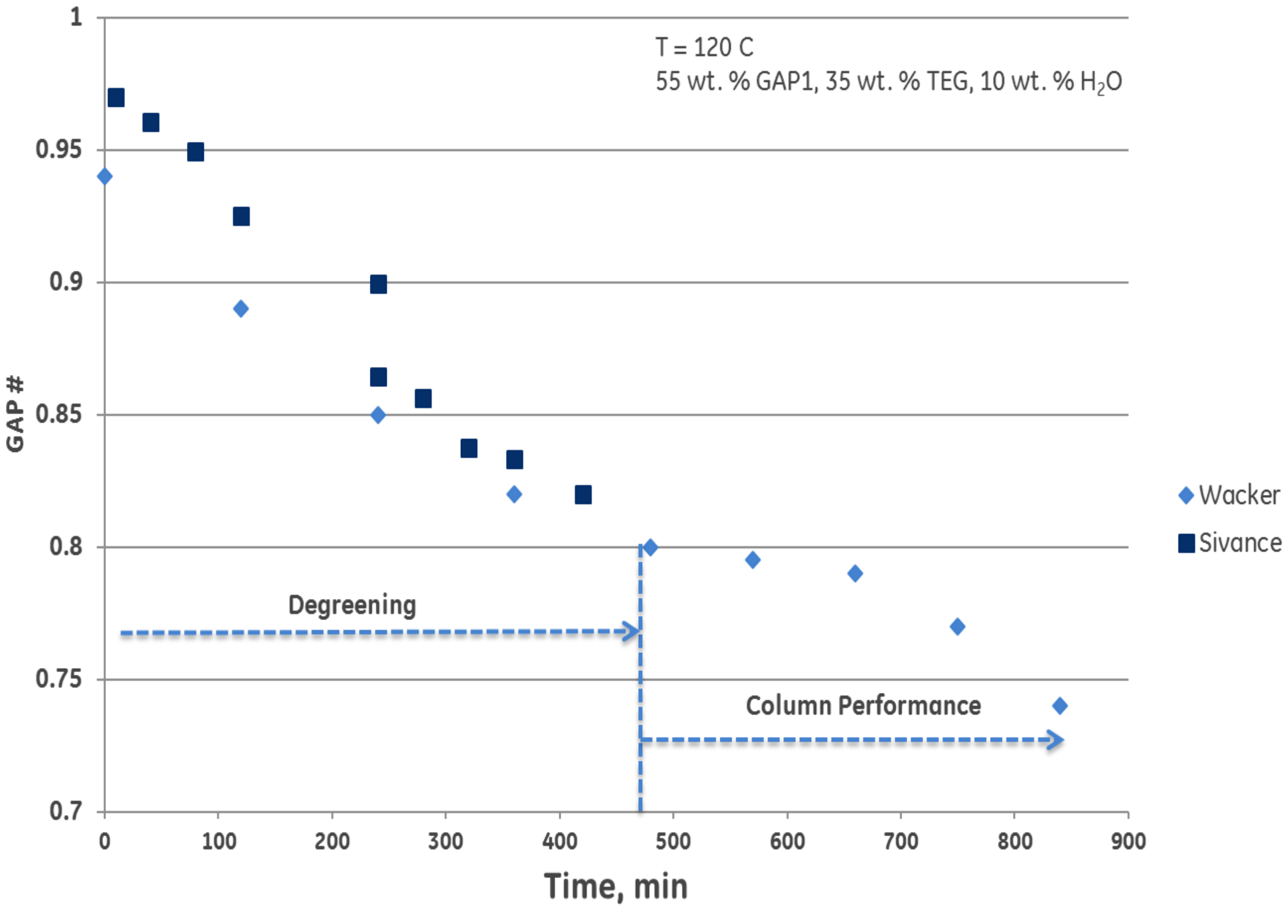
✓ **CO_2 Capture Efficiency (2 kW_e Bench)**: Wacker ~ Sivance

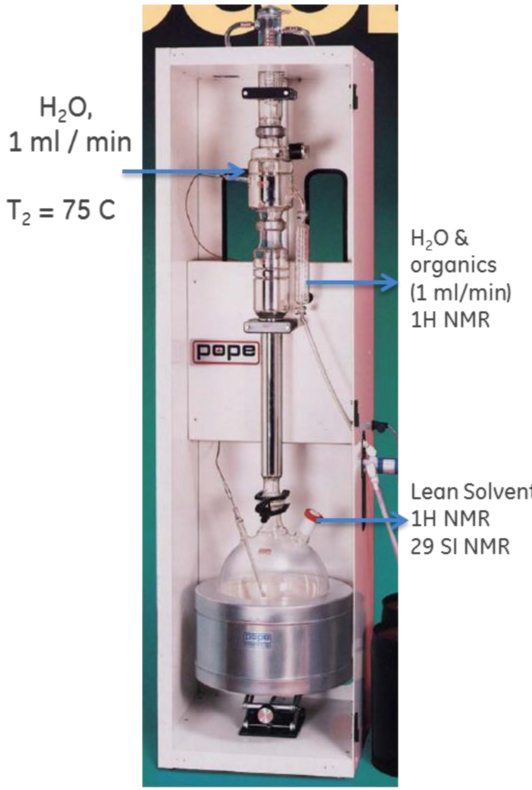
Hydrothermal Stability.. Early equilibration



✓ **Early Equilibration..** Reduction in GAP# without losing CO_2 Capacity

Hydrothermal Stability (lab).. Wacker vs. Sivance





T = 120 C
55 wt. % GAP1, 35 wt. % TEG, 10 wt. % H_2O

✓ **Hydrothermal Equilibration..** Wacker ~ Sivance

Wacker Qualification.. Summary

- **Thermal-degradation (lab)..** Wacker ~ Sivance

- **Oxidation**
  - **Lab (Parr reactor, 70 °C):**

    Wacker ~ 1/10 Sivance; no influence of Fe^{2+}
  - **Skid (2 kW, 1 ppm SO_2, L:G = 0.5; 125 °C desorption; 50-70 °C absorption):**

    Wacker (5 % O_2) ~ Wacker (20 % O_2)~ 1/10 Sivance (5 % O_2)

- **Hydrothermal Equilibration (lab)..** Wacker ~ Sivance

- **CO_2 Capture Efficiency (2 kW skid)..** Wacker ~ Sivance (80 %)

✓ Wacker Qualified as Supplier for GAP-1

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Host Evaluation.. Criteria to accommodate water-lean aminosilicone solvents

Unit Operation	Specifications
Absorber	Intercooling system to reject heat & maintain T < 70 ºC
Desorber	Steam stripping column with pre-flash system to reduce steam duty
MOC	Gaskets & seals compatible with GAP-1_m / TEG.
Water Management	Availability of water wash towers, partial and total condensers for precise water loading control. (Performance of the system is more sensitive to water content changes than the aqueous system.)
Heat Exchangers / Pumps	Designed to accommodate
Solvent Composition	% H_2O = 10 – 20 wt.%
Waste Water	System to collect all waste water for disposal

Minor modifications needed to typical aqueous pilots to accommodate water-lean aminosilicone solvents

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Techno-economical Analysis

- ***Scope:***

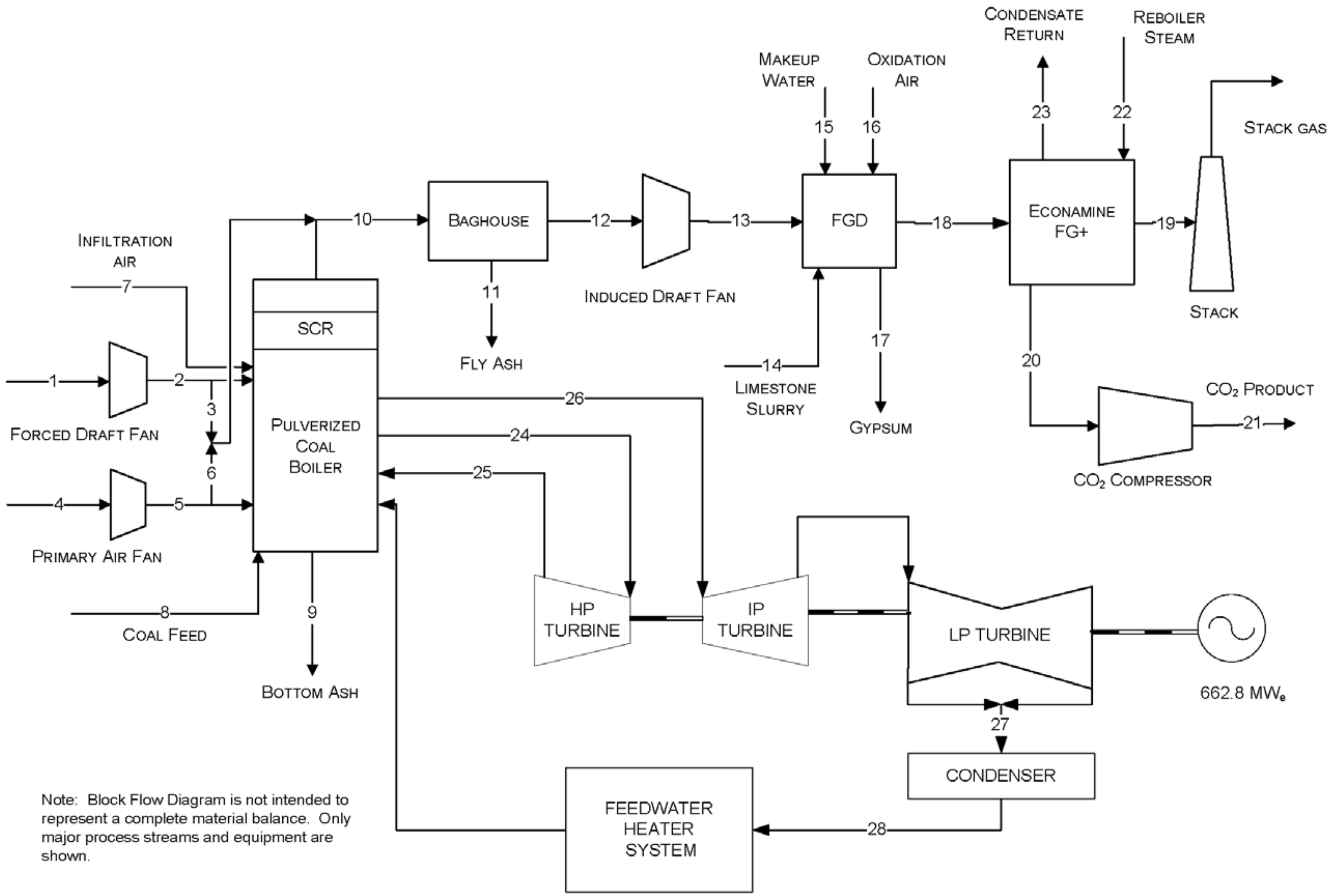
  Perform techno-economical comparison of the state-of-the art CO_2 capture technologies vs. aminosilicone solvent

- ***Methodology:***

  - Technologies Included: Enhanced Fluor Econoamine, KS-1 (MHI), MTR Membrane, TDA Adsorbent
  - Steam Conditions: Supercritical
  - Data for competitive technologies published by DOE/NETL

    (R. Stevens, 2012 NETL CO_2 Capture Technology Meeting)

Pulverized Coal Power Plant.. PFD Supercritical



Analysis Performed for Supercritical Coal Plant

Pulverized Coal Power Plant.. Evaluation Basis

	Case 11 w/o CO_2 Capture	Case 12 w/CO_2 Capture
Steam Cycle, MPa/°C/°C (psig/°F/°F)	24.1/593/593 (3500/1100/1100)	24.1/593/593 (3500/1100/1100)
Coal	Illinois No. 6	Illinois No. 6
Condenser pressure, mm Hg (in Hg)	50.8 (2)	50.8 (2)
Boiler Efficiency, %	88	88
Cooling water to condenser, °C (ºF)	16 (60)	16 (60)
Cooling water from condenser, °C (ºF)	27 (80)	27 (80)
Stack temperature, °C (°F)	57 (135)	32 (89)
SO_2 Control	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation
FGD Efficiency, % (A)	98	98 (B, C)
NOx Control	LNB w/OFA and SCR	LNB w/OFA and SCR
SCR Efficiency, % (A)	86	86
Ammonia Slip (end of catalyst life), ppmv	2	2
Particulate Control	Fabric Filter	Fabric Filter
Fabric Filter efficiency, % (A)	99.8	99.8
Ash Distribution, Fly/Bottom	80% / 20%	80% / 20%
Mercury Control	Co-benefit Capture	Co-benefit Capture
Mercury removal efficiency, % (A)	90	90
CO_2 Control	N/A	Econamine
Overall CO_2 Capture (A)	N/A	90.2%
CO_2 Sequestration	N/A	Off-site Saline Formation

DOE/NETL-2010/1397

Design basis according to DOE/NETL methodology

Pulverized Coal Power Plant.. Cost Estimation

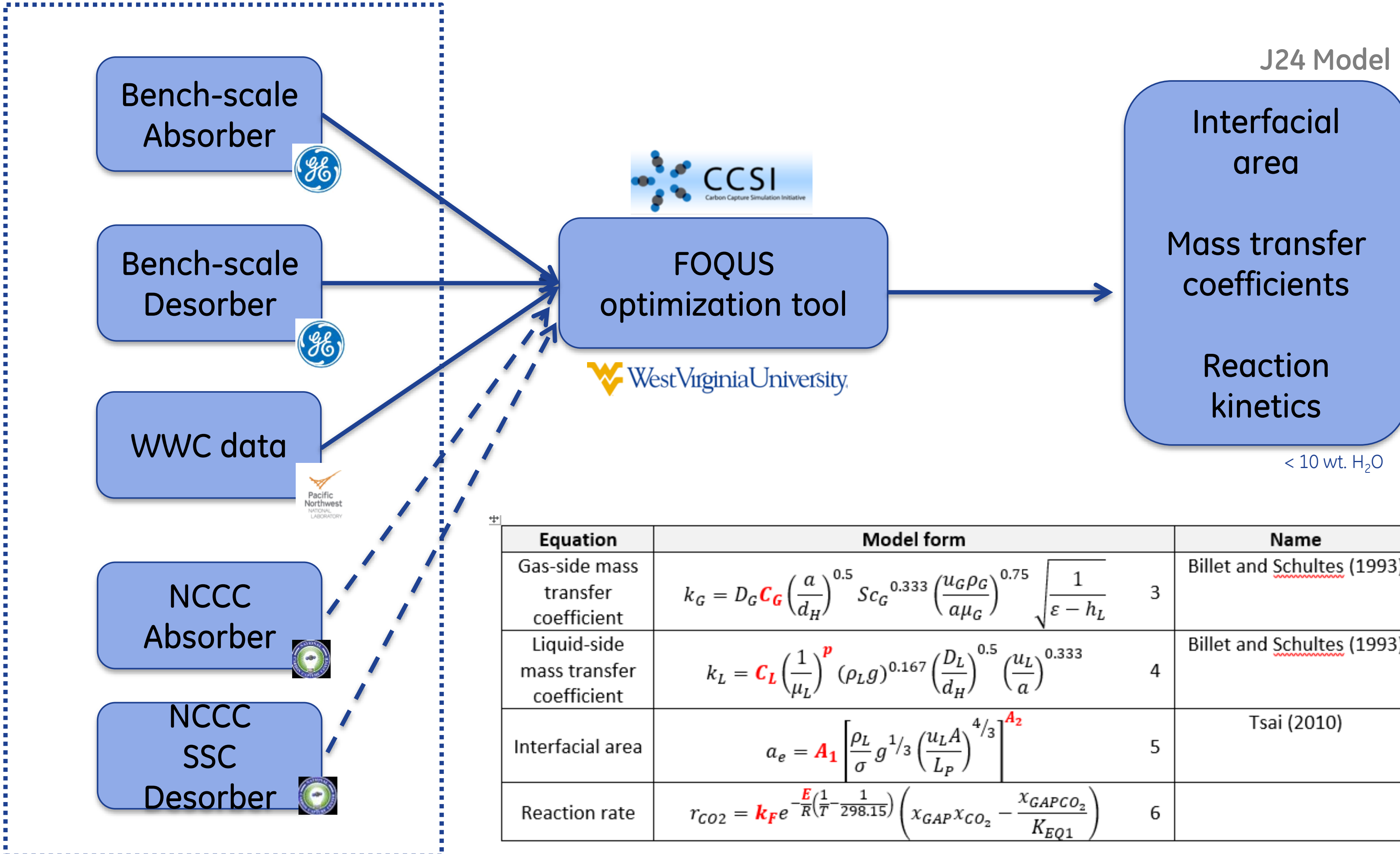
- 2011 $
- CO_2 transport, storage and monitoring included
- Financial Assumptions: High risk / investor own utilities (IOU)
- Financial outputs:

$$COE = \frac{\begin{matrix}\text{first year}\\ \text{capital charge}\end{matrix} + \begin{matrix}\text{first year}\\ \text{fixed operating}\\ \text{costs}\end{matrix} + \begin{matrix}\text{first year}\\ \text{variable operating}\\ \text{costs}\end{matrix}}{\begin{matrix}\text{annual net megawatt hours}\\ \text{of power generated}\end{matrix}}$$

$$\text{Removal Cost} = \frac{\{COE_{\text{with removal}} - COE_{\text{w/o removal}}\}\ \$/MWh}{\{CO_2\ \text{removed}\}\ \text{tons}/MWh}$$

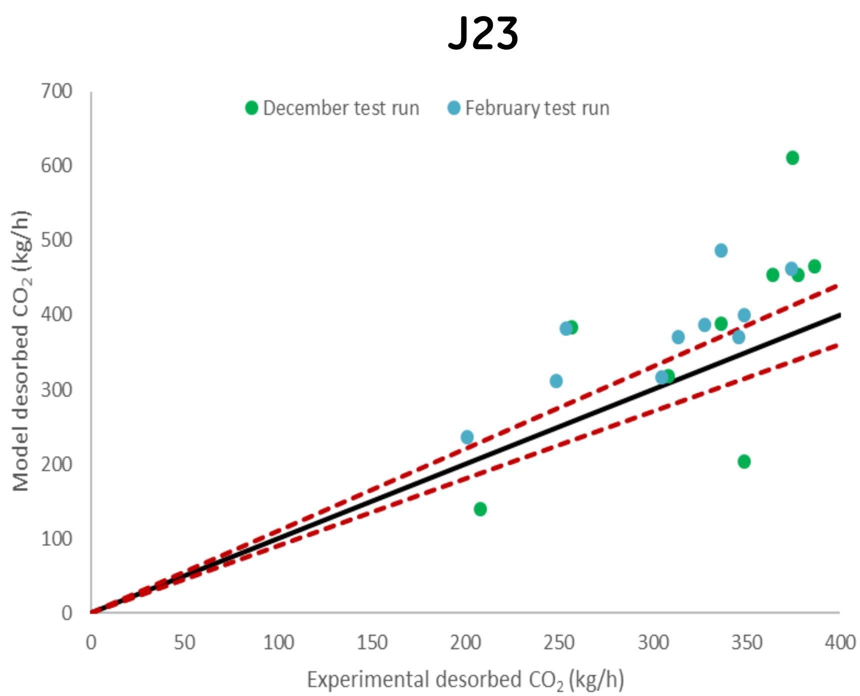
Cost Estimation according to DOE/NETL methodology

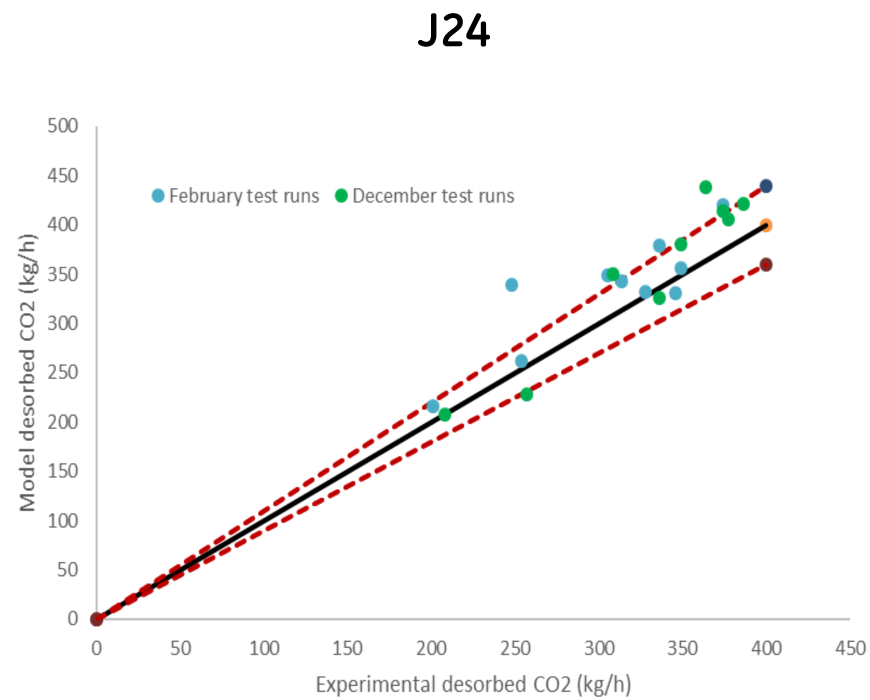
Process Modeling.. FOQUS Optimization



Equation	Model form	Name
Gas-side mass transfer coefficient	$k_G = D_G C_G \left(\frac{a}{d_H}\right)^{0.5} Sc_G^{0.333} \left(\frac{u_G \rho_G}{a \mu_G}\right)^{0.75} \sqrt{\frac{1}{\varepsilon - h_L}}$ 3	Billet and Schultes (1993)
Liquid-side mass transfer coefficient	$k_L = C_L \left(\frac{1}{\mu_L}\right)^{p} (\rho_L g)^{0.167} \left(\frac{D_L}{d_H}\right)^{0.5} \left(\frac{u_L}{a}\right)^{0.333}$ 4	Billet and Schultes (1993)
Interfacial area	$a_e = A_1 \left[\frac{\rho_L}{\sigma} g^{1/3} \left(\frac{u_L A}{L_P}\right)^{4/3}\right]^{A_2}$ 5	Tsai (2010)
Reaction rate	$r_{CO2} = k_F e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)} \left(x_{GAP} x_{CO_2} - \frac{x_{GAPCO_2}}{K_{EQ1}}\right)$ 6	

Process Modeling.. J24 Model tuning to 0.5 MW Data



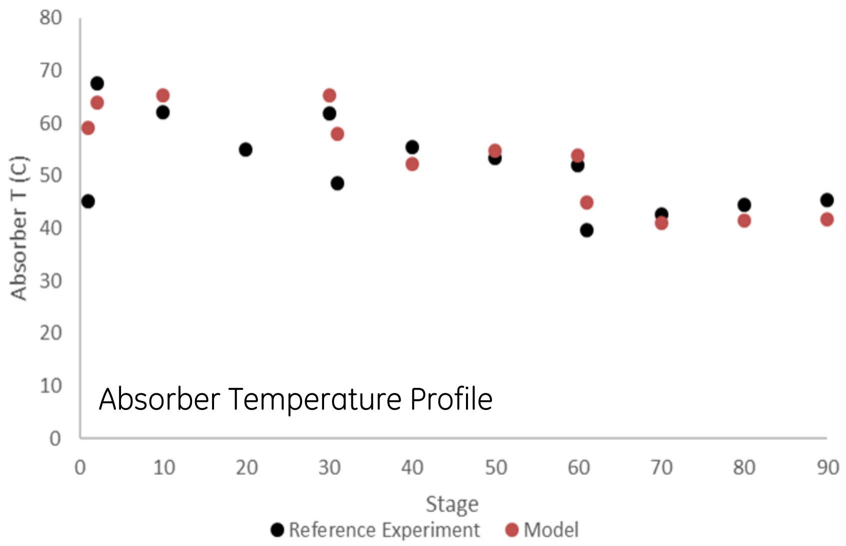


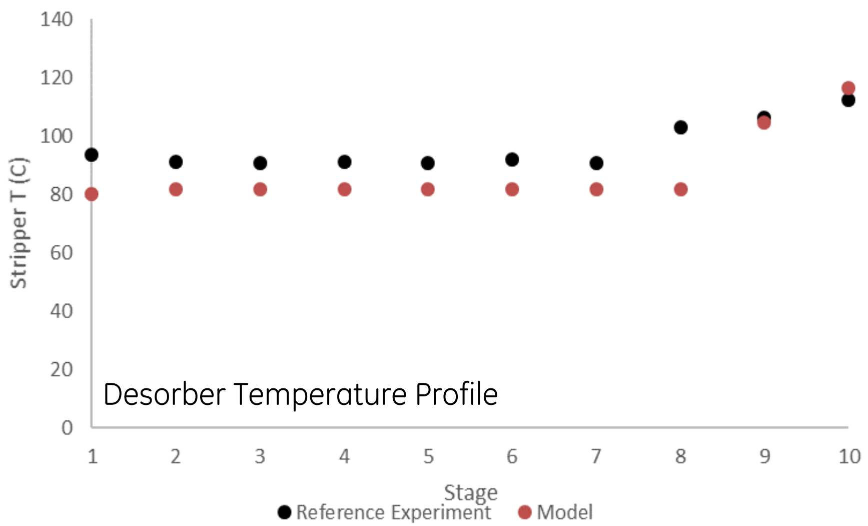
J24 Model:

- **Steam Stripper..** 40 stages with an upgraded reboiler
- **Absorber..** Intercoolers implementation
- **Solvent Properties..** Updated to accommodate higher water content

J24 Model captures well system behavior at 0.5 MW Pilot

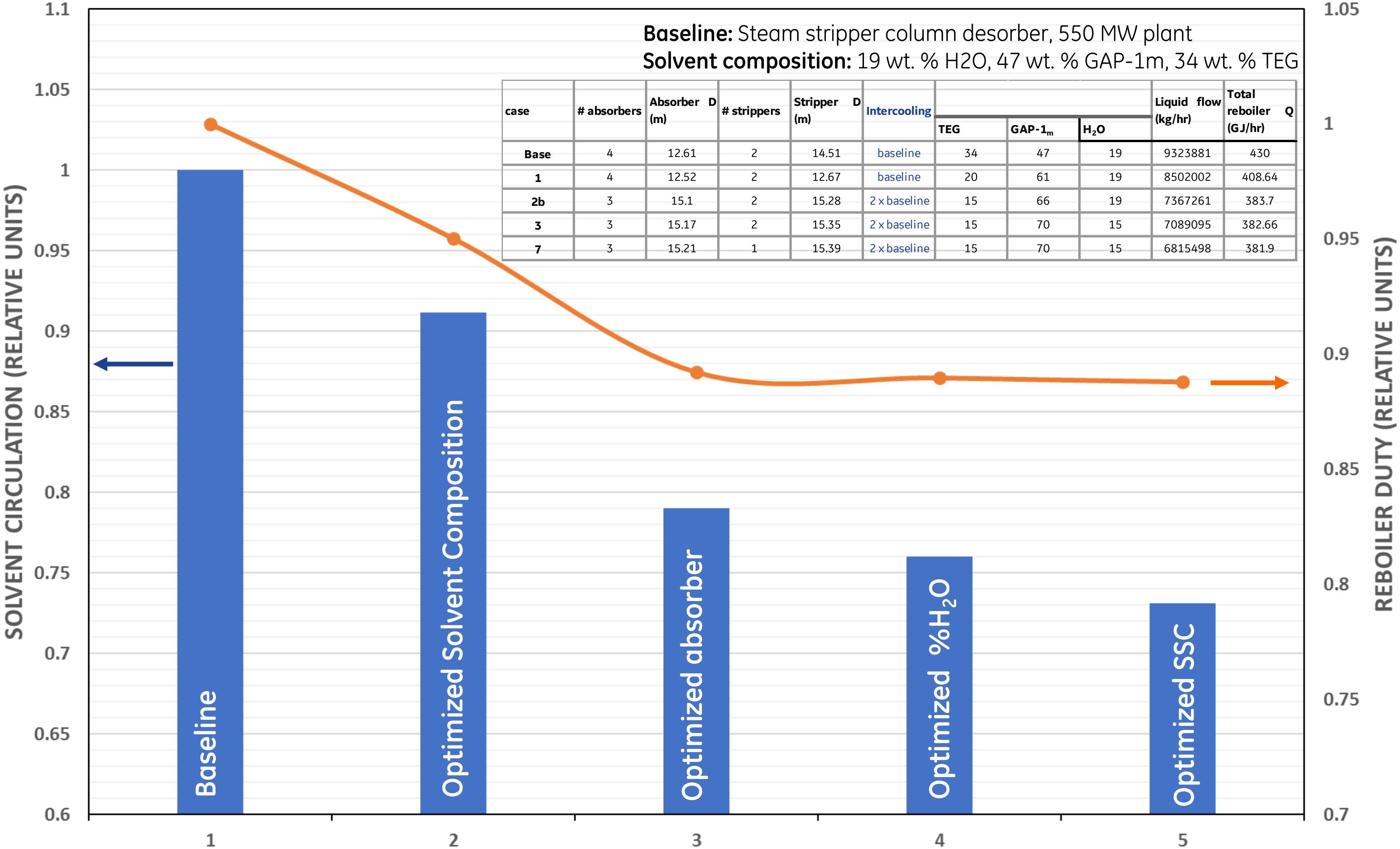
Process Modeling.. J24 Model tuning to 0.5 MW Data





J24 Model captures well system behavior at 0.5 MW Pilot

Process Optimization.. Composition & Absorber



Baseline: Steam stripper column desorber, 550 MW plant

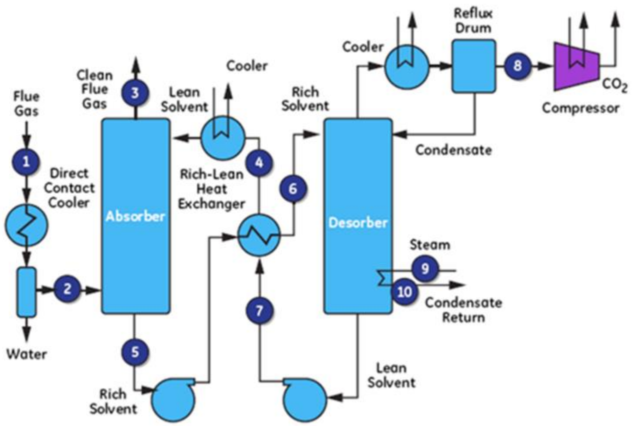
Solvent composition: 19 wt. % H2O, 47 wt. % GAP-1m, 34 wt. % TEG

case	# absorbers	Absorber D (m)	# strippers	Stripper D (m)	Intercooling	TEG	GAP-1_m	H_2O	Liquid flow (kg/hr)	Total reboiler Q (GJ/hr)
Base	4	12.61	2	14.51	baseline	34	47	19	9323881	430
1	4	12.52	2	12.67	baseline	20	61	19	8502002	408.64
2b	3	15.1	2	15.28	2 x baseline	15	66	19	7367261	383.7
3	3	15.17	2	15.35	2 x baseline	15	70	15	7089095	382.66
7	3	15.21	1	15.39	2 x baseline	15	70	15	6815498	381.9

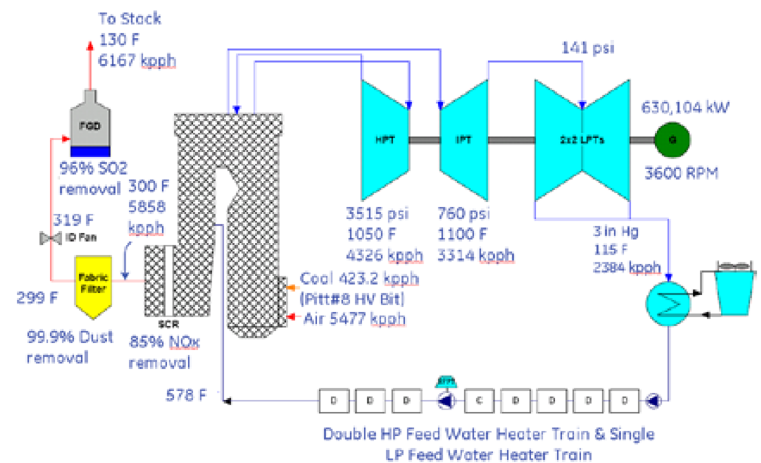
Process Optimization = f (absorber, SSC, solvent composition, intercooling)

Technical Approach.. Process & Plant Modeling

ASPEN PLUS: CO_2 Capture Island
GE Global Research



ThermoFlow: SC Power Plant
GE Power & Water

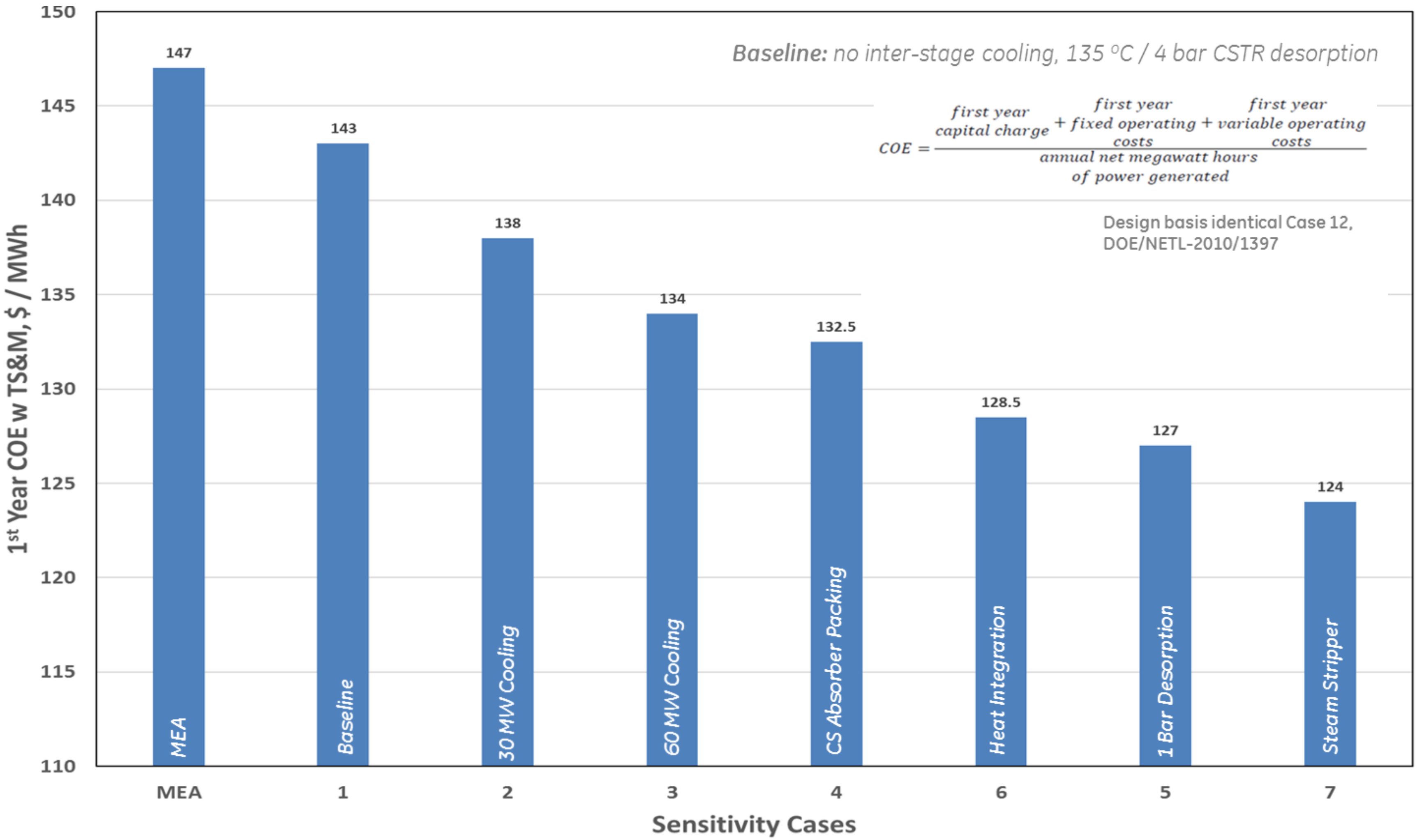


- ✓ **Absorber**… Packing, intercooling, MOC
- ✓ **Desorber…** SSC, temperature, MOC
- ▪ **Solvent** … Reclaiming, cost

- ✓ **Tune model to DOE/NETL-2010/1397**
- ✓ **Steam extraction**… Location, T
- ✓ **FGD**… Efficiency, CAPEX
- ▪ **Heat Integration**.. Cooling water, steam

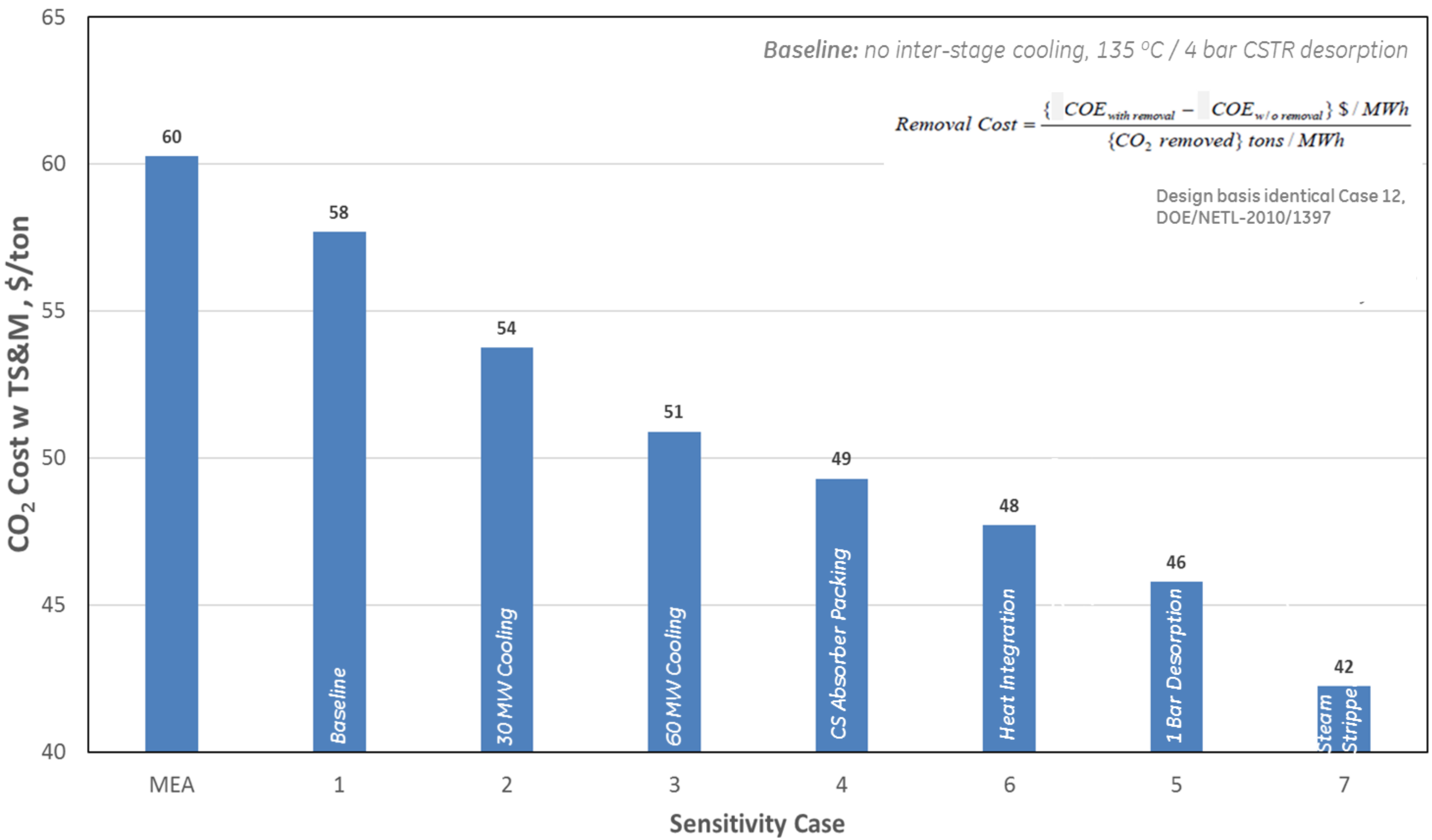
Dynamic interplay between the CO_2 Capture Island and Power Plant

Sensitivity Analysis.. 1st Year COE entitlement



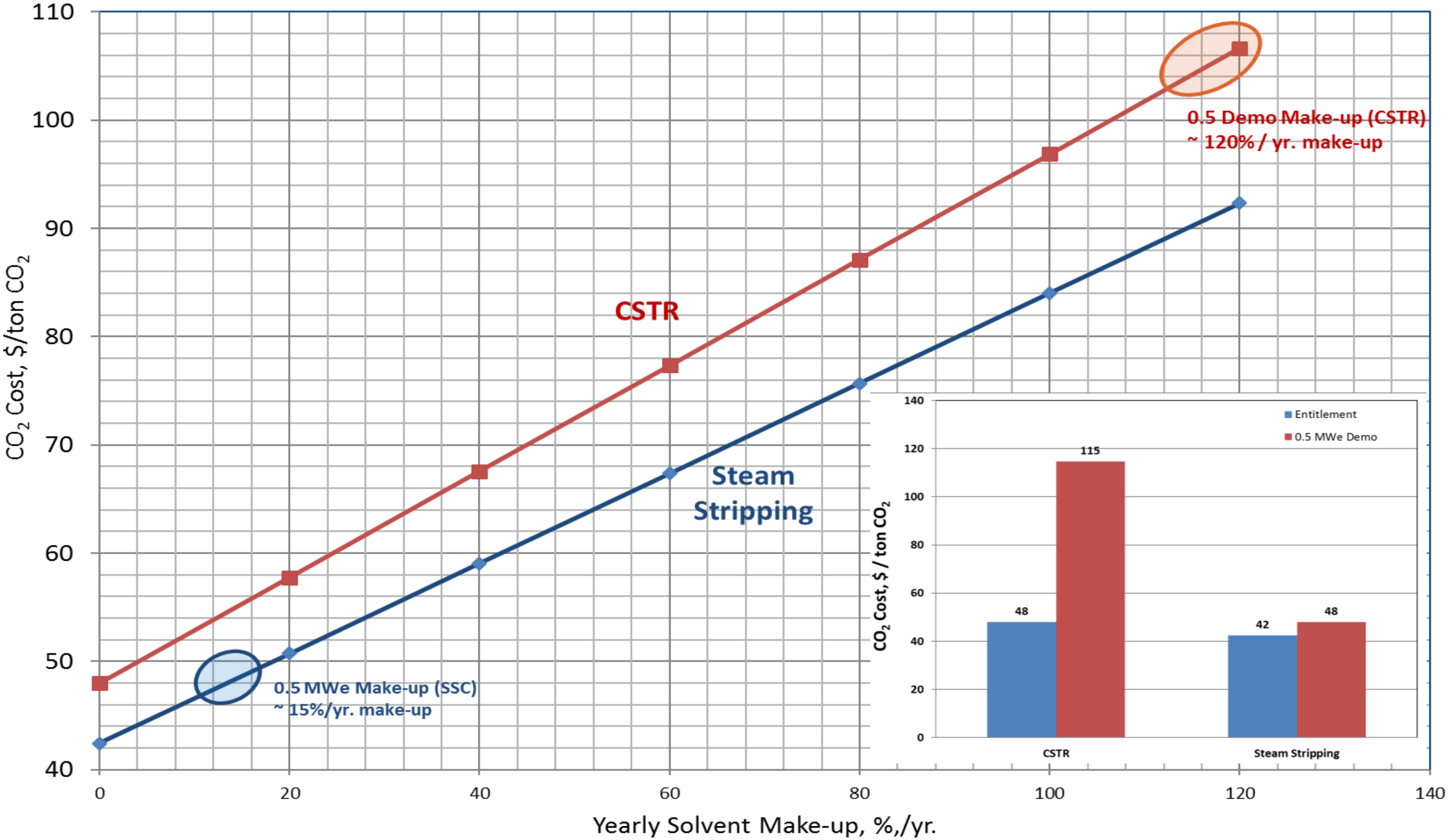
Over 20 % Improvements in Entitlement COE over MEA Fluor

Sensitivity Analysis.. CO_2 Removal Cost $_{entitlement}$



30% reduction in Entitlement CO_2 Cost vs. MEA

CO_2 Removal Cost.. CSTR vs. Steam Stripping

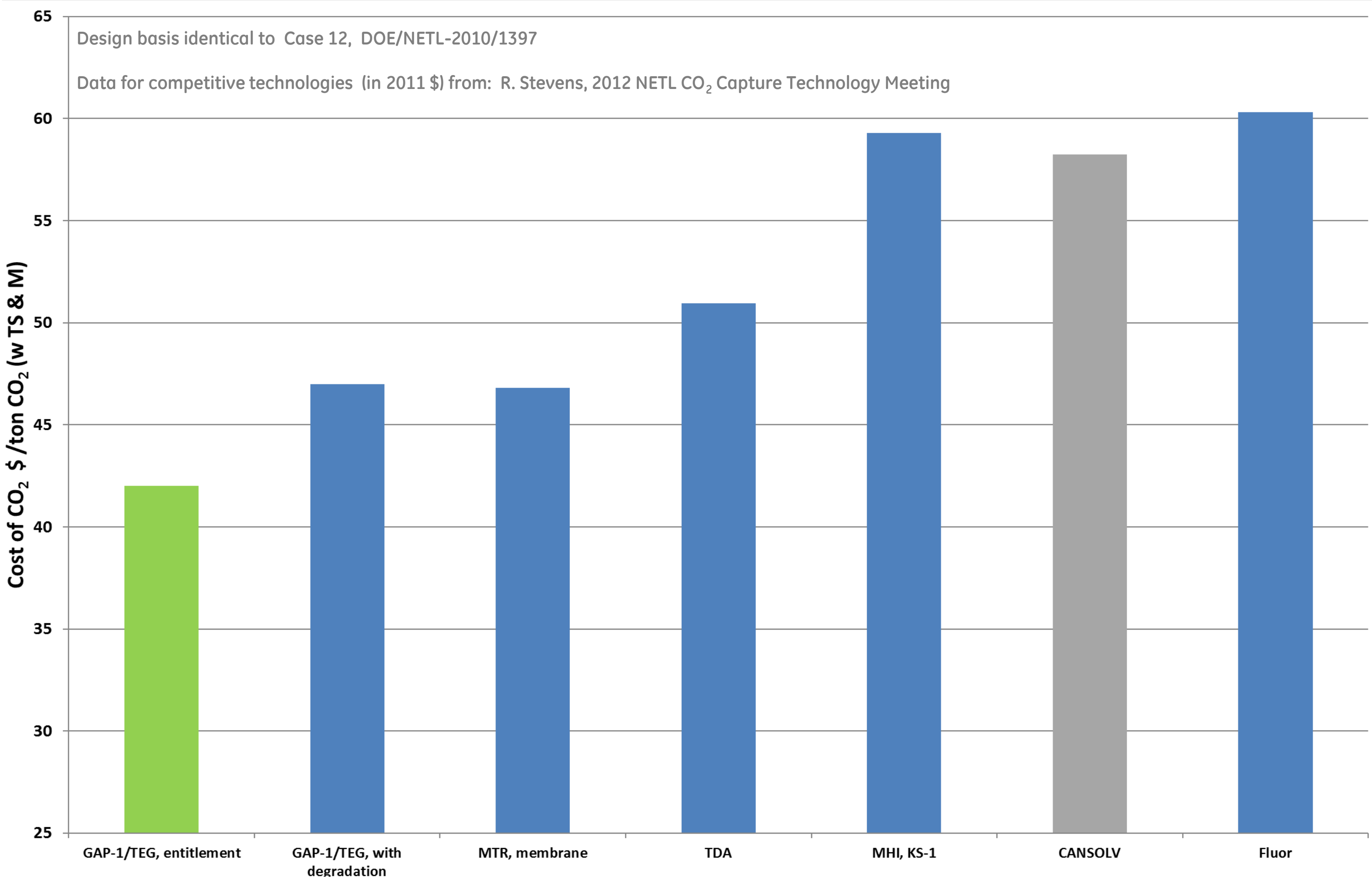


CSTR CO_2 cost.. dominated by solvent make-up

Steam Stripping CO_2 Cost.. $42 / tCO_2 (entitlement)

$48 / tCO_2 (with degradation)

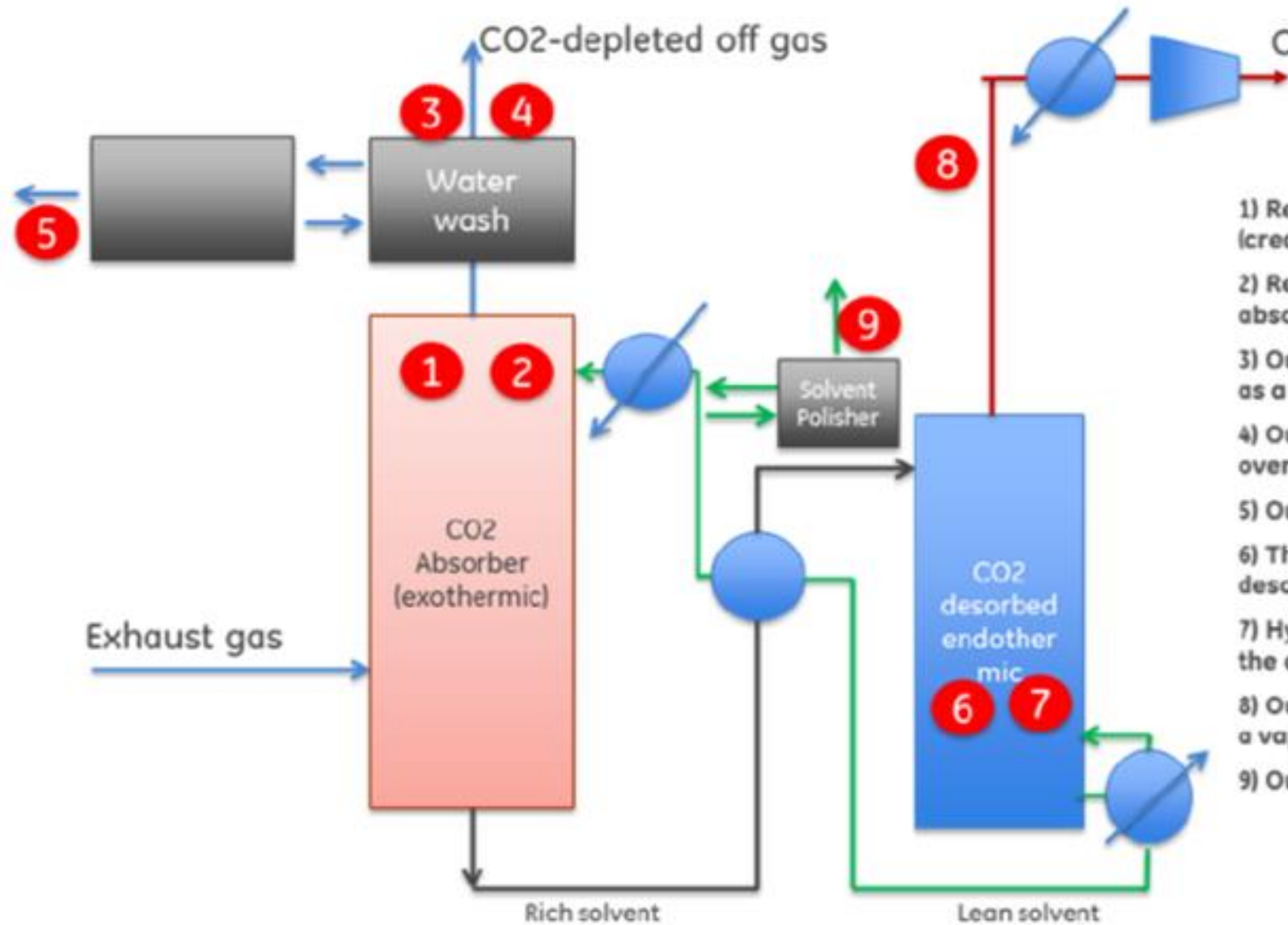
Competitive Assessment.. CO_2 Cost Removal



Agenda

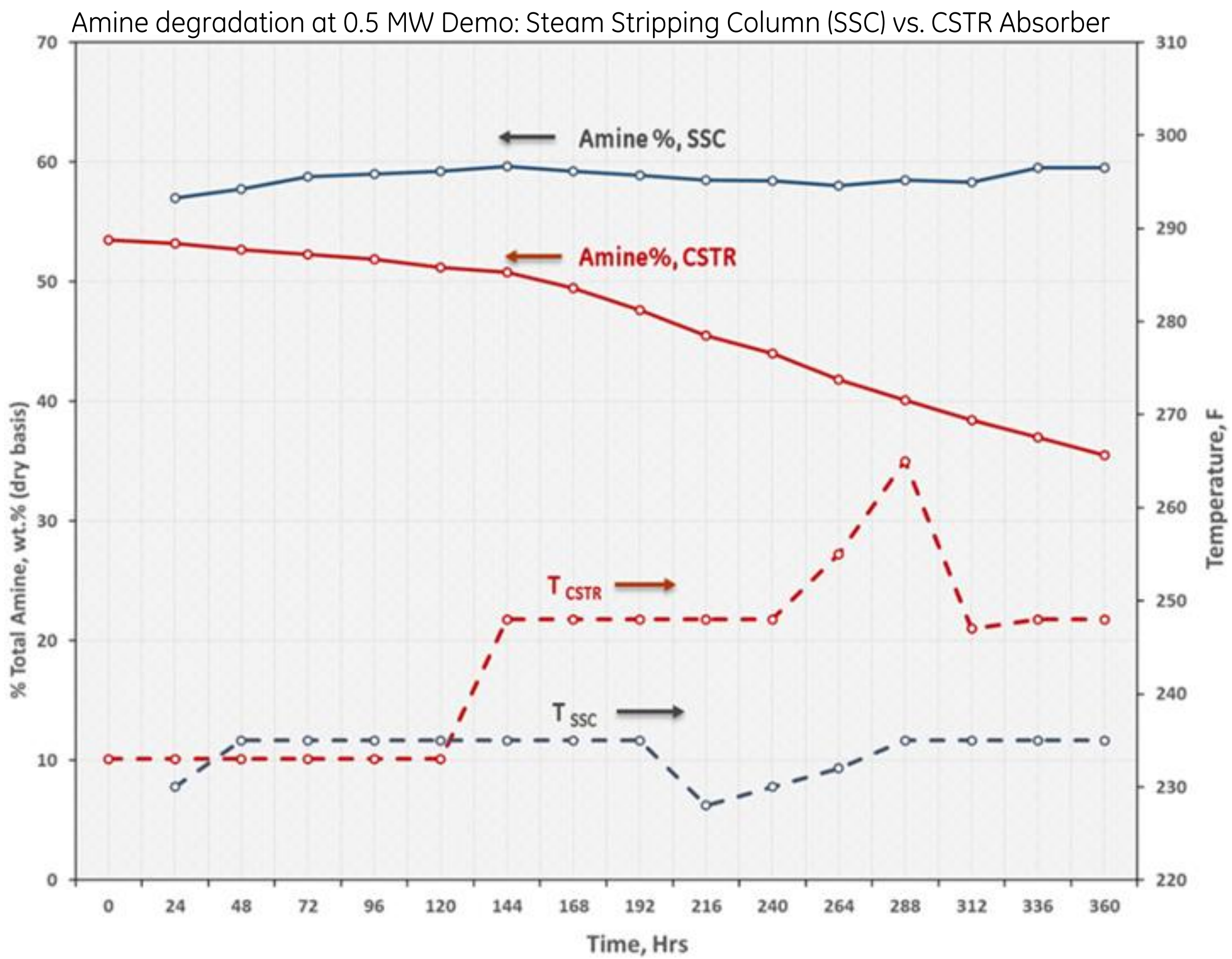
• Program Overview..	Feasibility study for 10 MW demo
• GE Aminosilicone..	Water lean CO_2 Capture Solvent
• Solvent Manufacturing..	Wacker qualified
• Host Evaluation..	Criteria to run water-lean solvent
• Techno-economic Analysis..	20 % Cost-out vs. MEA
• **Technology GAP Analysis..**	Solvent management & Gen 2 Solvent

Technology GAP Analysis.. Solvent Management



1) React with SO_2 in the absorber (create HSS)
2) React with O_2 and NO_x in the absorber (creates ammonia)
3) Out with the absorber overhead as a vapor component
4) Out with the absorber overheads as an entrained liquid
5) Out with Water Wash.
6) Thermal degradation in the desorber (creates Urea)
7) Hydro Thermal degradation in the desorber (creates D4)
8) Out with desorber overhead as a vapor component
9) Out with solvent purge residual

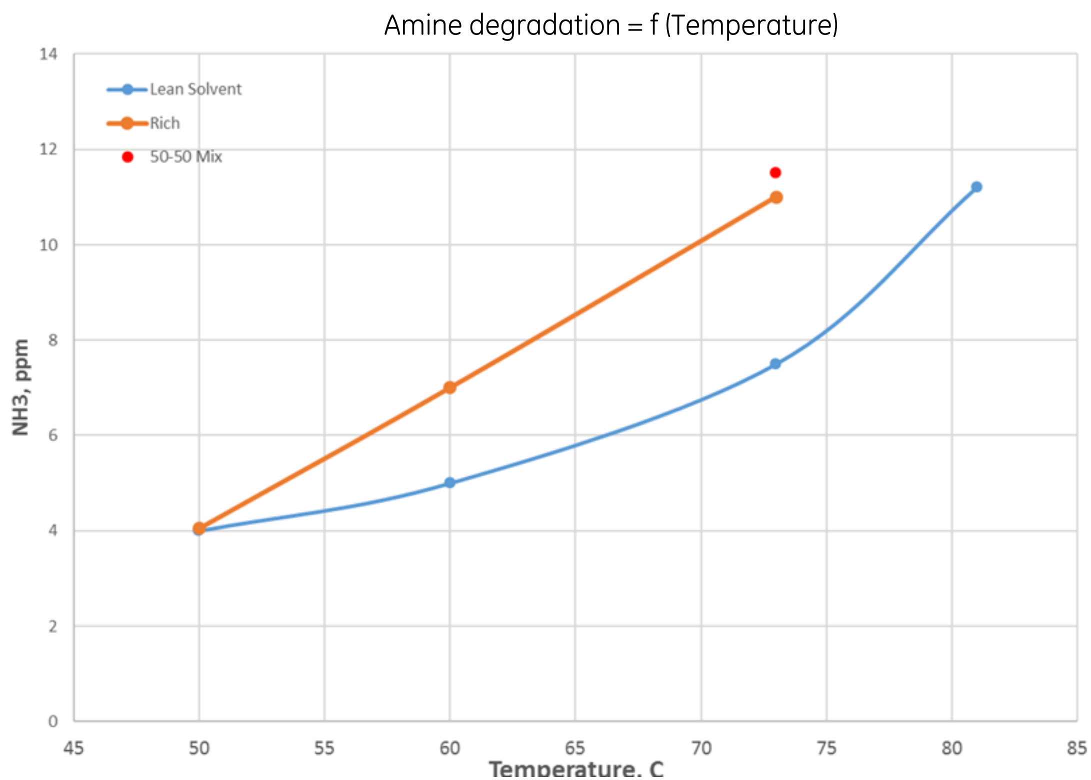
Technology GAP.. Solvent thermal stability

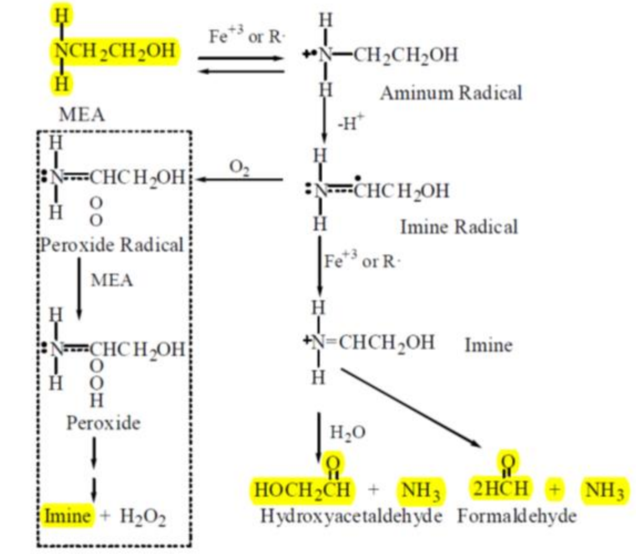


✓ **Recommendations:**

- Implement controlled water addition with SSC (TRL 5)
- Optimize water content to reduce steam duty / corrosivity of working solution

Solvent Management.. Oxidative Stability

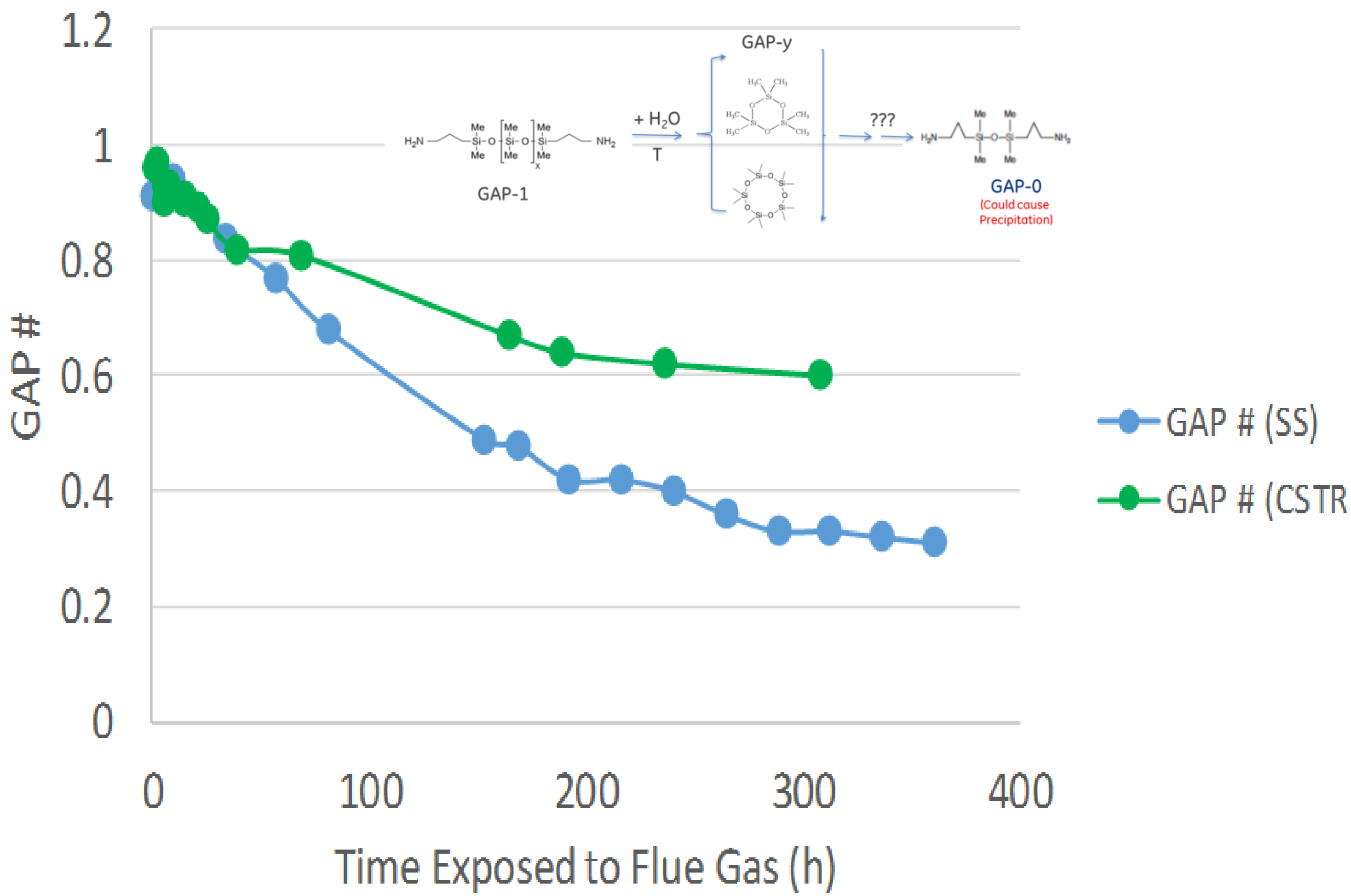




✓ **Recommendations:**

- Optimized absorber inter-stage cooling (TRL 6)
- Controlled water addition.. Reduced absorber temperature through evaporative cooling
- Development of oxidation inhibitors (TRL 2)

Solvent Management.. Hydrothermal Stability



✓ **Recommendations:**

- GAP number of starting material ~ 0.3 (equilibration value) (TRL 4)

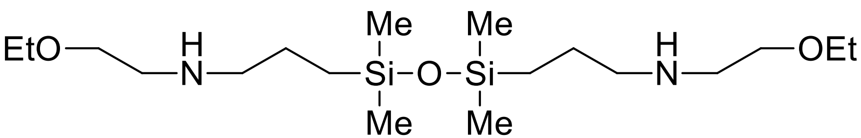
Technology GAP.. Future R&D Directions

Solvent Attribute	Baseline[1]	GAP-1 / TEG (Gen 1)	Adv. Aminosilicone (Gen 2)	Process Impact[2] (Gen 2 vs. Gen 1)
CO_2 Working Capacity (wt.%)	4	5	10	-30 % CAPEX; -11% OPEX
Solvent Make-up (% / yr)	100	75	20	-40% OPEX
Viscosity (CO_2 loaded, cP)	1	576	100	-40% absorber; -30% RLHX[3]
Heat of Reaction (KJ/Kg)	1825	2263	1900	-12 % reboiler duty
CO_2 Cost ($/t$CO_2$) **COE** (cents / kWh)	72 (13.7)	48 (11.6)	40 (10.6)	

Gen 2 Solvent..

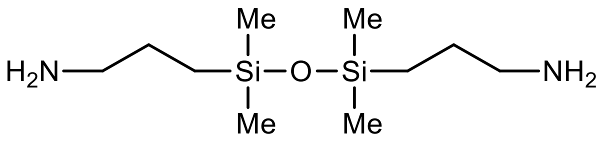
- ✓ Improved Working capacity.. No co-solvent
- ✓ Solvent Management.. No equilibration & reduced thermal degradation
- ✓ Viscosity reduction.. 4 X

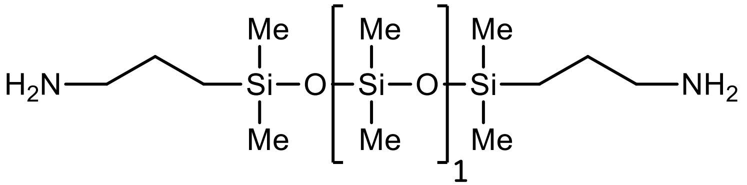
Technology GAP.. Future R&D Directions



GEN 2 : **EEAP** (EthoxyEthylAminoPropyl GAP)

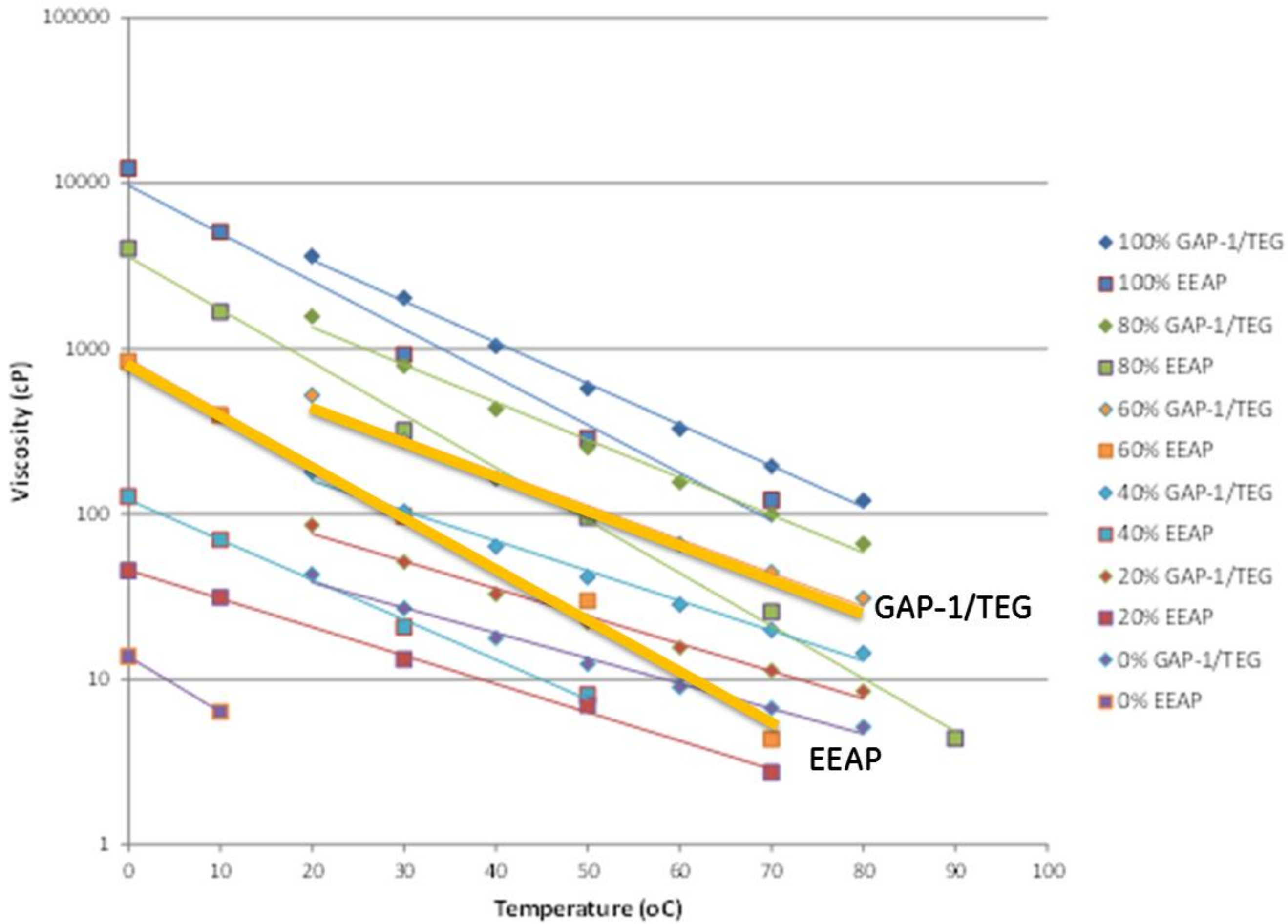
Same family of aminosilicones as GAP-0 and GAP-1





- Single component like GAP-0, not a mixture of homologs like GAP-1
- However, fully reacted EEAP remains as a flowable liquid
- No need for co-solvent

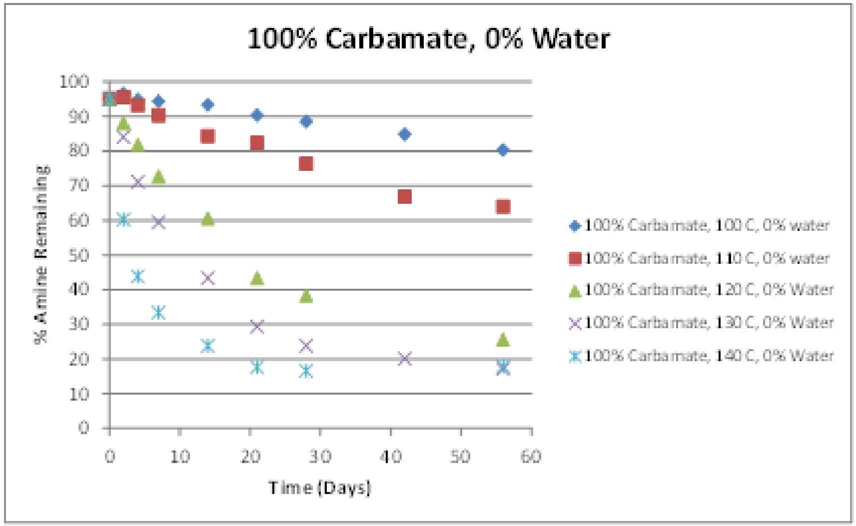
Gen 2 Solvents.. Viscosity



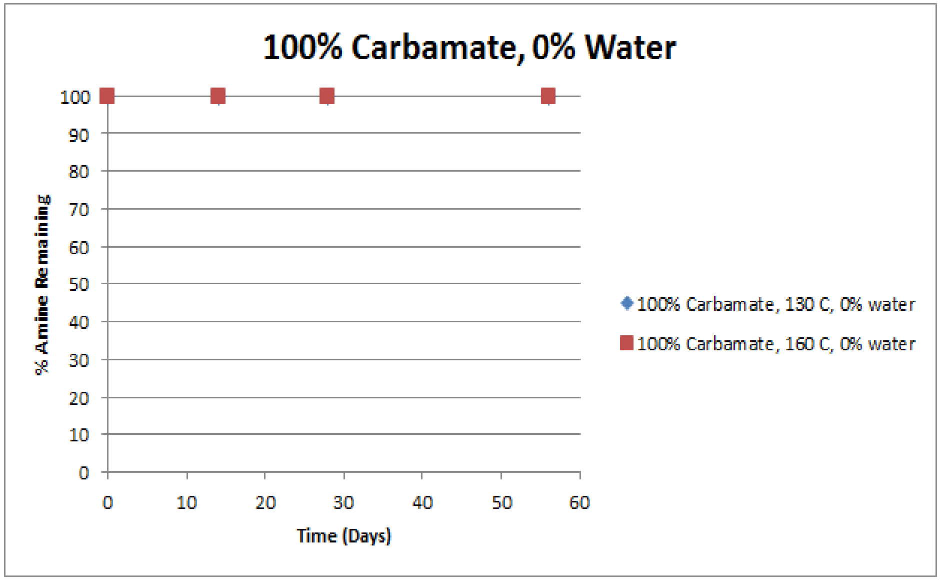
✓ **Gen 2 Solvents:** 2-3 X reduction in viscosity of the rich solvent

Gen 2 Solvents.. Thermal Stability

Gen 1: GAP-1 / TEG

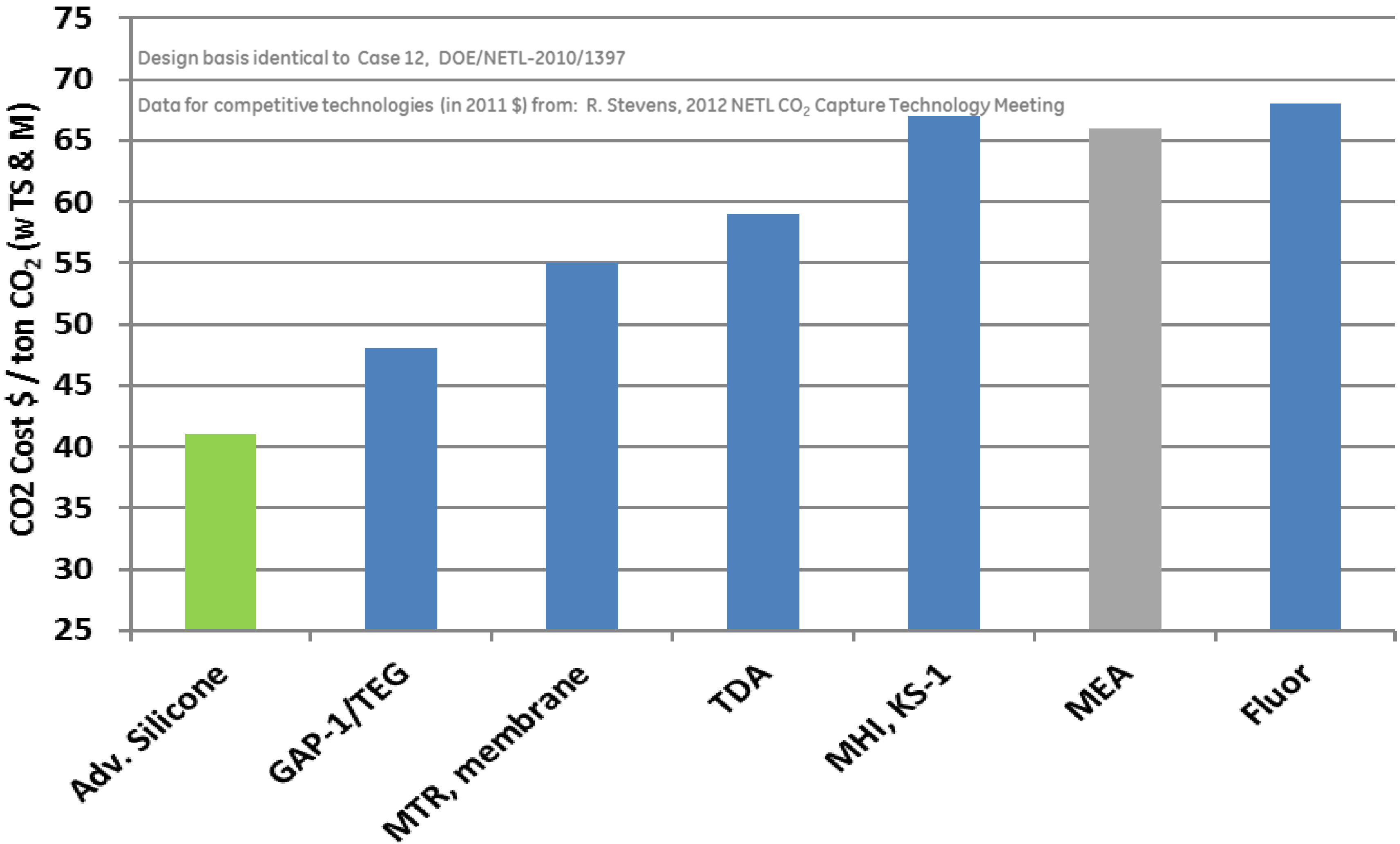


Gen 2: EEAP



✓ **Gen 2 Solvents:** No thermal degradation of the rich solvent @ 160 °C

Gen 2 Solvents.. Preliminary TEA



- ✓ **Gen 2 Solvents –** 20% potential CO_2 cost reduction vs. GAP-1 / TEG technology through increased working capacity, and reduced solvent make-up & viscosity

Executive Summary

- Performed feasibility evaluation of the of the aminosilicone solvent technology for scale-up at 10 MW

- **Aminosilicone Solvent**
  - ✓ **Non-aqueous solvent..** Improved CO_2 working capacity, Low volatility, low corrosivity
  - **Solvent degradation…** Thermal oxidative & hydrolysis

Suggested Actions: Improve solvent management through low T absorption / desorption, solvent mfg cost-out

- **Supplier Qualification**
  - ✓ **Qualification Process..** Solvent management (thermal, oxidation, equilibration) & CO_2 Capture Efficiency
  - ✓ **Performance..** Wacker ~ Baseline (Sivance); Wacker solvent showed improved oxidation stability

Suggested Actions: Wacker quailed as supplier for GAP/TEG-1

- **Techno-economical Analysis**
  - ✓ **Process modelling..** Updated ASPEN model for process optimization of the SSC (WVU)
  - ✓ **TEA..** \$42/tCO_2 (entitlement with SSC); \$ 48/tCO_2 (SSC & solvent degradation)
    CO_2 cost for CSTR dominated by solvent degradation

Suggested Actions: Develop Gen 2 solvent as path to \$40/tonne CO_2

- **GAP Analysis**
  - ✓ **Technology Gaps..** Solvent management
  - ✓ **Recommendations..** Controlled water addition with SSC for improved thermal & oxidation stability; adjust GAP# for starting material, oxidation inhibitors, solvent reclamation
  - ✓ **Future R&D..** Develop & scale-up co-solvent free water lean aminosilicone solvent (Gen 2)

Suggested Actions: Improve specific steam duty through water loading optimization & advanced flow scheme; demonstrate solvent management & reclamation at TRL 6 before proceeding with the next scale pilot.