Pilot-Scale Silicone Process for Low-Cost Carbon Dioxide Capture

Final Scientific/Technical Report

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Disclaimer:

Executive Summary

GE Global Research has developed, over the last 8 years, a platform of cost effective CO_2 capture technologies based on a non-aqueous aminosilicone solvent (GAP-1_m). As demonstrated in a previous funded DOE project (DE-FE0007502), the GAP-1_m solvent has increased CO_2 working capacity, lower volatility and corrosivity than the benchmark aqueous amine technology. The current report describes the cooperative program between GE Global Research (GE GRC), and the National Carbon Capture Center (NCCC) to design, construct, and operate a pilot-scale process using GAP-1_m solvent to demonstrate its performance at 0.5 MW_e.

(i) Performance of the GAP-1_m solvent was demonstrated in a 0.5 MW_e pilot with real flue gas for over 900 hrs. of operation using two alternative desorption designs: a Continuous Stirred Tank Reactor (CSTR), and a Steam Stripper Column (SSC). The CSTR is a one-stage separation unit with reduced space requirements, and capital cost. The alternative is a multi-stage separation column, with improved desorption efficiency. Testing the two desorber options allowed us to identify the most cost effective, and space efficient desorber solution.

(ii) *<u>CSTR Campaign</u>:* The CSTR desorber unit was designed, fabricated and integrated with the pilot solvent test unit (PSTU), replacing the PSTU Steam Stripper Column at NCCC. Solvent management and waste water special procedures were implemented to accommodate operation of the non-aqueous solvent in the PSTU.

Performance of the GAP-1_m solvent with the CSTR was demonstrated for over 500 hrs. while varying temperature of the desorption (230 – 265 °F), solvent circulation rate (GAP-1_m : CO_2 (molar) = 1.5 – 4), and flue gas flow rates (0.2 – 0.5 MW_e). Solvent carry-over in the CO_2 product was minimized by maintaining water content below 5 wt.%, and desorption pressure at 7 psig. CO_2 capture efficiency achieved was 95% at 0.25 MW_e (GAP-1_m : CO_2 = 4 (molar), 230 °F desorption), and 65% at 0.5 MW_e (GAP-1_m : CO_2 (molar) = 1.5, 248 °F). Solvent loss was dominated by thermal degradation of the rich solvent.

(iii) *<u>Steam Stripper Column Campaign</u>:* Higher expected cost of the solvent vs. aqueous amines makes solvent management a top priority to maintain the low cost for the process. During the testing of the GAP-1_m solvent with the CSTR, thermal degradation of the rich solvent was found to be the main mechanism in solvent loss. Small amounts of water in the working solution were found to be an effective way to enable steam stripping, thereby lowering desorption temperature, and hence reducing thermal degradation. Steam stripping also increased working capacity by 30% due to a more efficient desorption. The concept was first tested in a glass stripping column (lab scale,

GE GRC), optimized in a continuous bench scale system (2 kW_e, GE GRC), and demonstrated in a 0.5 MW_e PSTU at NCCC. No special system modifications were required to the PSTU to accommodate the testing of the non-aqueous GAP-1 solvent with the regenerator column. SSC was found to be more robust towards solvent entrainment (H_2O < 35 wt.%). 90 – 95% CO_2 capture efficiency was achieved under stoichiometric conditions at 0.5 MW_e (235 ^oF desorption, 2 psig and 19 wt. % H_2O). Both CO_2 capture efficiency and specific duty reached optimum conditions at 18 wt.% H_2O. Low amine degradation (< 0.05 wt.%/day) was recorded over 350 hrs. of operation. Controlled water addition to GAP-1_m solvent decreased the desorption temperature, thermal degradation, and improved the CO_2 working capacity due to more efficient absorption and desorption processes. Under these conditions, the GAP-1_m solvent exhibited a 25% increased working capacity, and 10% reduction in specific steam duty vs. MEA, at 10 ^oF lower desorption temperature.

(iv) *<u>Techno-economic Analysis:</u>* The pilot-scale PSTU engineering data were used to update the capture system process models, and the techno-economic analysis was performed for a 550 MW coal fired power plant. The 1st year CO_2 removal cost for the aminosilicone-based carbon-capture process was evaluated at \$48/ton CO_2 using the steam stripper column. This is a 20% reduction compared to MEA, primarily due to lower overall capital cost. CO_2 cost using the CSTR desorber is dominated by the economics of the solvent make-up. The steam stripper desorber is the preferred unit operation due to a more efficient desorption, and reduced solvent make-up rate. Further reduction in CO_2 capture cost is expected by lowering the manufacturing cost of the solvent, implementing flowsheet optimization and/or implementing the next generation aminosilicone solvent with improved stability and increased CO_2 working capacity.

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4.0 Steam Stripping Column (SSC) Campaign

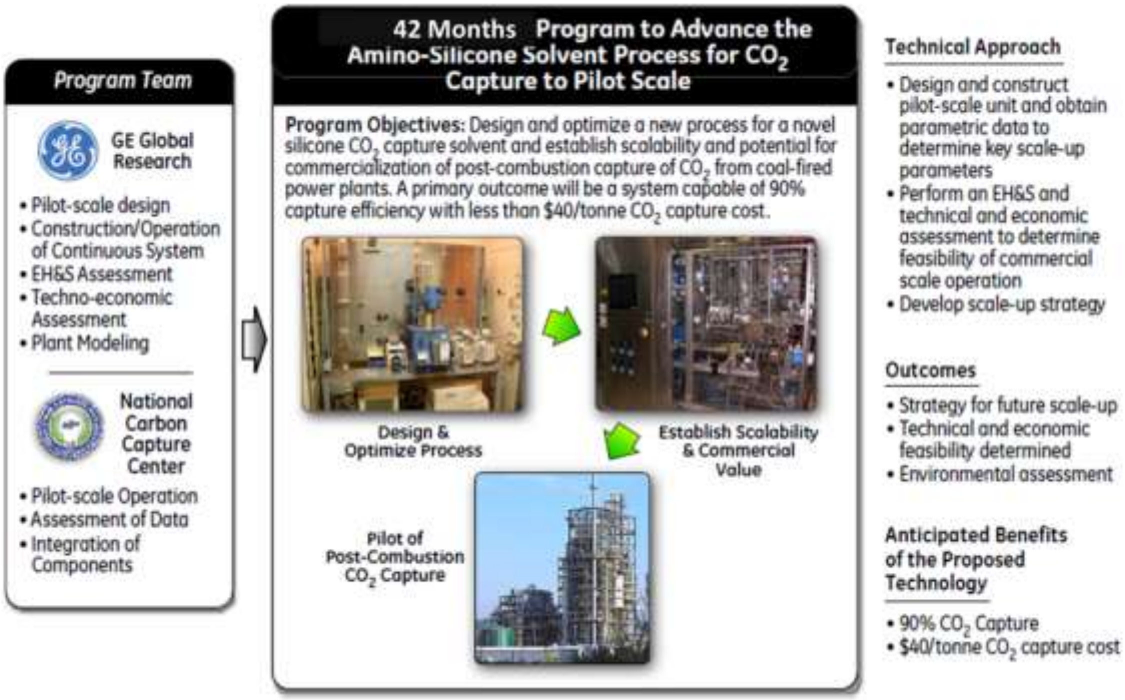
6.0 Technology EH&S Assessment

1. Project Objectives and Timeline

The primary objective of the cooperative agreement between GE Global Research, National Carbon Capture Center (NCCC) and Department of Energy was to design, construct, and operate a pilot-scale process using a novel aminosilicone based CO_2 capture solvent (GAP-1_m/TEG). **Figure 1** and **Figure 2** describe the overall objectives of the program, and program timeline, respectively.

Performance of the GAP-1_m/TEG solvent was demonstrated in a 0.5 MW_e pilot with real flue gas for over 900 hrs of operation using two alternative desorption designs: a Continuous Stirred Tank Reactor (CSTR), and a Steam Stripper Column (SSC). The CSTR desorber was designed, fabricated and integrated with the pilot solvent test unit (PSTU), replacing the PSTU Steam Stripper Column at NCCC. During the testing of the GAP-1_m/TEG solvent with the CSTR, thermal degradation of the rich solvent was found to be the main mechanism in solvent loss. Small amounts of water in the working solution were found to be an effective way to enable steam stripping, lower desorption temperature, and hence reduce thermal degradation. The concept was first tested in a glass stripping column (GE GRC), optimized in a continuous bench scale system (2 kW_e, GE GRC), and demonstrated in a 0.5 MW_e pilot (NCCC). No special system modifications were required to the PSTU to accommodate the testing of the non-aqueous GAP-1_m/TEG solvent with the regenerator column.

Data obtained from the system included solvent stability, effects of flue gas contaminants, and recommended operating conditions for both CSTR and SSC desorbers. The pilot-scale engineering data was used to update the capture system process models in collaboration with CCSI and West Virginia University. The updated models were used to complete the techno-economic analysis and to develop a scale-up strategy to evaluate the progress in meeting the DOE goal of CO_2 capture cost from coal-fired power plants at less than $40/tonne of CO_2.



Program Objectives: Design and optimize a new process for a novel silicone CO_2 capture solvent and establish scalability and potential for commercialization of post-combustion capture of CO_2 from coal-fired power plants. A primary outcome will be a system capable of 90% capture efficiency with less than \$40/tonne CO_2 capture cost.

Figure 1. Pilot-Scale Silicone Process for Low-Cost Carbon Dioxide Capture: Project Objectives

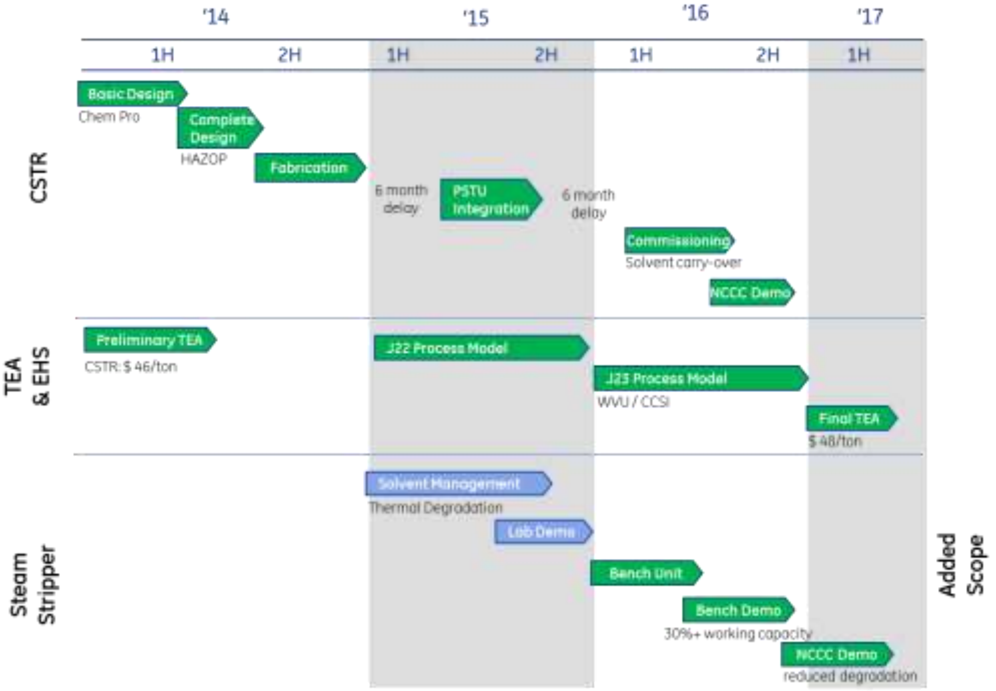


Figure 2. Pilot-Scale Silicone Process for Low-Cost Carbon Dioxide Capture: Overall Timeline

2. GE Aminosilicone Technology

The proposed technology is to use an aminosilicone-based solvent for CO_2-capture from the flue gas of a pulverized coal power plant. In previous GE Global Research work, as part of a prior DOE project (DE-NT0005310) an aminosilicone solvent was identified that demonstrates superior performance for CO_2 capture. This material consists of an aminosilicone oligomer known as GAP (3-aminopropyl end-capped polydimethylsiloxanes [PDMS]). It was found that the best performance was for a material where the average value for x is 1. The structure of this material, known as GAP-1 (1,5-Bis(3-aminopropyl 1,1,3,3,5,5-hexamethyl trisiloxane)), is shown in **Figure 3**.

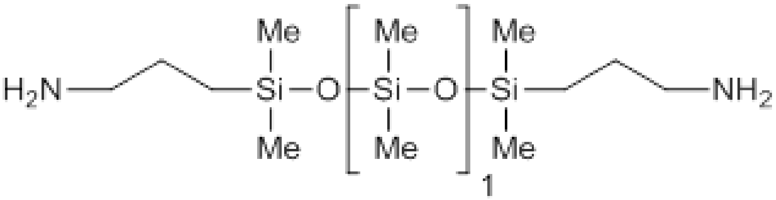


Figure 3. GAP-1 (1,5-Bis(3-aminopropyl) 1,1,3,3,5,5-hexamethyl trisiloxane).

GAP-1 readily reacts with CO_2 to form a carbamate (**Figure 4).**

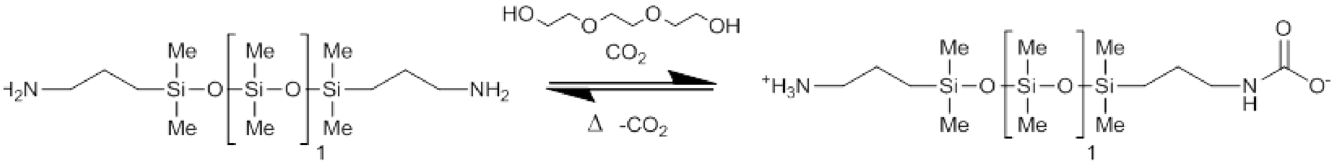


Figure 4. GAP-1 material reacting with CO_2

The GAP-1 synthesized for this project is actually a statistical mixture of GAP molecules with x values of 0 to 3, and will be distinguished from pure GAP-1 by the subscript "m" (GAP-1_m). GAP-1_m consists of 40 wt.% GAP-0, 33 wt.% GAP-1, 19% GAP-2, and 8% GAP-3, as determined by ^1H NMR, with the average molecular weight being that of GAP-1. At elevated temperatures CO_2 is reversibly desorbed from GAP-1_m, permitting reuse of the CO_2 capture solvent. However, the viscosity of GAP-1_m increases significantly upon absorption of CO_2, and can solidify at high CO_2 loadings. In order to mitigate these issues, it was found that a suitable CO_2 capture solvent could be produced by diluting GAP-1_m in a co-solvent. Using triethylene glycol (TEG) as a co-solvent, a CO_2 capture solvent comprised of 60% (by wt.) GAP-1_m with 40% TEG demonstrated improved thermal stability and volatility relative to MEA with a similar capacity for CO_2. The use of a co-solvent ensures that the viscosity of the aminosilicone-based solvent is acceptable even at high CO_2 loadings, and inhibits solidification of the aminosilicone.

GAP-1_m/TEG exhibits a number of desirable properties as a CO_2 capture solvent when compared to MEA. **Figure 5** shows the vapor pressure of both MEA and GAP-1_m. As shown, both GAP-1_m and TEG are significantly less volatile than MEA. This lower volatility simplifies CO_2 desorption and potentially reduces the solvent loss in both clean flue gas and CO_2 streams.

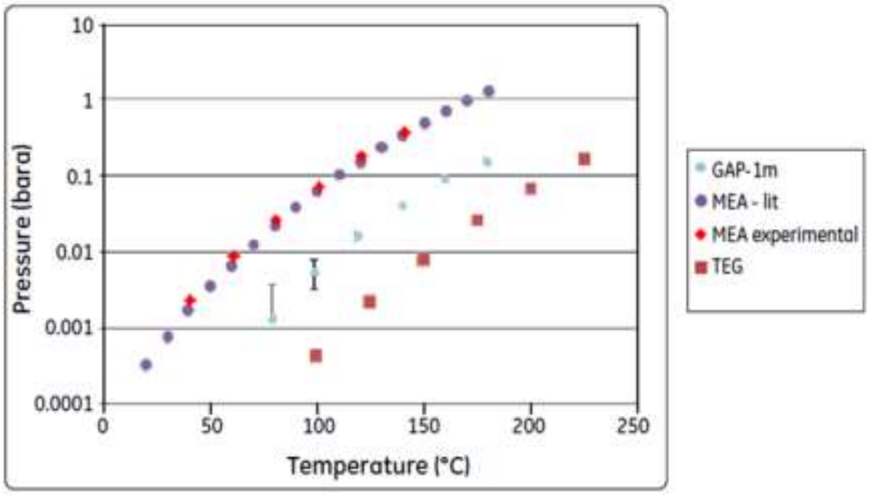


Figure 5. **Vapor Pressure**: MEA vs. GAP-1_m/TEG solvent

Thermal stability tests were performed in prior DOE funded projects, in which GAP-1_m (lean solvent) was heated at temperatures from 120 to 160°C for over 80 days, in the presence of air. **Figure 6** shows the results when compared to MEA. At 120 ^oC, it was observed by GC that there was no detectable degradation of the material. At 150°C, lean aminosilicone solvent exhibits one order of magnitude lower thermal degradation rate than MEA.

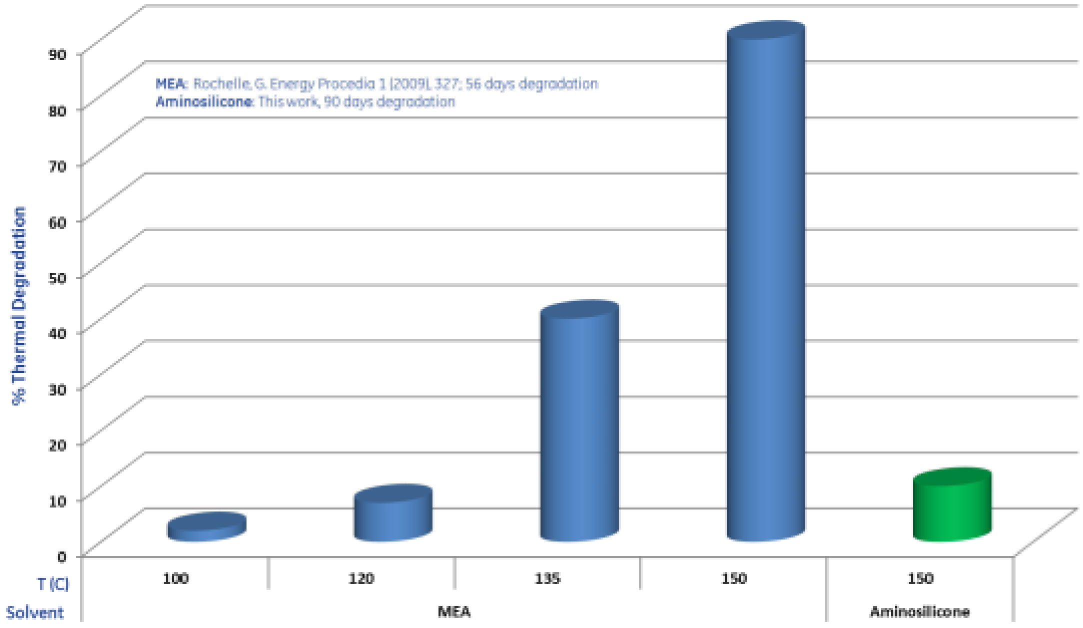


Figure 6. **Thermal Degradation:** MEA vs. GAP-1_m/TEG solvent (lean)

More recent studies were completed looking at the effects of water and CO_2 on thermal degradation. It was found that high concentration of carbon dioxide results in elevated thermal degradation rates. This is shown in **Figure 7**. Solvent that is fully loaded with CO_2 (the blue curves), shows a higher rate of thermal degradation over a range of temperatures, than the partially loaded samples (the green curves). Additionally, it was determined that the addition of water (at 5-10 wt.%) decreased the rate of thermal degradation for both the 100% loaded solvent and the 25% loaded solvent.

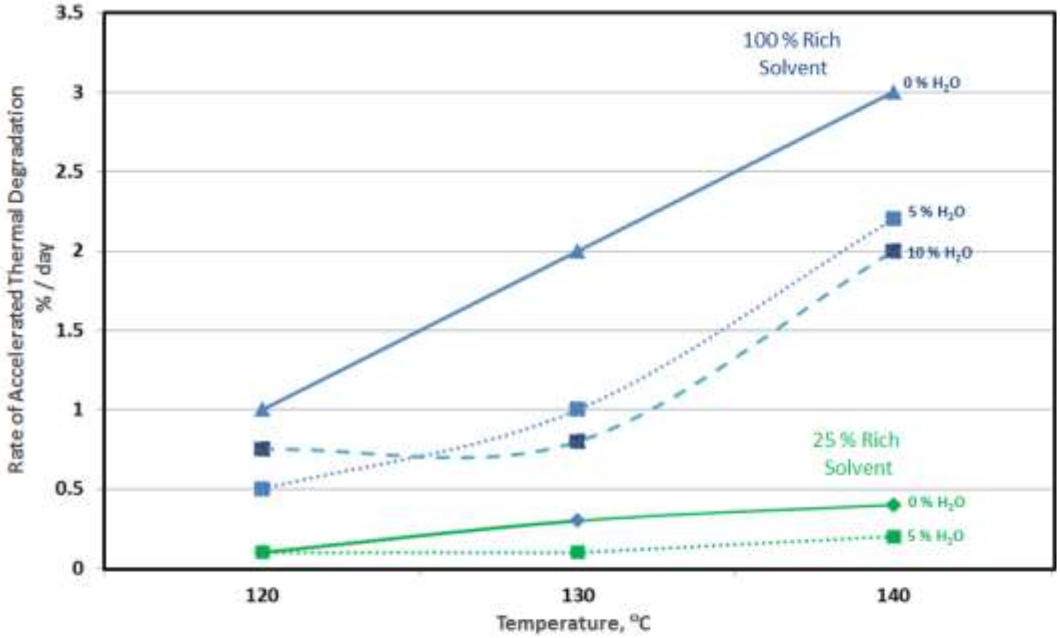


Figure 7. **Thermal Degradation:** GAP-1_m/TEG solvent (rich)
Rate of thermal degradation as a function of temperature, percent CO_2 loading, and water loading (2 kW bench scale process)

In order to better understand why CO_2 would promote thermal degradation, and why water would inhibit it, various analytical techniques were used to determine the products of thermal degradation. The route for thermal degradation identified is shown in **Figure 8**.

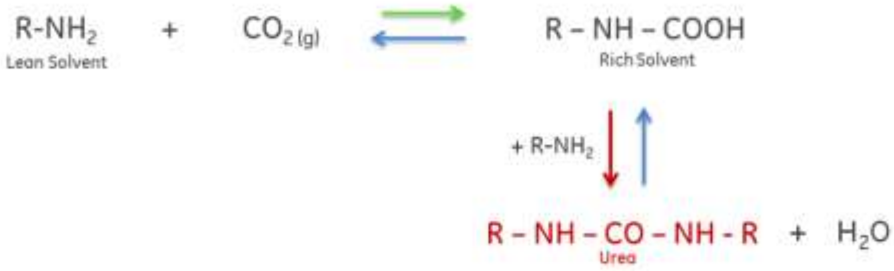


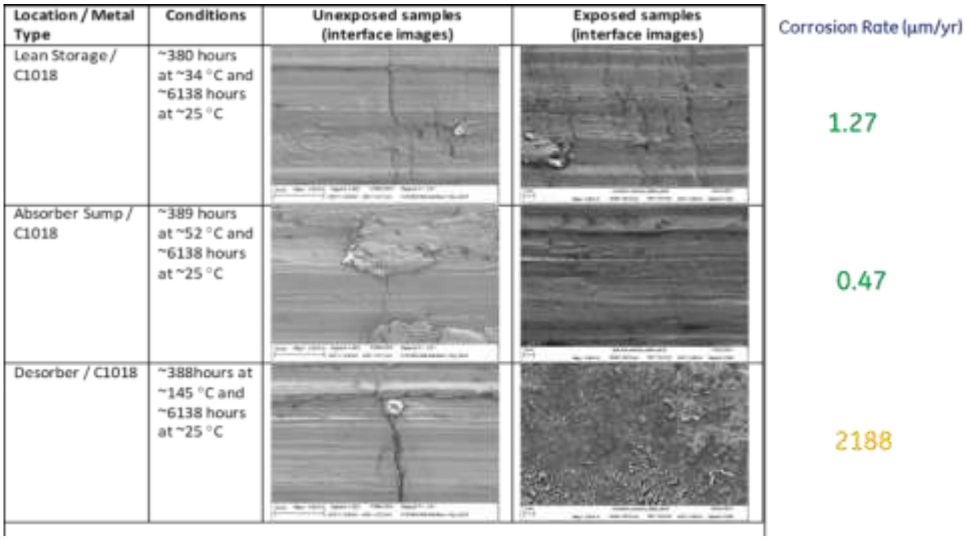
Figure 8. **Thermal Degradation of GAP-1_m/TEG solvent (rich):** Proposed Mechanism

Lean aminosilicone solvent can react with CO_2 to form a carbamate (CO_2-rich solvent). The carbamate molecule can then react with a CO_2-lean molecule in a side reaction to form urea and water, where two amine groups are inactive in the urea form. Increasing the concentration of CO_2-rich solvent pushes the equilibrium of the side reaction to favor the formation of urea, therefore increasing the rate of thermal degradation of the solvent. However, water is also a product of the side reaction. So adding water to the solvent should help push the equilibrium of the side reaction back to favoring the non-urea form. In summary, we found that the rate of thermal degradation of the rich solvent is proportional to temperature, CO_2 content of the solvent leaving the desorber and inversely proportional to water content (eq. [1]).

$$Rate\ of\ thermal\ degradation \sim \frac{T \times \%CO_{2,lean}}{\%\ H_2O} \qquad [1]$$

Finally, corrosivity studies conducted in our bench scale system [DE-FE0007502] have shown that GAP-1_m/TEG is significantly less corrosive than MEA under the absorber and rich/lean heat exchanger conditions, decreasing capital costs by using less expensive materials of construction (**Figure 9**).

Figure 10 shows the CO_2 capture process that was developed to take advantages of the unique properties of the aminosilicone solvent (increased CO_2 capacity, lower volatility and lower corrosivity). A CSTR desorber was proposed as a low CAPEX / low footprint alternative to the typical regenerator system. The system was previously demonstrated in the 2 kW_e demo [DE-FE0007502], and it was the initial design choice for the 0.5 MW_e pilot.



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

Figure 9. **GAP-1_m/TEG Corrosivity**

Corrosion rates measured in the bench scale demo (2 kW_e)

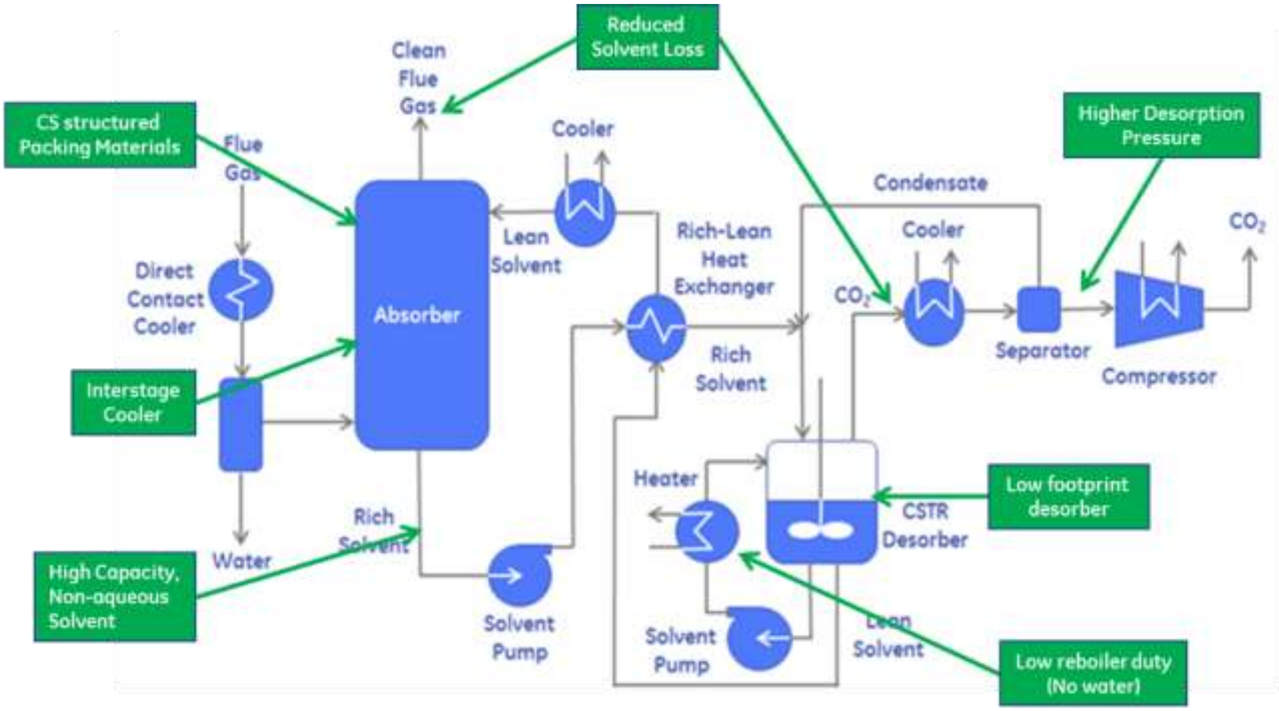


Figure 10. **CO_2 Capture Process for GAP-1_m/TEG**

CSTR – continuous stirred tank reactor

3. CSTR Campaign

A CSTR desorber system was designed, fabricated and integrated with the equipment available (absorber / water wash column, rich lean exchanger, lean cooler) at the NCCC. The system was designed to operate continuously, using flue gas provided by the NCCC. The conceptual design of the hybrid system in shown in **Figure 11**.

The skid design included a desorber that replaced the stripper column currently at the NCCC. The desorber consists of a continuous stirred-tank reactor into which the CO_2-rich solvent from the absorption column feeds. The reactor has an agitator to keep the content of the reactor well mixed. The reactor also has a recycle loop with a heat exchanger. This loop is used to heat the contents of the reactor and to increase mass transfer of the desorbed CO_2 from the solvent to the gas phase. The skid also includes a partial condenser that recovers solvent vapor from the CO_2 leaving the reactor vessel.

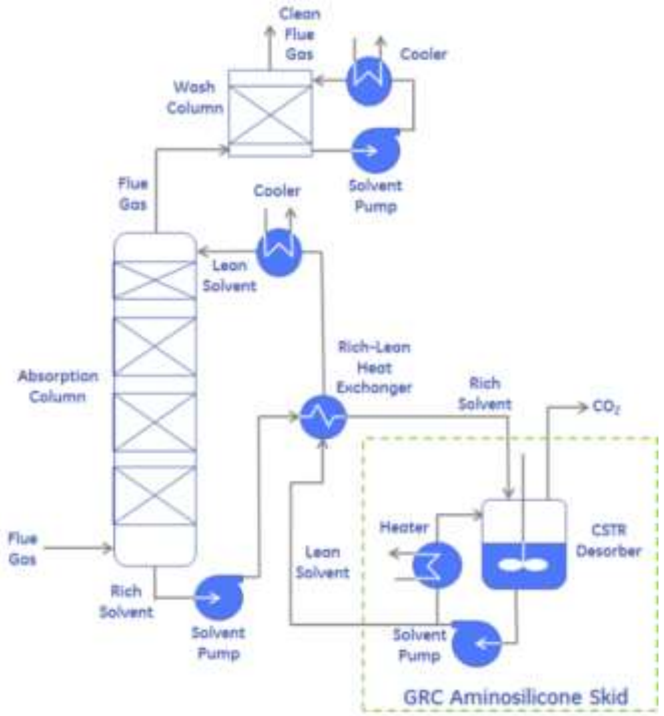


Figure 11. **CSTR – PSTU Integration:** Conceptual Design

3.1. CSTR System

The overall timeline of the CSTR campaign is shown in **Figure 12**.

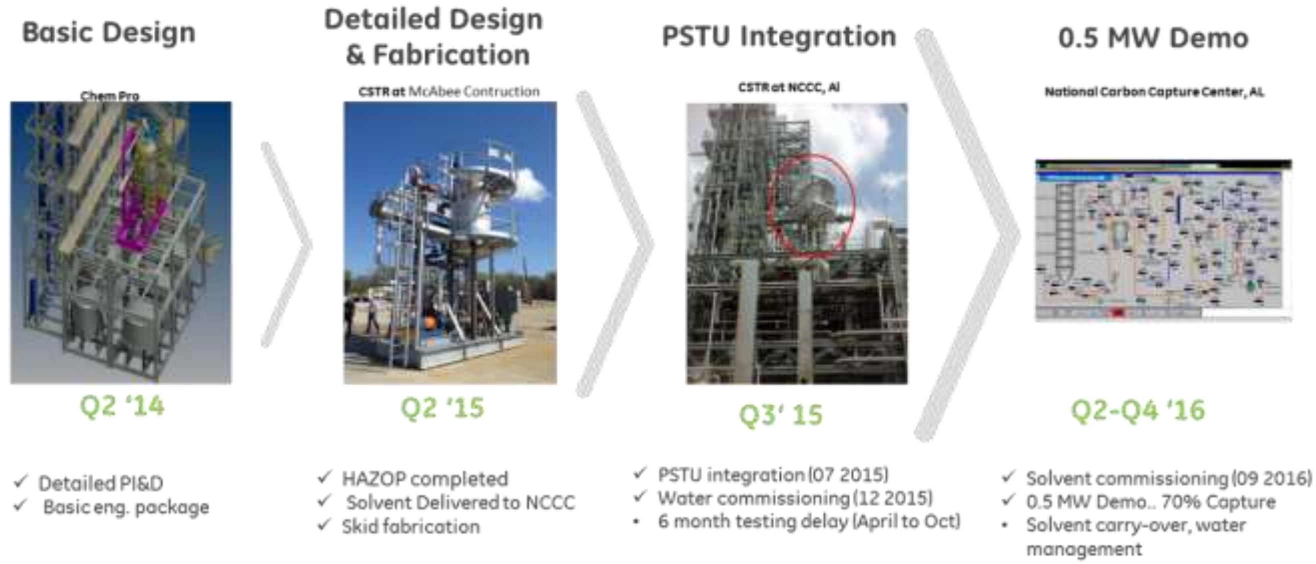


Figure 12. **CSTR Campaign:** Overall Timeline

3.1.1. CSTR System Design and Fabrication (Q1 2014 – Q2, 2015)

GE Global Research contracted ChemPro Group, an engineering firm, to complete the basic and detailed engineering package for the CSTR system. The initial design package included detailed P&IDs, equipment specifications for all major equipment (including pumps, heat exchangers, and the continuous stirred-tank reactor), and material and energy balances. The basic engineering package has also shared with the NCCC for review, to ensure that the skid can be integrated with the existing PSTU equipment. **Figure 13** shows an aerial view of the mezzanine level of the PSTU, with the proposed location of the CSTR skid. **Figure 14** shows a 3D model of the CSTR skid, incorporated into the PSTU. **Figure 15** shows the 3D model of the CSTR skid structure. The basic engineering design was completed in Q2 2014, and the detailed engineering was completed in Q3 2014. McAbee Construction, contracted by ChemPro, completed the skid fabrication in Q1 2015 (**Figure 16**)

Figure 13. **CSTR Design:** PSTU showing the footprint of the GE skid

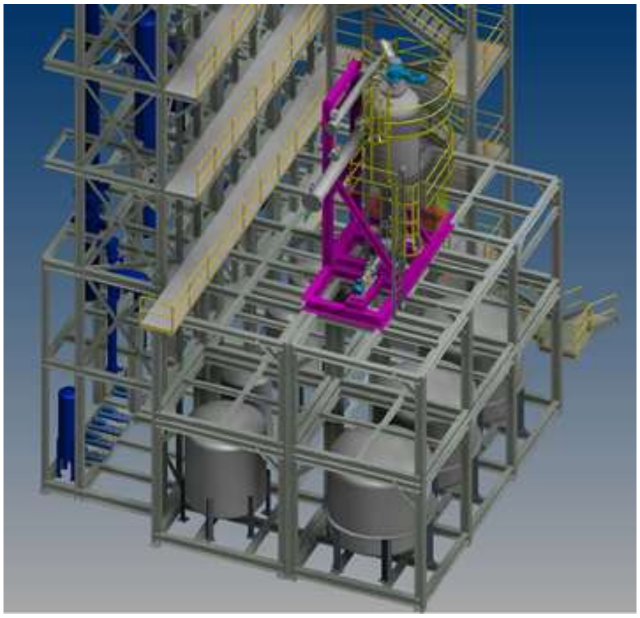


Figure 14. **CSTR Design:** GE CSTR – PSTU Integration (3D model, Chempro)

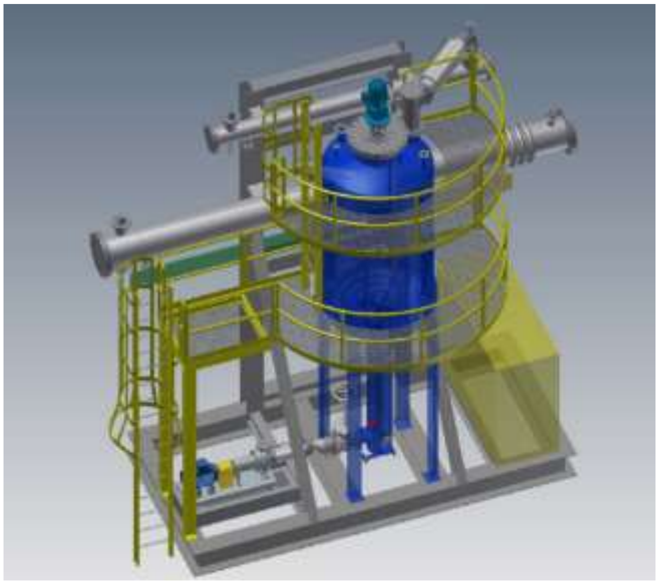


Figure 15. **CSTR Design:** Skid Structure (3D model, Chempro)

Figure 16. CSTR Fabrication: Skid during commissioning (Q1 2015, McAbee)

3.1.2. Material Selection

Compatibility of materials of construction is crucial for the integrity of the capture system. Some of the ubiquitous and critical components are seals and gaskets. From prior work, it was found that Viton® seals did not withstand prolonged exposure to aminosilicones. EPDM was considered as a replacement material for seals and gaskets on the PSTU, but it was unclear if this material would withstand a heated mixture of GAP-1_m/TEG.

To evaluate the EPDM elastomer, small samples of the white rubber were placed in flasks with various solvents, as shown in **Table 1**, and heated for 6-10 days at 140 °C under N_2. Both pure GAP-0 and GAP-1_m (Samples A and B) showed little effect on the EPDM sample with only a very small amount of white hazy material being formed/extracted after 10 days at 140 °C. While no apparent damage was done to the rubber sample C, the GAP-1_m/TEG mixture generated a scummy layer that contained black specks that floated on the solvent mixture.

Table 1. Test samples for EPDM stability

Sample	Solvent	Observation
A	GAP-0	Small amount of white hazy material extracted from rubber. No apparent dimensional or color change and rubber sample was still elastomeric. Some absorption of solvent into rubber as seen by weeping after surface removal of solvent.
B	GAP-1m	Small amount of white hazy material extracted from rubber. No apparent dimensional or color change and rubber sample was still elastomeric. Some absorption of solvent into rubber as seen by weeping after surface removal of solvent.
C	GAP-1m/TEG (60:40)	Scum/rag level floating on top of solvent with black material present. However, there was no apparent dimensional and only a very slight color change and rubber sample was still elastomeric. Some absorption of solvent into rubber as seen by weeping after surface removal of solvent.
D	TEG	Small amount of white hazy material extracted from rubber. No apparent dimensional or color change and rubber sample was still elastomeric. Some absorption of solvent into rubber as seen by weeping after surface removal of solvent.
E	GAP-1m/TEG (60:40)	Scum/rag level floating on top of solvent with black material present. However, there was no apparent dimensional and only a very slight color change and rubber sample was still elastomeric. Some absorption of solvent into rubber as seen by weeping after surface removal of solvent.

Believing that the TEG was responsible for this effect, EPDM sample D was heated for 6 days with pure TEG with no rag/scum layer or black specks appearing. Repeating the C sample with E, black material appeared after 2-3 days and did not appear to increase for the 6 day duration of the heating. In all cases, regardless of the condition of the solvent, the EPDM samples remained viable and unchanged based on visual and tactile inspection.

A B C D E

Figure 17. **Material Qualification:** Gasket & seal material selection EPDM samples and solvents after thermal treatment in solvent. See **Table 1** for sample description.

A more quantifiable measure of the rubber integrity was made via tensile testing. For these tests, dog bone shaped samples were cut from a 3mm thick EPDM sheet. **Figure 18** and **Table 2** show the results obtained from virgin EPDM rubber samples. **Figure 19** and **Table 3** summarize the results for EPDM rubber aged at 140 ºC for 7 days in a 60/40 mixture of GAP-1_m/TEG.

The virgin material showed a maximum load of 38 N and mean tensile stress of ~3.9 MPa and a tensile strain of ~1590% which is representative of a strong elastomer. After soaking in the solvent mixture, the maximum load jumped to ~62 N with a tensile stress increased to ~6.2 MPa and the stress increased to over 3000%. While the dimensions of the samples remained the same, it was apparent that some solvent had plasticized the rubber, thereby increasing its toughness.

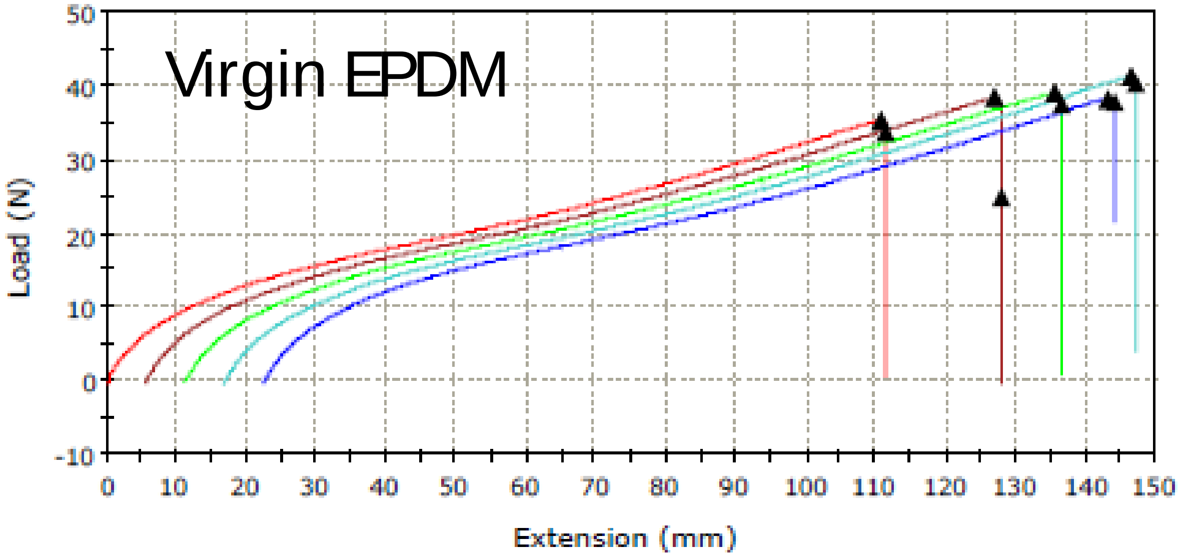


Figure 18. **Material Qualification:** Instron tensile plot (EPDM virgin samples)

Table 2. **Material Qualification:** Virgin EPDM Instron

	Maximum Load	Tensile stress at Maximum Load	Tensile strain at Maximum Load	Load at Break (Standard)	Tensile stress at Break (Standard)	Tensile strain at Break (Standard)
Sample	(N)	(MPa)	(%)	(N)	(MPa)	(%)
1	35.28	3.56	1449.73	33.64	3.4	1460.07
2	38.23	3.86	1589.43	24.79	2.5	1599.77
3	38.87	3.93	1624.85	37.33	3.77	1636.82
4	41.15	4.16	1699.95	40.13	4.05	1708.12
5	38.15	3.85	1583.57	37.61	3.8	1596.63
Coefficient of Variation	5.47157	5.47157	5.71596	17.30884	17.30884	5.64438
Maximum	41.15	4.16	1699.95	40.13	4.05	1708.12
Mean	38.33	3.87	1589.51	34.7	3.51	1600.28
Median	38.23	3.86	1589.43	37.33	3.77	1599.77
Minimum	35.28	3.56	1449.73	24.79	2.5	1460.07
Range	5.87	0.59	250.22	15.35	1.55	248.04
Standard Deviation	2.09745	0.21186	90.85557	6.00627	0.60669	90.32598

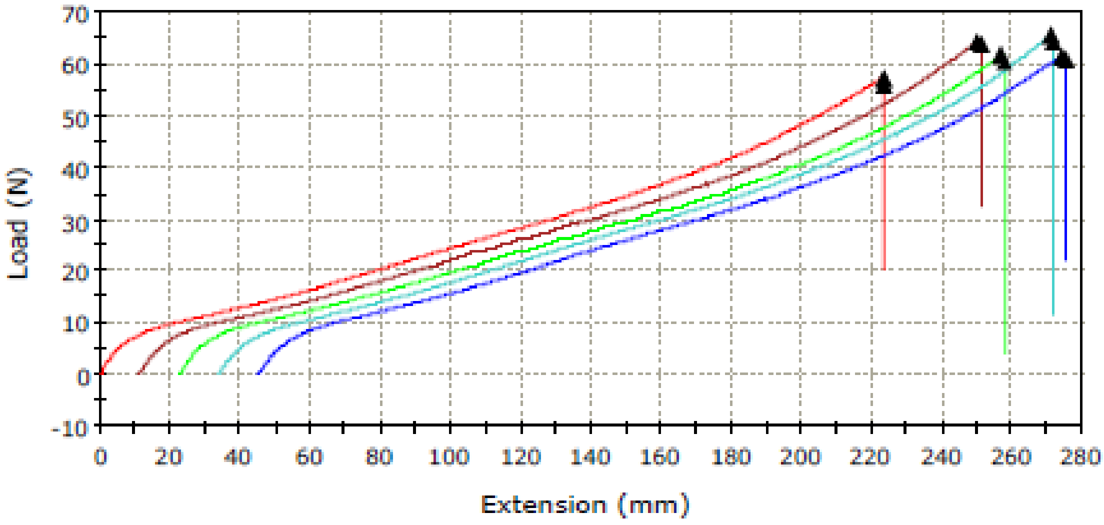


Figure 19. **Material Qualification:** Instron tensile plot (EPDM aged samples)
EPDM rubber aged at 140 ºC for 7 days in a 60/40 mixture of GAP-1/TEG.

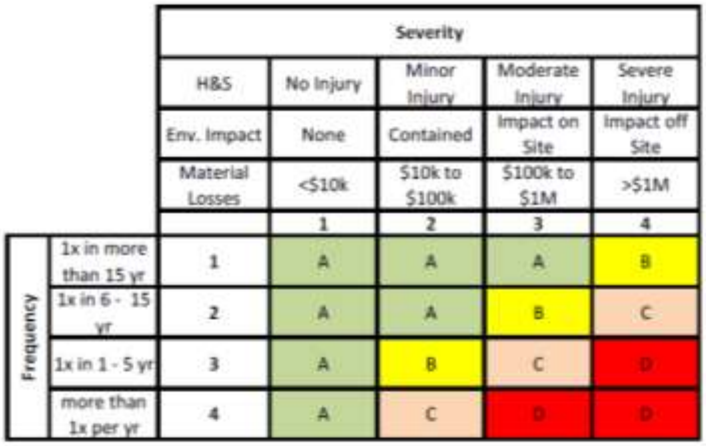
Table 3. **Material Qualification:** Aged EPDM Instron
EPDM rubber aged at 140 ºC for 7 days in a 60/40 mixture of GAP-1/TEG.

	Maximum Load	Tensile stress at Maximum Load	Tensile strain at Maximum Load	Load at Break (Standard)	Tensile stress at Break (Standard)	Tensile strain at Break (Standard)
Sample	(N)	(MPa)	(%)	(N)	(MPa)	(%)
1	57.18	5.78	2920.15	55.65	5.62	2925.59
2	63.95	6.46	3120.51	63.63	6.43	3135.83
3	61.42	6.2	3065.5	60.55	6.12	3075.29
4	65.45	6.61	3111.72	64.21	6.49	3119.84
5	61.29	6.19	3006.72	60.71	6.13	3015.43
Coefficient of Variation	5.08924	5.08924	2.7293	5.56863	5.56863	2.80969
Maximum	65.45	6.61	3120.51	64.21	6.49	3135.83
Mean	61.86	6.25	3044.92	60.95	6.16	3054.4
Median	61.42	6.2	3065.5	60.71	6.13	3075.29
Minimum	57.18	5.78	2920.15	55.65	5.62	2925.59
Range	8.27	0.84	200.36	8.56	0.86	210.24
Standard Deviation	3.148	0.31798	83.1049	3.3941	0.34284	85.81913

3.1.3. Hazard and Operability Study (HAZOP)

A detailed hazard and operability study (HAZOP) of the skid design was conducted on 12/3 and 12/4 of 2014 at the NCCC. For the HAZOP, an independent facilitator and scribe where hired to guide the process. The facilitator sectioned the P&IDs for the skid into 11 nodes, each node corresponding to a portion of the skid dedicated to a unique function. The team, which included representatives from GE Global Research, the NCCC, and ChemPro group, evaluated possible failure modes for each node. For this evaluation, the frequency (F) of each failure mode occurring and the severity (S) in terms of health and safety, environment impact, and material loss were estimated on a scale of 1 to 4 (with 4 being the worst), and the resulting risk rank (R) was determined by calculating F×S. **Table 4** shows the matrix that was used for this evaluation, including guidelines for rating frequency and severity and the color coded region showing the resulting risk rank. Red risk ranks (D) are considered extreme risks, while green risk ranks (A) are considered minor. It should be noted that the risk for each failure mode was evaluated without taking into account existing safety measures or future abatement methods. After the risk was determined for each failure mode, recommendations were made by the team to abate the risk.

Table 4. **HAZOP study:** risk matrix

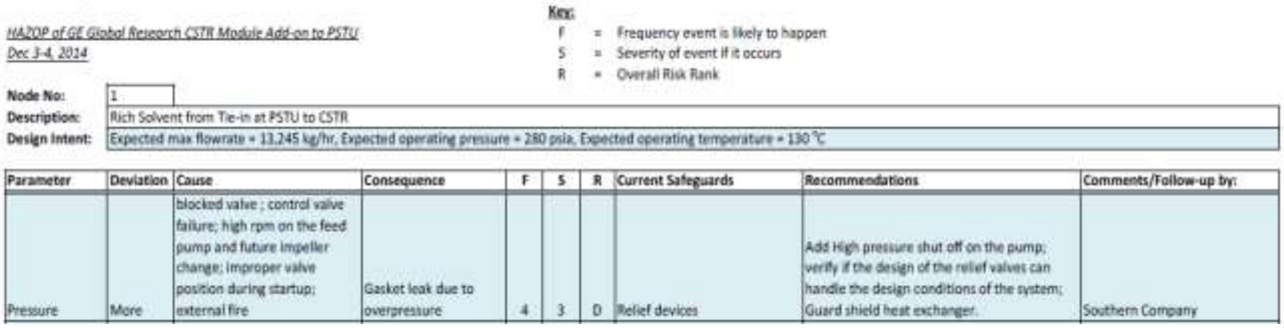


			Severity			
		H&S	No Injury	Minor Injury	Moderate Injury	Severe Injury
		Env. Impact	None	Contained	Impact on Site	Impact off Site
		Material Losses	<$10k	$10k to $100k	$100k to $1M	>$1M
			1	2	3	4
Frequency	1x in more than 15 yr	1	A	A	A	B
	1x in 6 - 15 yr	2	A	A	B	C
	1x in 1 - 5 yr	3	A	B	C	D
	more than 1x per yr	4	A	C	D	D

In the HAZOP, 39 failure modes were identified. However, of these failure modes, only 1 received a D risk rating and another received a C risk rating.

Figure 20 shows the results of the analysis for the failure mode that received a risk rating of D. This failure mode is caused by the high pressure in the solvent feed to the CSTR resulting in a gasket leak in the rich/lean heat exchanger. As shown in **Figure 20**, a number of causes for high pressure in the solvent feed were identified. Additionally, recommendations were given to abate the risk, such as having a high pressure shut off on the feed pump, and shielding the rich/lean heat exchanger to contain any solvent that might escape.

Figure 21 shows the results of the analysis for the failure mode that received a risk rating of C. This failure mode is caused by the over-pressure of the CSTR. As shown in **Figure 21**, the CSTR is already equipped with an indicating rupture disk in case of over pressure. One of the recommendations was to have a signal from the indicating rupture disk sent to the control room, so that the operator can see if the rupture disk has released. The design team implemented all recommendations from the HAZOP team during commission phase of the project.



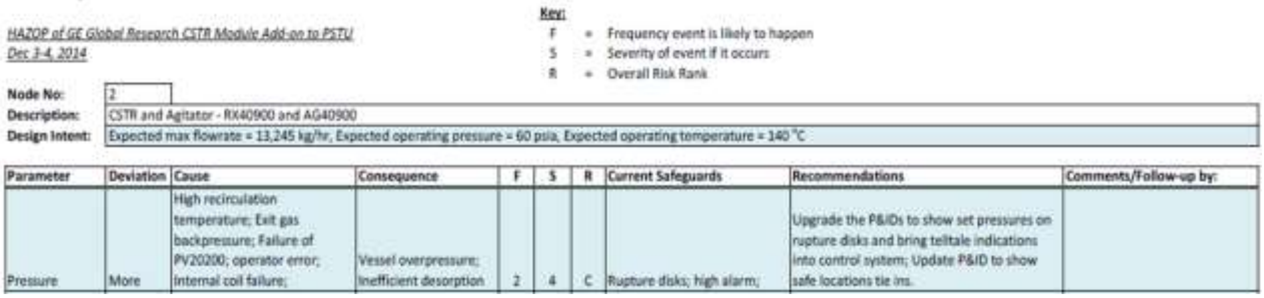
HAZOP of GE Global Research CSTR Module Add-on to PSTU
Dec 3-4, 2014

Key:
F = Frequency event is likely to happen
S = Severity of event if it occurs
R = Overall Risk Rank

Node No:	1
Description:	Rich Solvent from Tie-in at PSTU to CSTR
Design Intent:	Expected max flowrate = 13,245 kg/hr, Expected operating pressure = 280 psia, Expected operating temperature = 130 °C

Parameter	Deviation	Cause	Consequence	F	S	R	Current Safeguards	Recommendations	Comments/Follow-up by:
Pressure	More	blocked valve ; control valve failure; high rpm on the feed pump and future impeller change; improper valve position during startup; external fire	Gasket leak due to overpressure	4	3	D	Relief devices	Add High pressure shut off on the pump; verify if the design of the relief valves can handle the design conditions of the system; Guard shield heat exchanger.	Southern Company

Figure 20. **HAZOP study:** Failure mode analysis for high pressure in the solvent feed



HAZOP of GE Global Research CSTR Module Add-on to PSTU
Dec 3-4, 2014

Key:
F = Frequency event is likely to happen
S = Severity of event if it occurs
R = Overall Risk Rank

Node No:	2
Description:	CSTR and Agitator - RX40900 and AG40900
Design Intent:	Expected max flowrate = 13,245 kg/hr, Expected operating pressure = 60 psia, Expected operating temperature = 140 °C

Parameter	Deviation	Cause	Consequence	F	S	R	Current Safeguards	Recommendations	Comments/Follow-up by:
Pressure	More	High recirculation temperature; Exit gas backpressure; Failure of PV20200; operator error; Internal coil failure;	Vessel overpressure; Inefficient desorption	2	4	C	Rupture disks; high alarm;	Upgrade the P&IDs to show set pressures on rupture disks and bring telltale indications into control system; Update P&ID to show safe locations tie ins.	

Figure 21. **HAZOP study:** Failure mode analysis for high pressure in the CSTR

3.1.4. Pilot Scale Solvent Supply

Two separate sources of GAP-1_m solvent were identified as potential suppliers for the solvent to be used in the pilot test operation. Solvent samples were received at GE GRC and the qualification process included full compositional analysis, performance evaluation for CO_2 capture uptake, and thermal stability tests. The supplier of choice was down selected based on consideration of shipping costs, scale-up capacity, on-time delivery, and reliability.

Part of the evaluation of the GAP-1_m from the domestic supplier entailed thermal stability testing with several levels of β-isomer contamination. Samples supplied contained <1%, 4%, 8% and 12% β-isomer. The most stable mixture of the four materials was the large-scale batch of GAP-1_m that had the highest beta content at ~12%. **Figure 22** summarizes the 3-month test in which the sample containing 12 % β-isomer was heated at 150 °C for 90 days with periodic sampling for GC analysis. A modest decrease in GAP-0 content with a concomitant increase in GAP-1, GAP-2 and GAP-3 was observed. This was in stark contrast to the 1%, 4% and 8% samples in which a precipitous drop was seen in the first 2 weeks. 20-40% of the GAP-0 was lost with a doubling of the GAP-1 and GAP-2 content during this time period. 12% beta GAP-1m met also the qualifications for total CO_2 uptake and impurities profiles and it was selected to be produced for the pilot scale program. 10 Mt of GAP-1_m solvent was delivered to NCCC site in Q2 2015 (**Figure 23**).

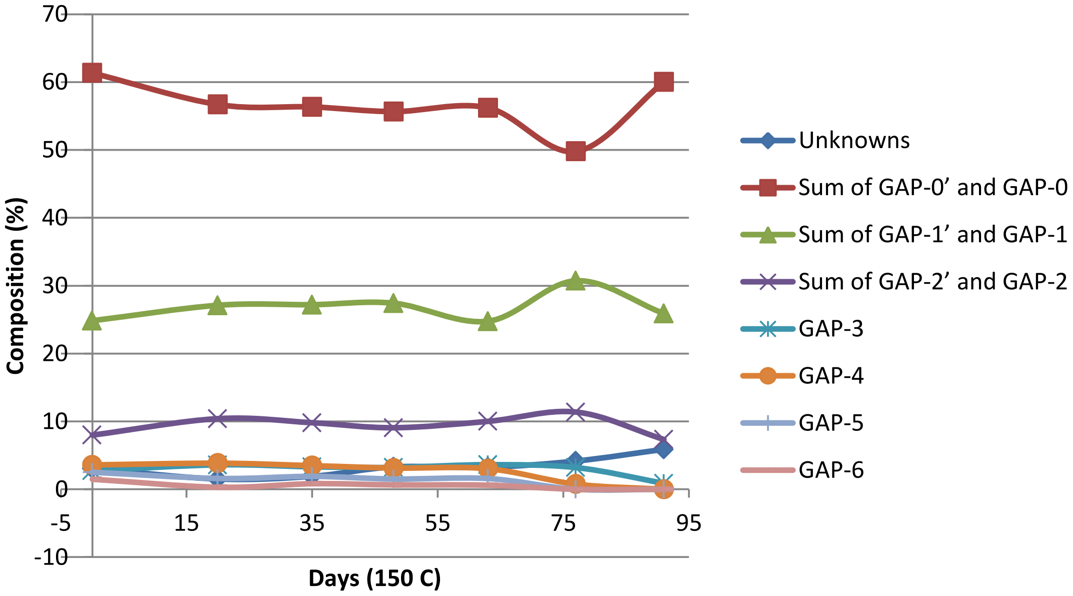


Figure 22. **Solvent Supply:** Qualification (Thermal stability)

Thermal stability of GAP-1_m with ~12% Beta Isomer

Figure 23. **Solvent Supply:** Solvent delivered at NCCC (10 Mt, Q2 2015)

3.1.5. Waste Water Process Development

During operation of the PSTU with the GAP-1_m/TEG solvent, there were two potential sources of waste water from the process, as shown in Figure 24. At the exit to the absorption tower, a water wash tower is used to capture any aminosilicone and TEG leaving the column as vapor or aerosol. As these components accumulate in the wash water, a fraction of the wash water is purged so that clean make-up water can be added. The second source of waste water is water that evaporates from the solvent during heating in the desorber. The CO_2 and water stream generated will pass through a partial condenser to recover the majority of the aminosilicone, but a small amount of aminosilicone will remain in the CO_2 stream and condense out with the water in the total condenser. During the design phase of the CSTR system, two methods were explored to minimize the solvent loss in the aqueous effluents: (i) purification through activated carbon bed, and (ii) water recycle in the lean storage tank. The two methods are discussed below.

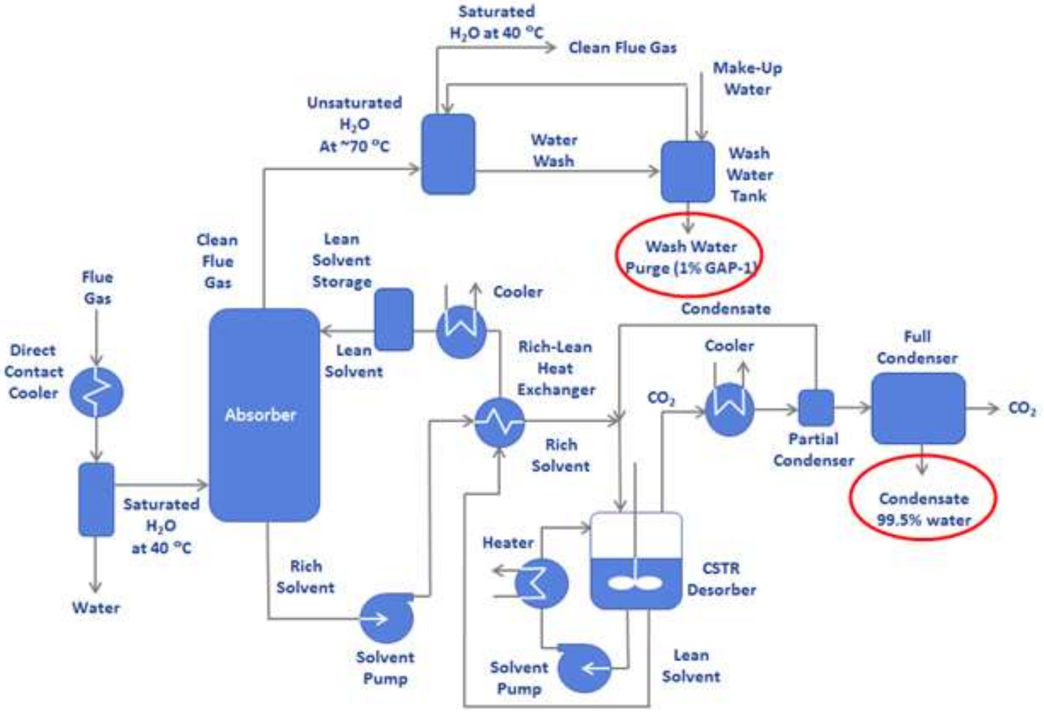


Figure 24. **GAP-1m/TEG Process Flow Diagram:** Waste water streams

3.1.5.1. Waste Water Purification: Activated Carbon Adsorption

Both lab and bench scale experiments were performed to evaluate the efficiency of using activated carbon for the removal of aminosilicones from waste water streams. Two methods were examined as potential analytical tools for the analysis of aminosilicones in water. The first was high pressure liquid chromatography – electro spray/time-of-flight mass spectrometry (HPLC-ES/ToF MS) and the second was total organic carbon (TOC). Synthetic waste water sample was prepared by mixing 3.0 g of GAP-0 and 323 g DI water. This mixture was heated at 70 ^{o}C for 24 h. The clear, water-white liquid was analyzed and then treated with carbon. 30 g of activated carbon (Norit SG II) was loaded into a chromatography column (20 x 150 mm bed of carbon), and 250 mL of synthetic waste water was passed through the column. **Table 5** shows that there was a large discrepancy between the two methods for the untreated sample. However, the treated material was in close agreement. This difference could be due to the fact that the concentration of the untreated sample exceeds the dynamic quantitative range for the mass spectrometer, even at 20-fold dilution. It is also possible that the response factors for the aminosilicones and aminosilanols are different than the cyclohexylamine standard used in the test.

Table 5. Waste Water Treatment by Activated Carbon Adsorption:
Analytical Method Comparison

Method	Before Treatment (ppm)	After Treatment (ppm)
HPLC-ES/ToF MS	16,432	113
TOC	26,184	84

HPLC-ES/ToF MS - high pressure liquid chromatography – electro spray/ time-of-flight mass spectrometry; **TOC** - total organic carbon

While there is some difference in absolute measurements for aminosilicone content analysis between the TOC and HPLC methods, both appear to be acceptable methods for determining the presence of aminosilicones in aqueous solutions that range between ~100ppm and 3%. Although the TOC method cannot identify specific species in solution, it is a rapid and easily employed analytical procedure that can be deployed at the pilot plant site to provide a sense of the organic contamination in the waste water streams. In addition, it appears that under the conditions studied, activated carbon treatment of highly contaminated waste water (1.6-2.6% aminosilicone) is an effective means of greatly reducing the aminosilicone level.

In order to further test the efficacy of the carbon filter for removing aminosilicone and TEG from waste water, a series of experiments were commissioned to be performed at Engineering Performance Solutions, a company that specializes in testing materials for filtration.

For these experiments a small bed of the activated carbon used in the full-scale carbon bed was produced by taking the full-scale carbon pellets and grinding them down to a finer particle size. The smaller particles were then placed in a mini-column. Solutions were made of 0.5 wt.% aminosilicone in water, 0.5 wt.% TEG in water, and 0.25 wt.% aminosilicone and 0.25% TEG in water. Each of these solutions was run through a fresh bed at a flow rate that resulted in a contact time representative of the Empty Bed Contact Time (EBCT) of the full-scale process. The effluent from the carbon bed was measured using Total Organic Carbon (TOC) measurements, so that break-through curves could be generated for each solution. **Figure 25** shows the break-through curve for 0.5 wt.% aminosilicone in water. It was observed that the TOC was less than 10% of its final value for roughly 2000 bed volumes. The TOC then jumped to approximately 50% of its final value for another 5000 bed volumes, before complete breakthrough.

Figure 26 shows the corresponding curves for 0.5 wt.% TEG in water (Train 1) and 0.25 wt.% aminosilicone and 0.25 wt.% TEG in water (Train 2). The TEG appears to demonstrate 100% breakthrough almost immediately. Interestingly, for the mixture of aminosilicone and TEG in water, 100% breakthrough also appears almost immediately. This suggests that the TEG may interfere with the carbon beds ability to remove aminosilicone. Therefore, it was concluded that absorbers containing the tested activated carbon are not highly efficient in removing traces of aminosilicone from aqueous streams containing TEG.

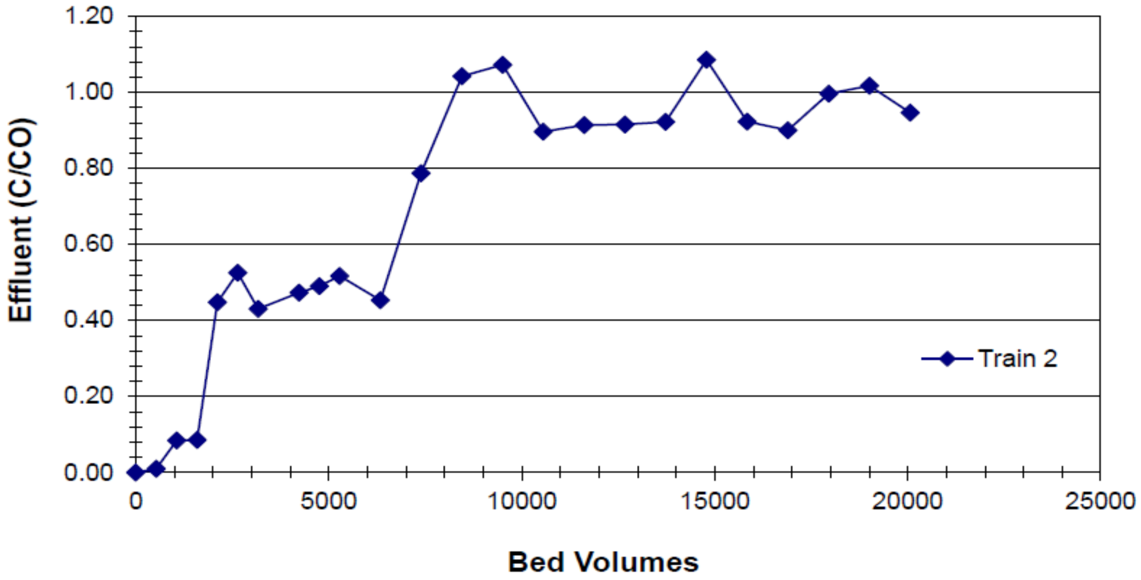


Figure 25. **Waste Water Purification:** Carbon bed test (GAP-1_m in water)
Breakthrough curve for 0.5 wt.% aminosilicone in water through carbon bed
Analysis based on total organic carbon (TOC) method

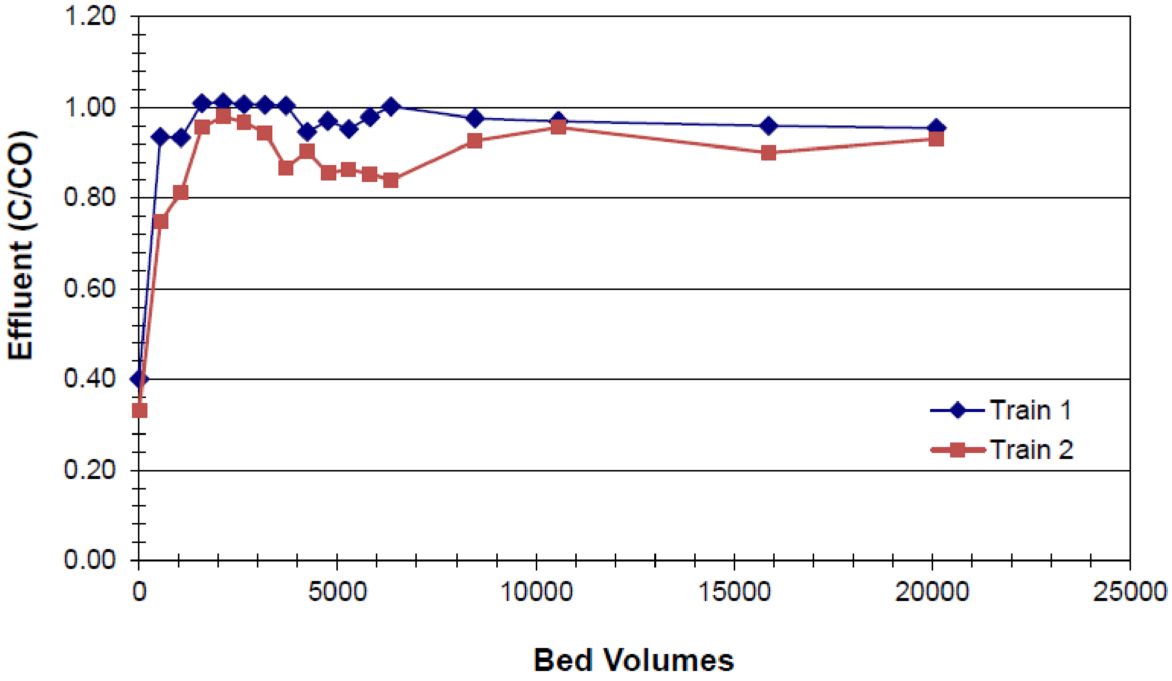


Figure 26. **Waste Water Purification:** Carbon bed test (TEG and GAP-1_m/TEG)
Breakthrough curves for: 0.5 wt.% TEG in water (Train 1) and 0.25 wt.% aminosilicone and 0.25 wt.% TEG in water (Train 2). Analysis based on total organic carbon (TOC) method

3.1.5.2. Waste Water Recycling Process

In order to minimize the waste water produced, it was determined that the waste water streams can be recycled back to the lean solvent storage tank, as shown in **Figure 27**.

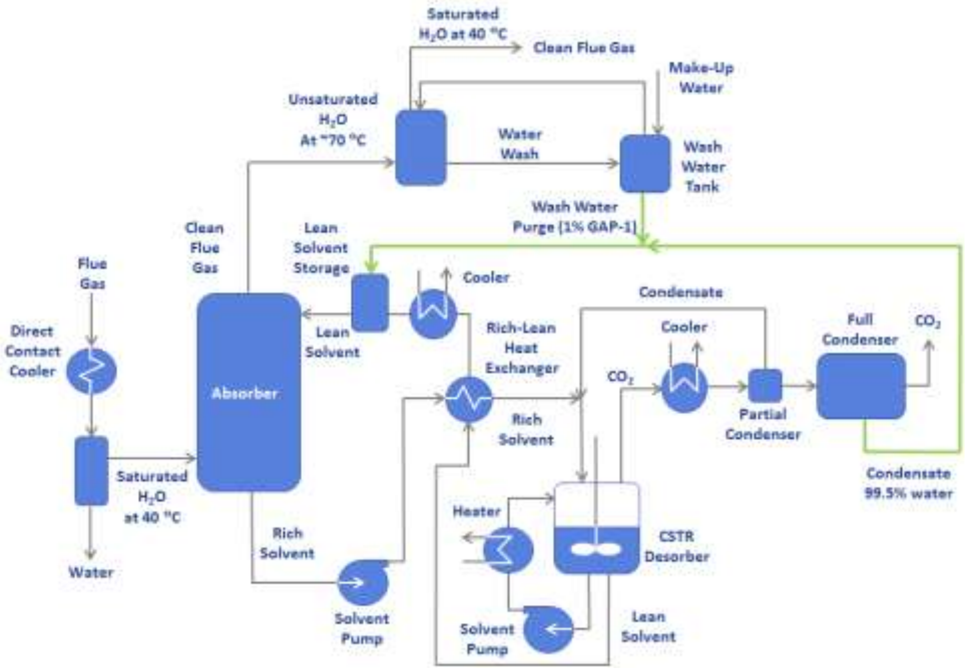


Figure 27. **Waste Water Recycle:** Process flow diagram
Waste water streams recycled to the lean solvent storage tank

Recycling the water to the lean solvent storage tank has several advantages. First, it has been shown that having controlled amount of water in the solvent decreases the rate of thermal degradation. Second, control amount of water lowers the partial pressure of CO_2 in the desorber headspace, and hence decreases the desorption temperature. Finally, recycling water reduces the solvent loss in the aqueous streams, and decreases the waste water produced during the operation. Based on all these advantages, this configuration was adopted during both CSTR and SSC campaigns.

3.2. Analytical Methods Development

GE Global Research and NCCC analytical team developed several analytical methods to assess the performance and degradation of the GAP-1_m/TEG solvent during the CSTR / SSC campaigns. **Table *6*** lists the method utilized during the campaign.

Table 6. Analytical Methods

Quantifier	Analytical Method
GAP-1_m/TEG in waste water	TOC
% CO_2 in rich solvent	Carbamate Titration
Free Amine	Amine Titration
GAP-1_m : TEG urea	^1H NMR
% H_2O	Karl Fisher Titration

Total Organic Carbon (TOC):

As described earlier, this technique was used to determine the level of aminosilicone present in the wash water samples. The sample was acidified, oxidized and combusted. While this procedure cannot differentiate between species present in the sample, it is a very common method used in water evaluation. As there were no other sources of carbon present beside the GAP-1_m/TEG sample, we were able to correlate the TOC to the amount of aminosilicone solvent present.

Carbamate Titration:

The extent of reaction of CO_2 with the amine solvent was determined by titrating the carbamate in the GAP-1_m/TEG solvent. A known amount of GAP-1_m/TEG solvent (1.5 – 3 g) was diluted with a pH adjusted methanol solution (50 mL, pH 11.3). Upon degassing CO_2, the pH of the methanol solution dropped depending on the CO_2 content. The mixture was then titrated back to a pH of 11.3 with potassium hydroxide. A fixed endpoint method was utilized. The sample weight, titrant normality, and volume of titrant consumed were all used to calculate the %CO_2 in the initial sample.

Amine Titration:

Free amine content was determined by titration with hydrochloric acid. Approximately 0.1 g of sample was added to a 10 mL 2-neck round bottom flask equipped with a magnetic stir bar and a pH electrode. The sample was diluted with approximately 8-10 mL of MeCN and stirred. pH measurements were recorded while adding hydrochloric acid solution (0.1 N). After the pH 7 end point was reached, titrant was added until a pH of 3 was achieved. The equivalence point was determined by plotting pH vs titrant volume.

^{1}H NMR

Samples were taken periodically for proton NMR analyses, to determine if the ratio of TEG : aminosilicone remained constant during the campaign, and to monitor for significant build-up of urea by-products. These tests were conducted at GE GRC on a 400 MHz instrument using $CDCl_3$ as the solvent. The ratio of O-CH_2CH_2-O protons in TEG to the CH_3-Si protons in GAP-X was determined, and the weight ratio of the two components defined. In addition, the integration of the resonance at ~3.2ppm showed the amount of urea that may have been formed due to thermal degradation.

3.3. CSTR – PSTU Integration and Water Commissioning (Q3-4 2015, Q2 2016)

CSTR system was delivered to NCCC site in June 2015, and its integration with the PSTU was completed in Oct. 2017. System integration proceeded in the following sequential steps: (i) rigging the CSTR system to the 4th floor of PSTU (**Figure 28** / **Figure *29***); (ii) pipe connections between the CSTR system and the PSTU, (iii) pressure testing of the CSTR reactor and auxiliary equipment with air, (iv) heat tracing and (v) process control interface development for CSTR-PSTU integrated system (**Figure 30**). A series of commissioning, start-up, and operating documents were created specific to the GE's CSTR system installed in the PSTU and transferred to NCCC. The list of procedures generated is listed in **Table 7**.

Table 7. **CSTR – PSTU Integration:** Operating Documents

Process Step	Operating Documents
Preparations for Start-up	• Verify Completion/Installation • Safety Check • Electrical and Instrument Continuity Check
Initial Start-up	• Preparation for Start-up with Water • Cooling Water & Tempered Water System Fill • Demineralized Water System Fill • Reactor/Recirculation System Fill • Steam System Fill • System Shutdown and Draining
Solvent Mixing and Loading	• Solvent Mixing Procedure • Inventory Solvent Storage Tank • Inventory Lean Solvent Storage • PSTU Solvent Filling Procedure • Filling GE System with Process Fluid
Process Start-up	• Normal Start-up • Normal Operation • Normal Shutdown • Emergency Shutdown
Draining and Cleaning Procedures	• Draining and Cleaning Procedures • Draining Procedure • Cleaning Procedure

Figure 28. **CSTR – PSTU Integration:** CSTR Rigging (Q3 2015)

Figure 29. **CSTR – PSTU Integration:** CSTR Installed at NCCC (Q3 2015)

Figure 30. **CSTR – PSTU Integration:** Process control interface

Commissioning of the PSTU – CSTR system was conducted in the following sequential steps: (a) cold water circulation (Q4 2015), (b) steam commissioning (12/2016 and Q2 2016), and (c) hot and cold solvent circulation (Q3 2016). During the cold water circulation and steam commissioning, the team identified and fixed two minor leaks in the rich-lean heat exchanger, and CSTR lid (around sight glasses). Finally, it was determined that the CSTR had been hooked up to intermediate pressure steam (<250 psig), instead of the medium pressure steam (<450 psig) specified in the design. Because of the lower pressure steam supply, a pressure control valve on the CSTR system that was designed for the higher expected pressure drop had to be removed, and the interlock system has modified to accommodate this change.

3.4. Solvent Commissioning (Q3 2016)

Commissioning of the CSTR - PSTU system with GAP-1_m/TEG solvent was conducted by flowing both cold and hot solvent through the absorber-desorber system to check the operability of both the CSTR system and the rest of PSTU (absorber, pump, rich-lean exchanger, lean cooler) with the non-aqueous GAP-1_m/TEG solvent. The team implemented strict waste water and solvent management procedures to address handling the non-aqueous GAP-1_m/TEG solvent in the PSTU. First, all the pressure relief points of the system were piped to containment drums to eliminate the risk of solvent leaks. Any waste water resulted from the process was transferred to collection tanks and disposed off-site. PSTU sump collecting rain water drainage was monitored through automatic TOC measurements. Flue gas was automatically turned off in case of over pressure or over temperature events. Finally, HAZOP and SOPs were updated after solvent commissioning and before starting the CSTR campaign.

During the first attempts at operation with flue gas, the liquid level in CSTR was difficult to control leading to solvent carry-over in the downstream mist separator and total condenser. The root cause of solvent carryover was determined to be the high solvent water content (11 wt.%). The rapid changes in liquid level were attributed to the development of CO_2 and water vapor bubbles in the solvent, which resulted in a reduction in the effective density of the solvent in the CSTR (**Figure *31***). Foam development was confirmed by visual inspection through the CSTR sight glass. To address this behavior, the water content of the solvent was reduced to approximately 5 wt. % prior to further testing. In addition, a manual valve mounted downstream of the recirculation pump was adjusted to increase the local pressure on the suction side of the recirculation pump and the lower transmitter of the pressure differential liquid level measurement. The result of this adjustment was stable CSTR operation at 5 wt.% water. Once the water loading was kept below 5 wt.%, CSTR continuous operation was commenced in Q4, 2016. **Figure 32** shows stable CSTR operation at 0.2 MW_e and 2.5 % wt.% H_2O.

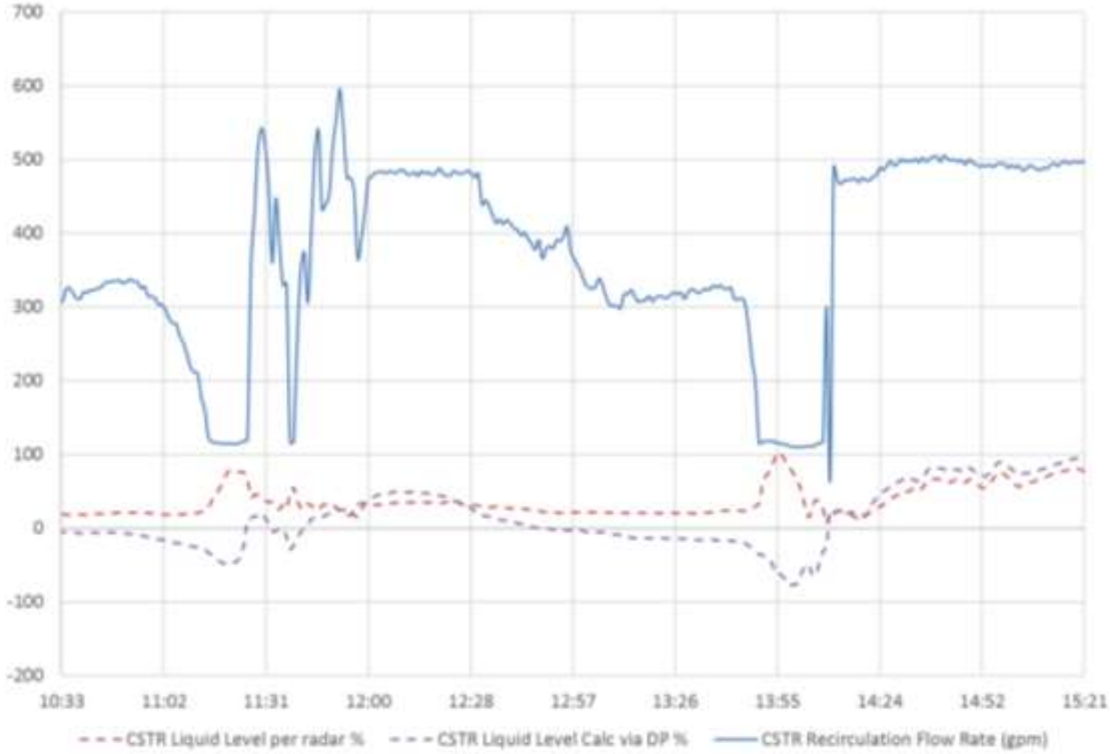


Figure 31. **CSTR Commissioning:** Solvent foaming at 11 wt.% H_2O

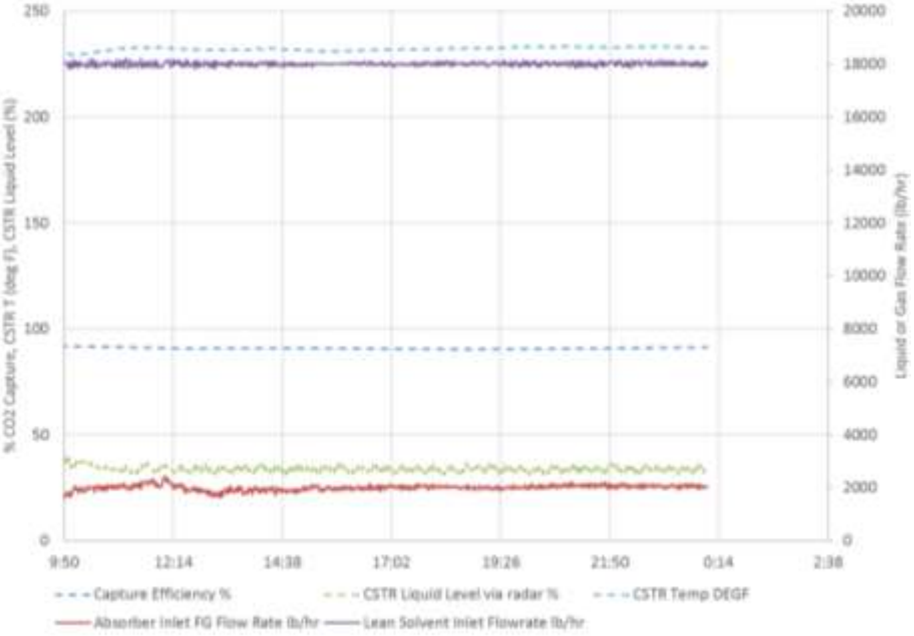


Figure 32. **CSTR Commissioning:** Stable operation at 2.4 wt.% H_2O and 0.2 MW_e

3.5. CSTR Campaign (Q4 2016)

500 hours of flue gas testing was performed in the NCCC PSTU with the CSTR while varying the stoichiometry (GAP : CO_2 = 2-4), and desorber temperature (230 F – 265 F). Liquid level in CSTR was kept constant at 33%. Water level was maintained below 5 wt.% to reduce solvent carryover in the overhead of CSTR, by manually transferring it from the mist separator tank (602) to the lean storage tank (401). Desorber pressure was varied between 7 to 10 Psig. Attempts to reduce desorber pressure below 7 Psig led to solvent carryover in the CSTR overhead. CO_2 capture efficiency has calculated based on the % CO_2 measured in the gas phase in the clean flue gas stream. Solvent degradation was evaluated based on the % amine measured in the lean solvent (**Figure 33**).

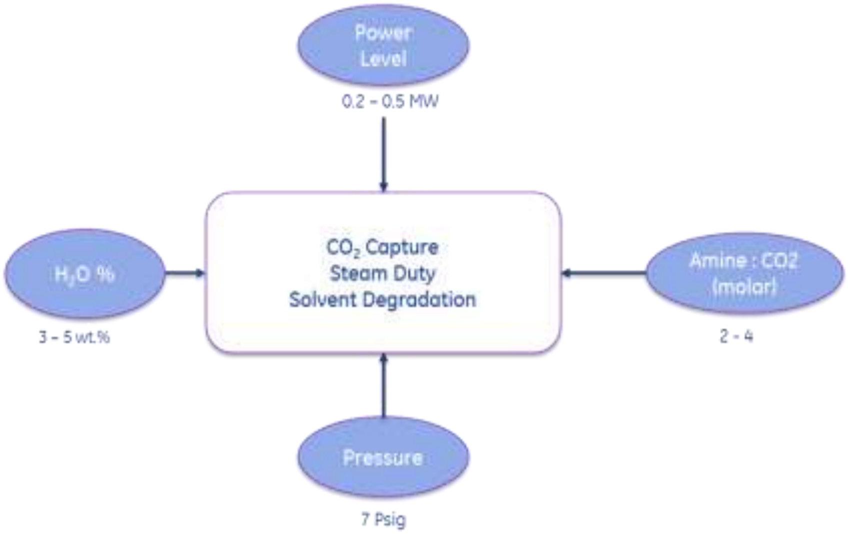


Figure 33. **CSTR Campaign:** Design of Experiments

Table 8: **CSTR Campaign:** Process Conditions

Condition	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Power Level (MW_e)	0.2			0.35	0.5	0.5	0.5
Flue Gas (FG) (lb./hr.)	2000	2000	2000	3750	5000	5000	5000
Liquid (lb./hr.)	12000	12000	12000	18000	1800	18000	18000
$D_{esorbed}$ (F)	233	233	233	248	248	255	265
$P_{desorber}$ (Psi)	7	7	7	7	7	7	7

Water Management: manual water addition from mist separator tank (602) to lean storage tank (401).

Table 9: **CSTR Campaign:** Flue gas conditions

	NO	**O_2**	**CO_2**	**NO_2**	**T**
	ppm	% vol.	% vol	ppm	F
Avg	34.2	6.6	12.6	0.55	134
Stdev.	8.1	0.8	0.5	0.21	2.9

Table 10: CSTR Campaign: Solvent Composition

Sample	Total Amine wt.%		CO_2 wt.%	TEG	Water
	wet	dry	wt.%	wt. %	wt.%
Initial	52.84	53.7	3.34	40.7	3.2
Condition 1	52.4	53.5	3.34	40.7	2.1
Condition 2	49.4	51.6	3.22	40.8	4.3
Condition 3	49.3	51.2	2.8	39.5	3.8
Condition 4	48.9	50.8	1.8	41.2	3.8
Condition 5	47.4	49.5	1.6	41.6	4.2
Condition 6	42.6	44.1	1.4	42.6	3.5
Condition 7	38.9	41.8	1.3	39.2	7.0

During the first week of the continuous CSTR campaign (Conditions 1-3, **Table 8** and **Table 9**) the system was operated at 0.2 MW_e, and a liquid flow rate that corresponded to a molar feed ratio of approximately 3.85 mol GAP-1_m/mol CO_2. CSTR temperature was held constant at 233 °F, and the lean solvent water content varied between 2 – 6 wt.%. During this period, CO_2 capture rates of 91-96% were observed. Higher CO_2 capture rates and lower absorber temperature correlated with increased solvent water content. Water level was maintaining by manually transferring the condensate accumulated in the total condenser (S-602) to the lean storage tank (401).

In the second week of the CSTR campaign, the gas flow rate was gradually increased to 500 pph (0.5 MW_e), as shown in **Table 8** (Conditions 4-7). Attempts were made to also increase the liquid flow rate to maintain constant molar GAP-1 : CO_2 ratio, but the PSTU rich solvent pump could not keep up with the higher liquid flow rate. Thus, the liquid flow rate was set to the maximum operable rate as limited by the rich solvent pump, which corresponded to a molar feed ratio of ~ 1.55 mol GAP-1_m/mol CO_2. CSTR temperature was increased from 233 ^oF to 265 ^oF.

During the third week of the continuous CSTR campaign, several attempts were made to operate the CSTR at lower pressure, to determine if higher desorption rates could be achieved at lower temperatures. However, operability of these test conditions proved to be problematic. Reducing CSTR pressure caused foaming of the liquid inventory in the CSTR. As this two-phase mixture entered the CSTR recirculation loop, the flow meter read a lower flow rate than expected, which tripped the interlocks that shut down the CSTR steam supply. As a result, steady state operation could not be achieved at low CSTR pressure. These conditions were explored more during the SSC campaign.

3.5.1. CSTR Campaign: 0.5 MW_e Demo

Performance of the CSTR with GAP-1_m/TEG solvent was demonstrated at 0.5 MW_e for 48 hrs. (**Figure 34**). Process conditions are listed in **Table 8** (Condition 5). GAP-1_m : CO_2 molar ratio was maintained at 1.5. Desorption conditions were kept constant at 248 ^oF and 7 Psig, respectively. Solvent composition is listed in **Table 10** (Condition 5). CSTR liquid level was kept constant at 33 % with no indication of solvent carry-over in the CSTR headspace. Specific steam utilization was 1.1 (lb. CO_2: lb. steam). CO_2 capture efficiency reached only 65% due to limited cooling capability of the lean cooler HX at higher flue gas flow rates.

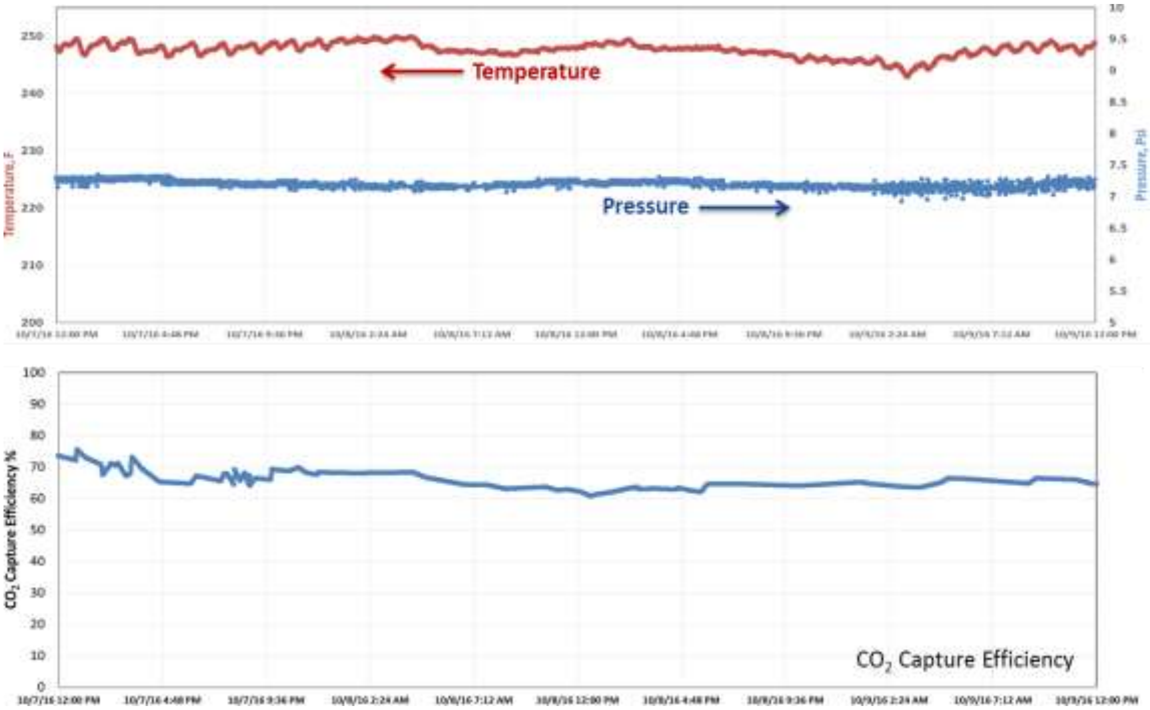


Figure 34. **CSTR Campaign:** 0.5 MW_e Demo
Process conditions listed in **Table 8** (Condition 5)

3.5.2 CSTR Campaign: Effect of stoichiometry and desorption temperature

CO_2 capture efficiency was greatly affected by amine to CO_2 stoichiometry and desorption temperature as shown in **Figure 35**.

CO_2 capture efficiency exceeded 90% under a large excess of amine (GAP : CO_2 = 3.85, 0.2 MW_e), even though the desorption temperature was only 233 ^oF. It dropped to 87% at lower amine excess (GAP : CO_2 = 1.9) even the desorption temperature increased to 248 ^oF. Increasing flue gas flow rate to 5000 pph while maintaining liquid flowrate at 18,000 pph decreased the amine to CO_2 stoichiometry to 1.55. This led to a CO_2 capture efficiency of 65%. Increase in desorption temperature to 265 ^oF at constant stoichiometry (GAP : CO_2 = 1.55) led to a marginal improvement in CO_2 capture efficiency of 71%.

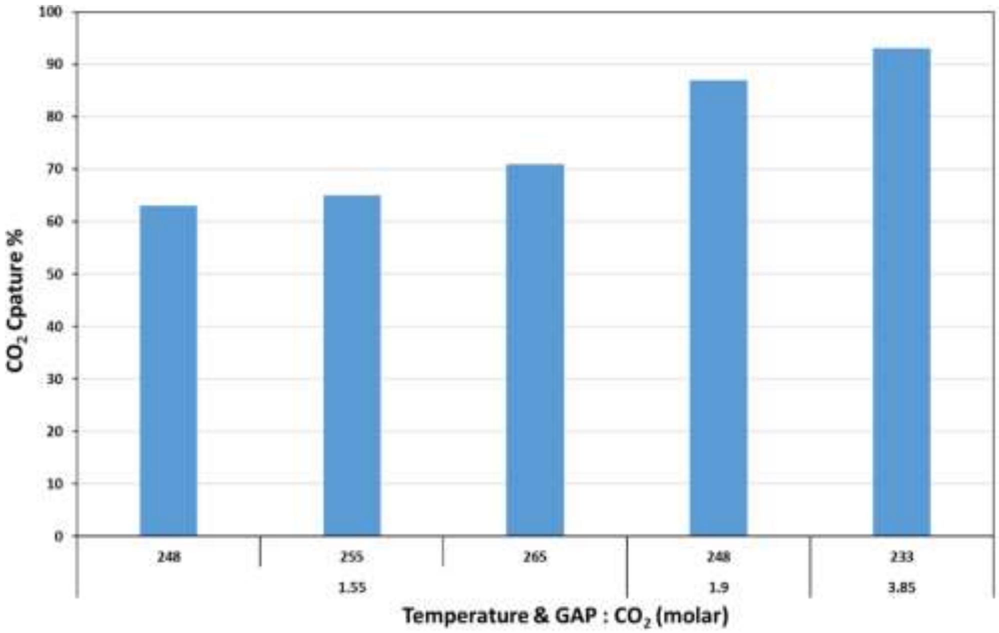


Figure 35. **CSTR Campaign:** CO_2 Capture Efficiency = f (T, GAP : CO_2 (molar))
Process conditions listed in **Table 8.**

Temperature increase and the maximum temperature in the absorber beds as a function of desorption temperature and amine to CO_2 stoichiometry are shown in **Figure 36**. For Conditions 1-3 (**Table 8**), lower desorption temperature (233 ^oF) and high excess of amine (GAP-1 : CO_2 =

3.85) led to overall lower absorber temperatures, and uniform absorption among the three absorber beds. Increasing desorber temperature from 233 °F to 248 °F and to 265 °F led to overall higher absorber temperatures (from 140 °F to 165 °F) and higher exotherms in the top bed, as the solvent entering the absorber top became leaner.

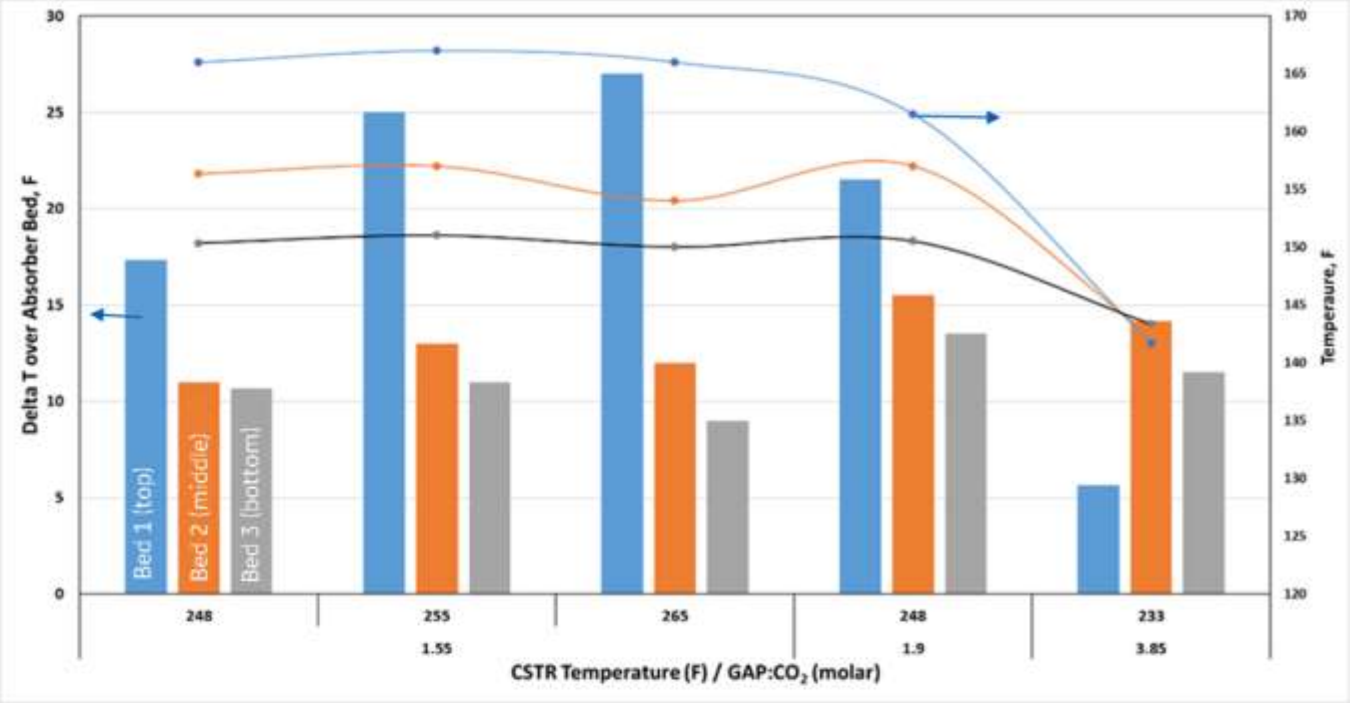


Figure 36. **CSTR Campaign:** Absorber operation = f (T, GAP : CO$_2$ (molar))

Process conditions listed in **Table 8.**

CO$_2$ loading in the lean and rich GAP-1$_m$/TEG working solution varied significantly as a function of desorption temperature and amine to CO$_2$ stoichiometry as shown in **Figure 37**. At low desorber temperature (233 °F) and high excess amine (Condition 1-3, **Table 8**), the active working capacity is very low due to an inefficient desorption process. Upon increasing the desorption temperature to 265 °F, the CO$_2$ content of the lean solvent dropped to 0.54 wt.% and active working capacity increased to 2.67%. However, this is only 30% of the theoretical working capacity of the solvent. As mentioned previously, we attributed this behavior due to insufficient cooling capacity of the lean cooler HX at 0.5 MW$_e$, and inability of the CSTR to be operated at higher water content and lower desorption pressure. These conditions were explored more during the SSC campaign.

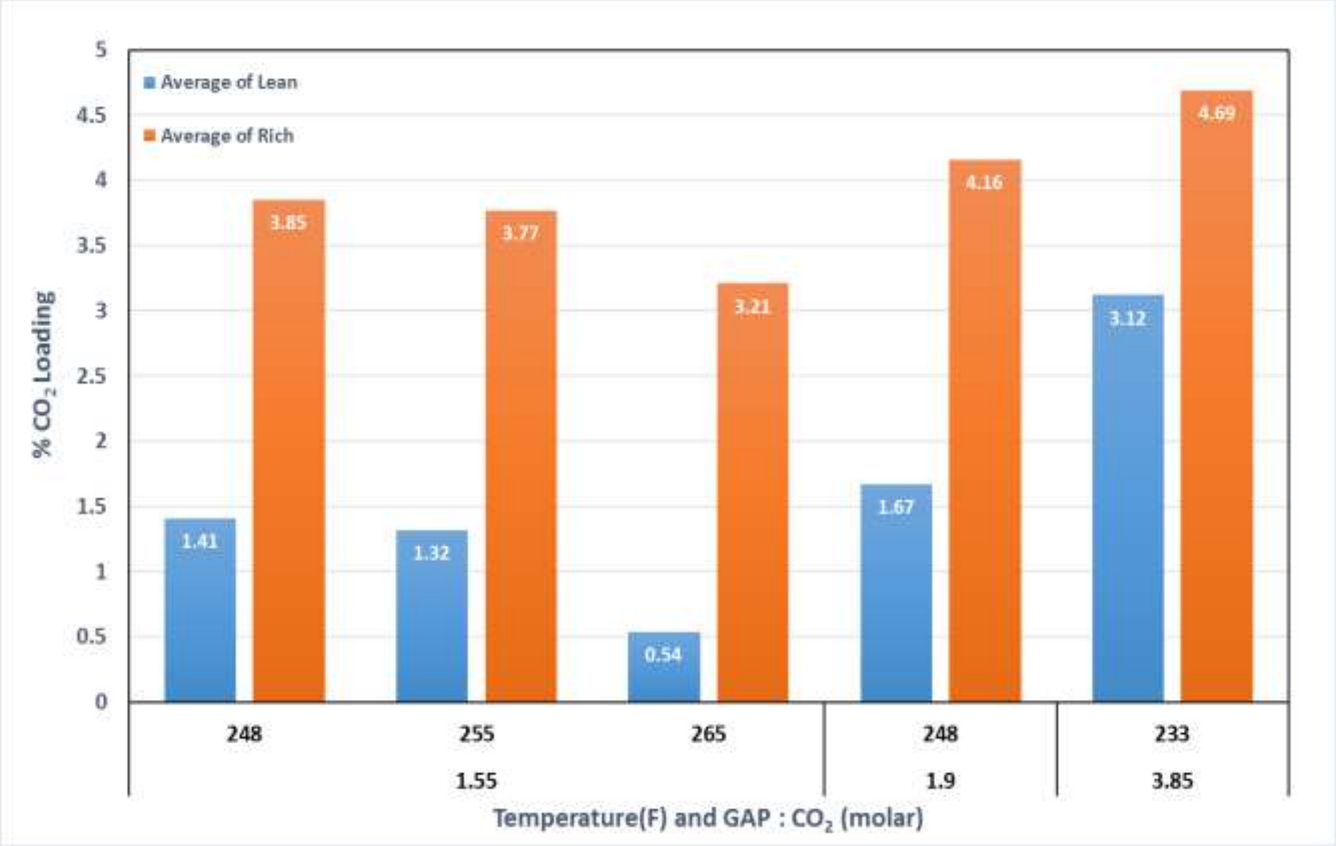


Figure 37. **CSTR Campaign:** Working Capacity = f (T, GAP : CO$_2$ (molar))
Process conditions listed in **Table 8.**

3.5.3. CSTR Campaign: Solvent Degradation

During the CSTR campaign, the solvent experienced desorption temperatures in the range of 233-262 °F, which caused thermal degradation to occur. The accumulation of degradation products in the solvent was monitored via the total amine content that was quantified in solvent samples taken throughout the test period and shown in **Figure 38**. The solvent lost approximately 15 wt. % amine capacity in the first two weeks of the CSTR campaign. The increased rate of degradation in the second week of the campaign is attributed to an increase in the CSTR operating temperature and reduced amount of water in the working solution. Before the third week of testing, some fresh GAP-1_m was loaded into the system to compensate for thermal degradation (not shown in **Figure *38***). Following this make up, the solvent lost approximately 5.4 wt.% amine capacity in the following week.

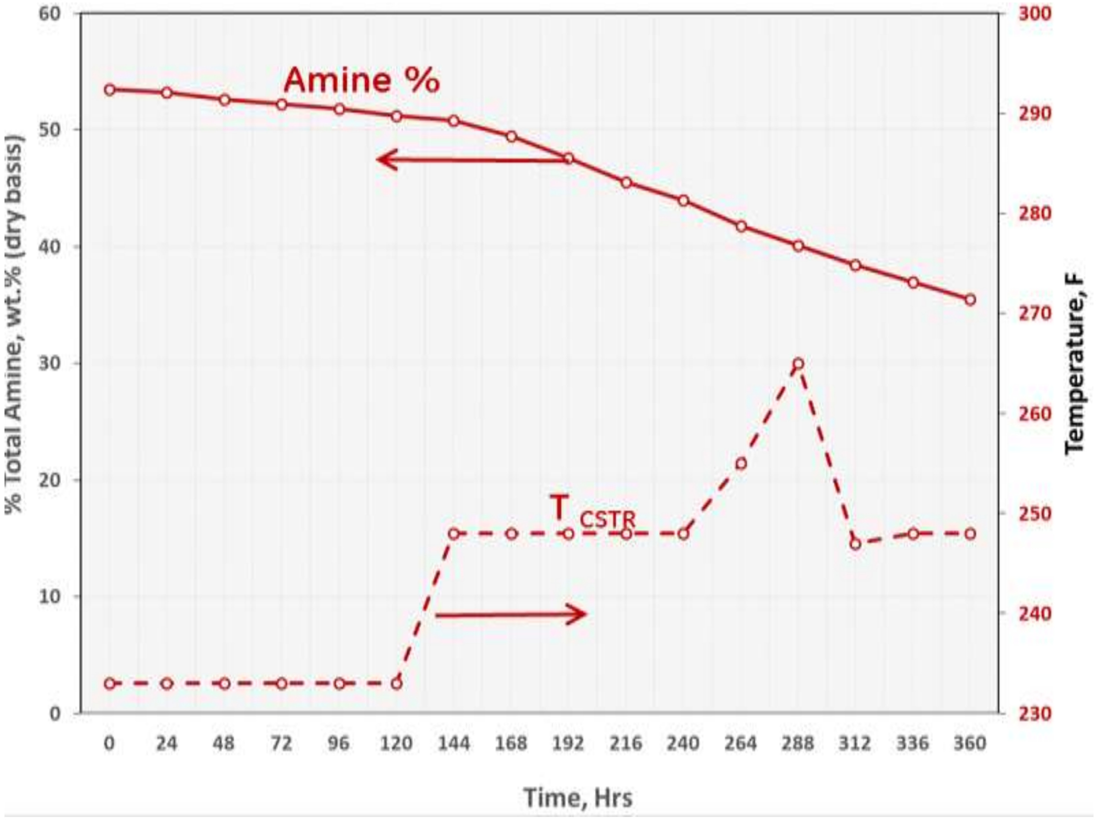


Figure 38. **CSTR Campaign:** Amine Degradation in Lean Solvent
Process conditions listed in **Table 8.**

At the end of the CSTR campaign, all samples collected at NCCC were shipped to GE for post-run analyses. These samples consisted of aminosilicone samples from the absorber as well as water samples from the 501 tank.

One of the analyses deemed critical to understanding the loss of amine, and therefore the carbon capture capacity of the solvent, was proton nuclear magnetic resonance (^{1}H NMR) spectroscopy.

It was previously shown that exposure of the aminosilicone carbamate to an elevated thermal environment resulted in the formation of urea-containing by-products. These by-products could be readily seen by ^1H NMR. In addition, this technique was also useful in determining the relative GAP-1_m/TEG ratios, the β-isomer content and the GAP number.

Figure 39 shows the visual transition the solvent underwent with increased time spent in the system. It is obvious that the solvent mixture became quite dark over time which is expected, as amines readily discolor upon oxidation to highly colored species. However, these color bodies may only be present in very small quantities, so deep discoloration may not be indicative of poor performance.

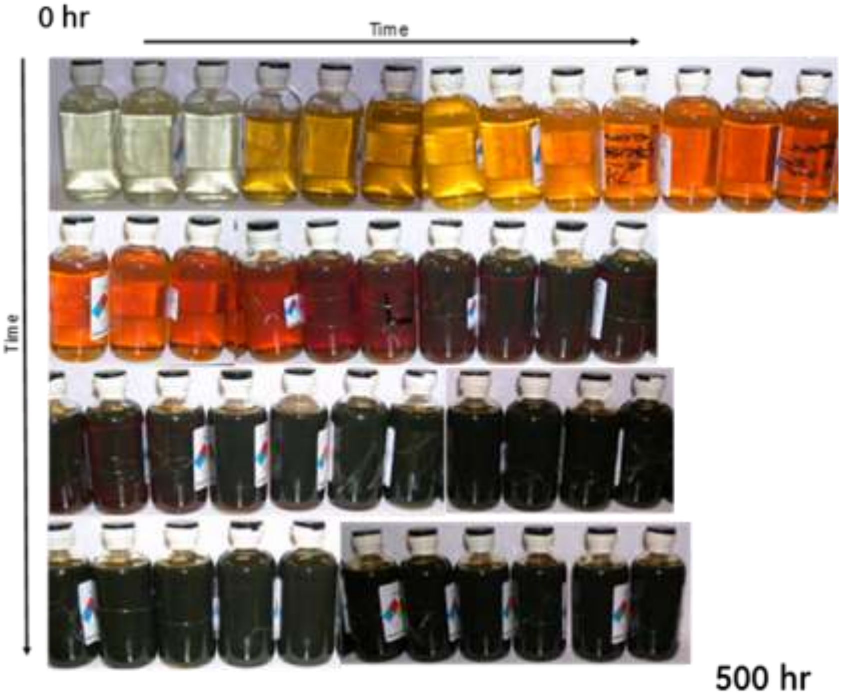


Figure 39. **CSTR Campaign:** Lean samples = f (time)

A variety of analyses were conducted to determine how the GAP-1_m/TEG solvent mixture performed and changed during the campaign. These tests included ^1H NMR and GC analyses, titrations, and CO_2 uptake experiments which provided information on the GAP # of the aminosilicone, the amine content of the system, mass balance of the components, and urea formation.

^1H NMR examination of the samples provided a wealth of information. First, the GAP-# was calculated based on the ratio of the methylene groups adjacent to the Si atom relative to the total number of methyl groups on silicon. The original aminosilicone solvent started with a GAP# of 0.96 indicating that it was very close to the desired starting # of 1. **Figure 40** shows that this value steadily decreased with time. This was expected as a re-equilibration reaction can occur under basic conditions and with heat and water present. This re-equilibration reaction not only generates an aminosilicone with a smaller average GAP-# but also results in the formation of cyclic silicones such as D_4 and D_5. Scheme 1 shows the process by which these materials are formed. There is a significant increase in the GAP # at 366 hours, but this corresponded to fresh solvent (with a GAP # of 0.96) being added to the system. The variation in values at 505 h is the result of samples taken when relatively fresh material from the SSC was added to the system.

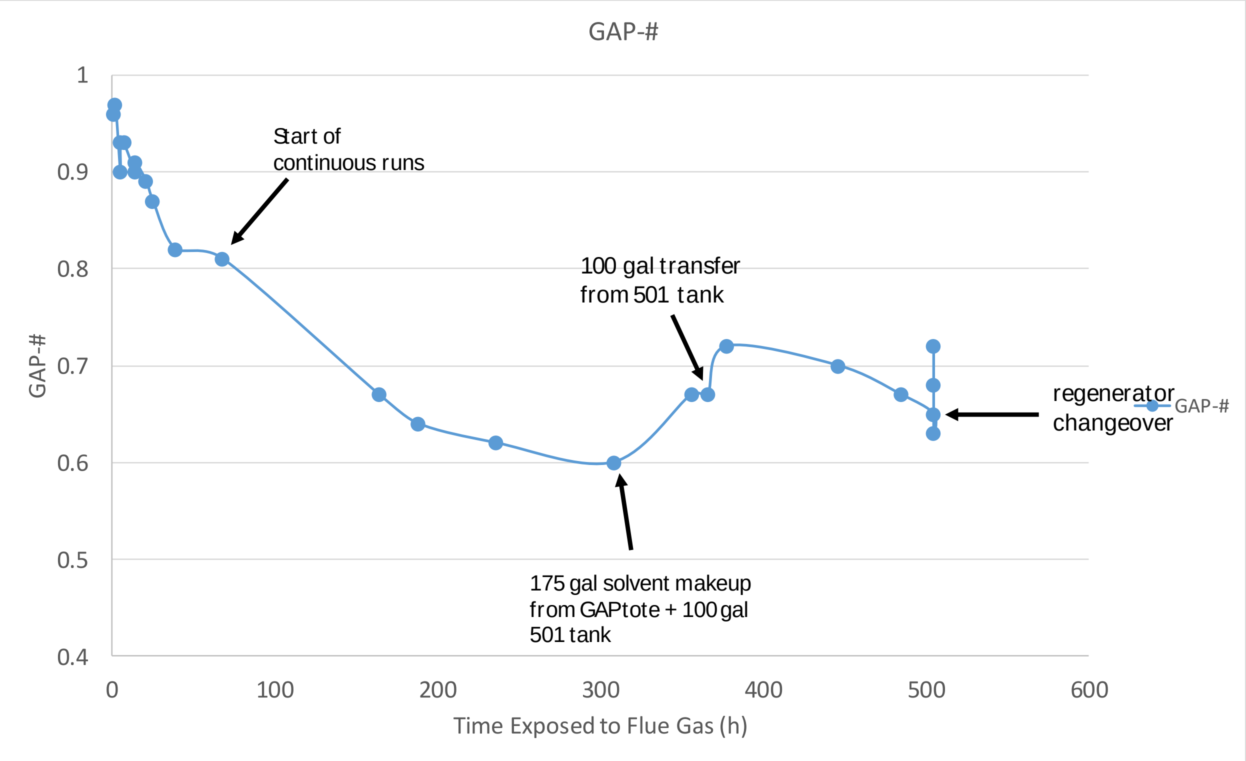
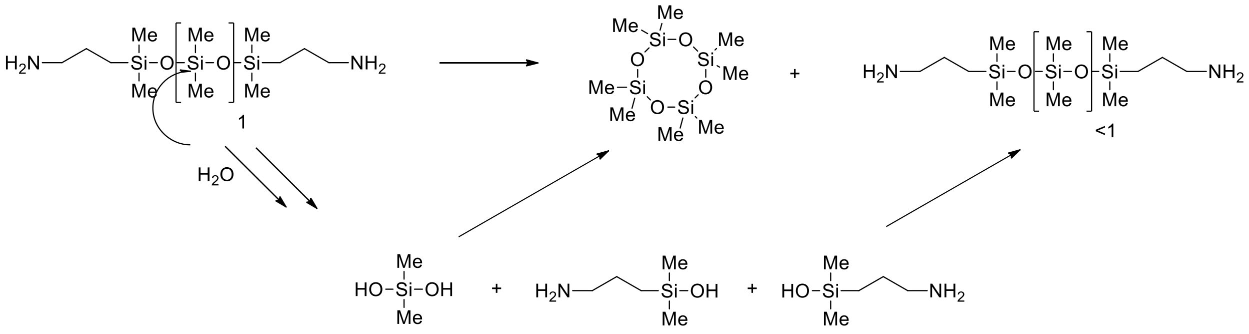


Figure 40. **CSTR Campaign:** GAP # = f (time)

Scheme 1. Re-equilibration of GAP-1



Amine and urea content could also be determined from NMR spectra. A series of aged samples are shown in **Figure 41**. The 1694 sample, with only 5 h exposure to flue gas showed very little urea present and the integration of the amine peak at 2.6 ppm indicated that 96% of the original amine was still present. As time progressed, more urea was formed. The peaks circled in red are confirmed urea peaks while those in green are likely other urea containing by-products. This conclusion is based on the peak shapes and chemical shift. More aged samples begin to show small amounts of other unidentified products, circled in blue.

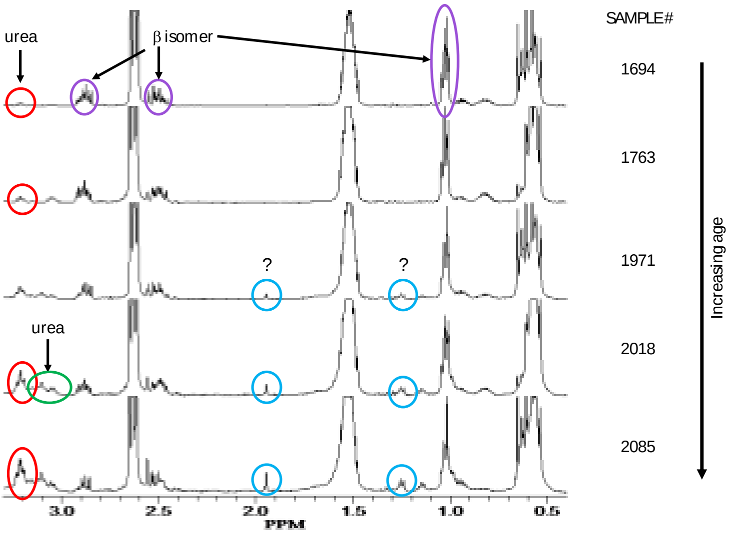


Figure 41. **CSTR Campaign:** ^{1}H NMR spectra of aged absorber samples

Figure 42 shows the increase in urea content of the solvent over time. The urea decomposition products may be formed via a variety of pathways as shown in Scheme 2. Whichever path is responsible; all indicate that high temperatures and low water levels intensify the problem.

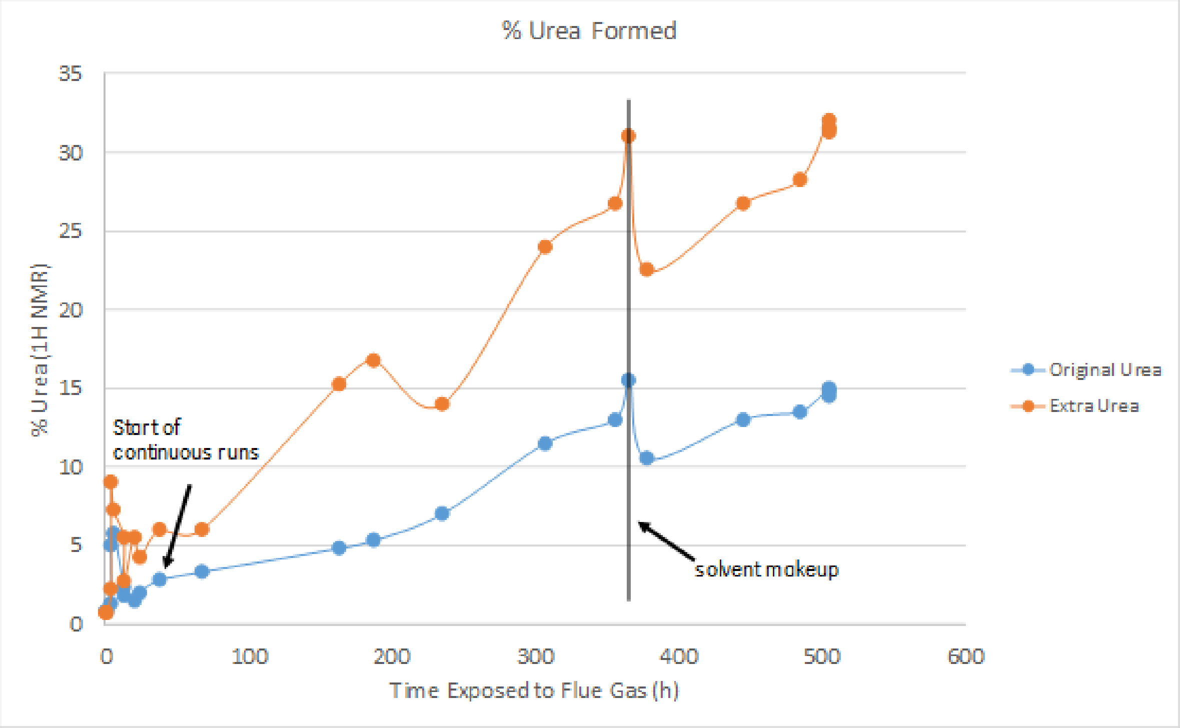
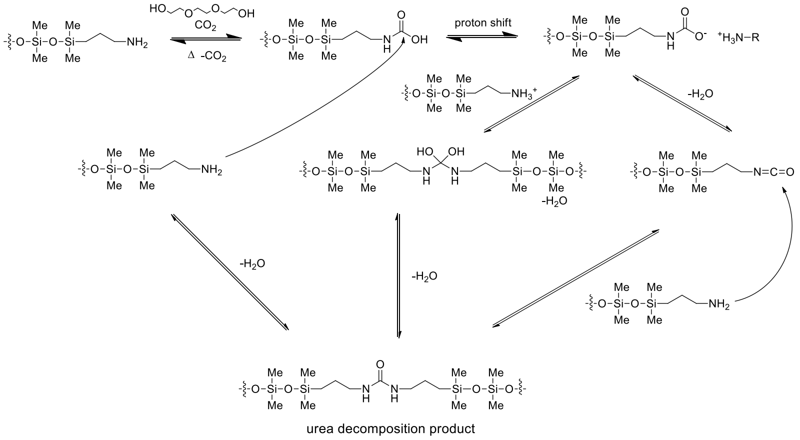


Figure 42. **CSTR Campaign:** Urea formation in absorber samples = f (time)

The blue line assumes only the urea that was circled in red in **Figure 41**. The orange line is likely the more accurate urea level that includes both the red and green circled peaks in **Figure 41**. The decrease in urea content at 366 h is again due to fresh solvent introduction into the system. The seemingly anomalous values in the orange curve at 164 and 188 h are unexplained at this point.

Scheme 2. Urea formation



The active amine content of the solvent mixture is the most critical parameter to assay. This value dictates the efficiency of the solvent mixture. **Figure 43** shows several plots relating to both the amine content of the solvent mixture as well as the component analysis or mass balance of the system. The orange curve represents the amine titration data obtained from NCCC. This is in weight percent of the total solvent mixture. In a perfect system of only GAP-1/TEG and no water, that value would start and remain at 60%. However, the initial loading of GAP-1/TEG started around 53.4% which is reflected in the curve. As the campaign progressed, the amine content decreased, which was commensurate with the increase in urea content. The blue curve shows the amount of amine remaining that was calculated from the NMR spectra. These numbers are higher because they represent the total amount of amine in the solvent mixture as determined by relative ratios of alpha and gamma protons on the aminopropyl functional group in GAP-X. This value should start at 100% and comes close at >97% with the early samples. Integration uncertainties account for ~3%. This curve follows the same trajectory as the % Amine NCCC curve except for a “bump” at 236 hours. It is unclear why there is this discrepancy. In both curves, the sharp increase in amine content at 378 hours is due to replenishment of the solvent.

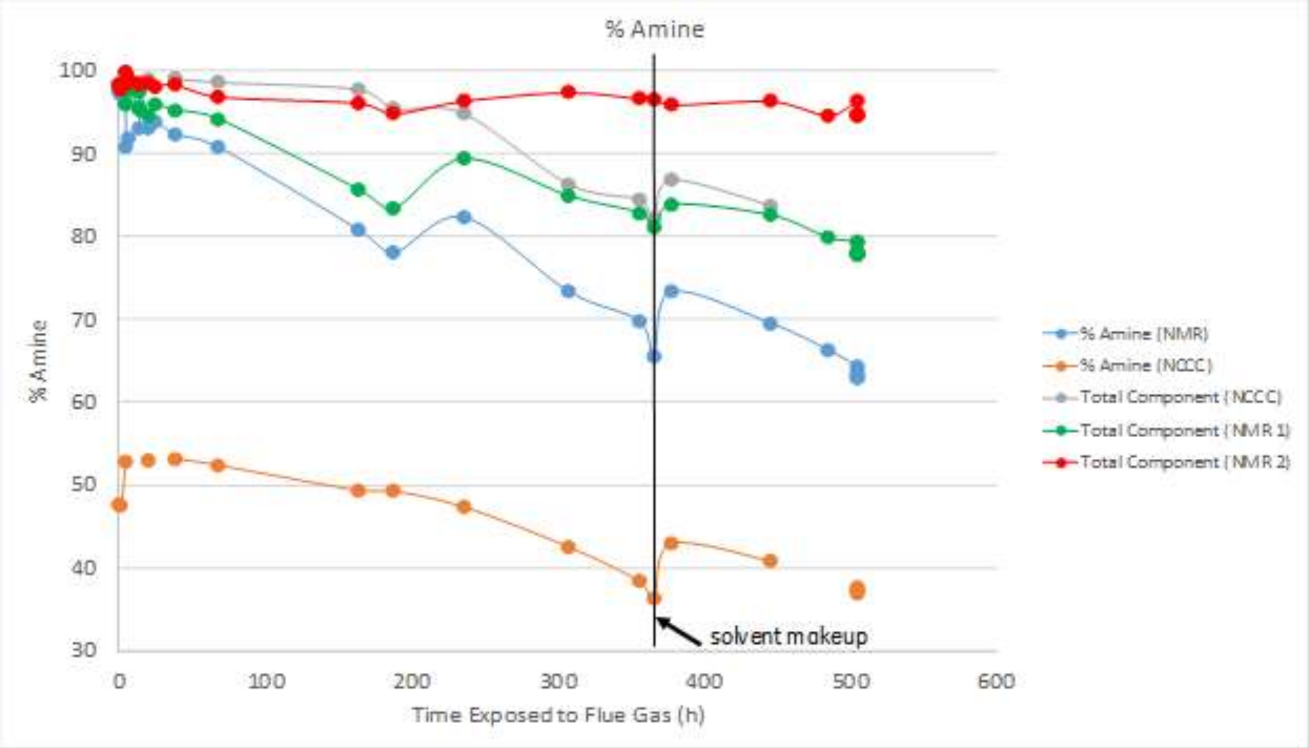


Figure 43. **CSTR Campaign:** Amine Content & Mass Balance = f (time)

The total component analysis provided by NCCC (gray curve), mirrored the % amine content closely. These data only accounted for the presence, or absence, of amine and did not consider any degradation products, such as urea. If only confirmed urea materials (red circled compounds in **Figure 41**) were added to the amine total, then the green curve in **Figure 43** was obtained. This shows comparable values to the gray curve at extended times; with only about 80% of the mass accounted for at the end of the campaign. However, if all the suspected urea derivatives were included in the mass balance calculation, then the red curve is obtained. This shows that about 95% of all the material is accounted for. This result also indicates that thermal degradation to urea-containing materials constitutes the major decomposition pathway. This does not rule out oxidative degradation, which is surely occurring, but it does imply that this is a less important reaction.

To identify and more fully characterize the decomposition products generated during operation, GC (gas chromatography) and LC/MS (liquid chromatography/mass spectrometry) were employed on the absorber samples. **Figure 44** shows the change in a series of GC chromatograms taken of aged absorber samples. Early samples showed the expected homologous series of GAP-X aminosilicones along with the β-isomer. As the campaign progressed, by-product peaks began appearing and the higher homologues of the GAP-X series began diminishing. The latter observation is consistent with re-equilibration occurring to give lower GAP-# materials and cyclic silicones. The by-product peaks may be indicative of the urea-containing decomposition products, but GC/MS was unable to unambiguously identify them.

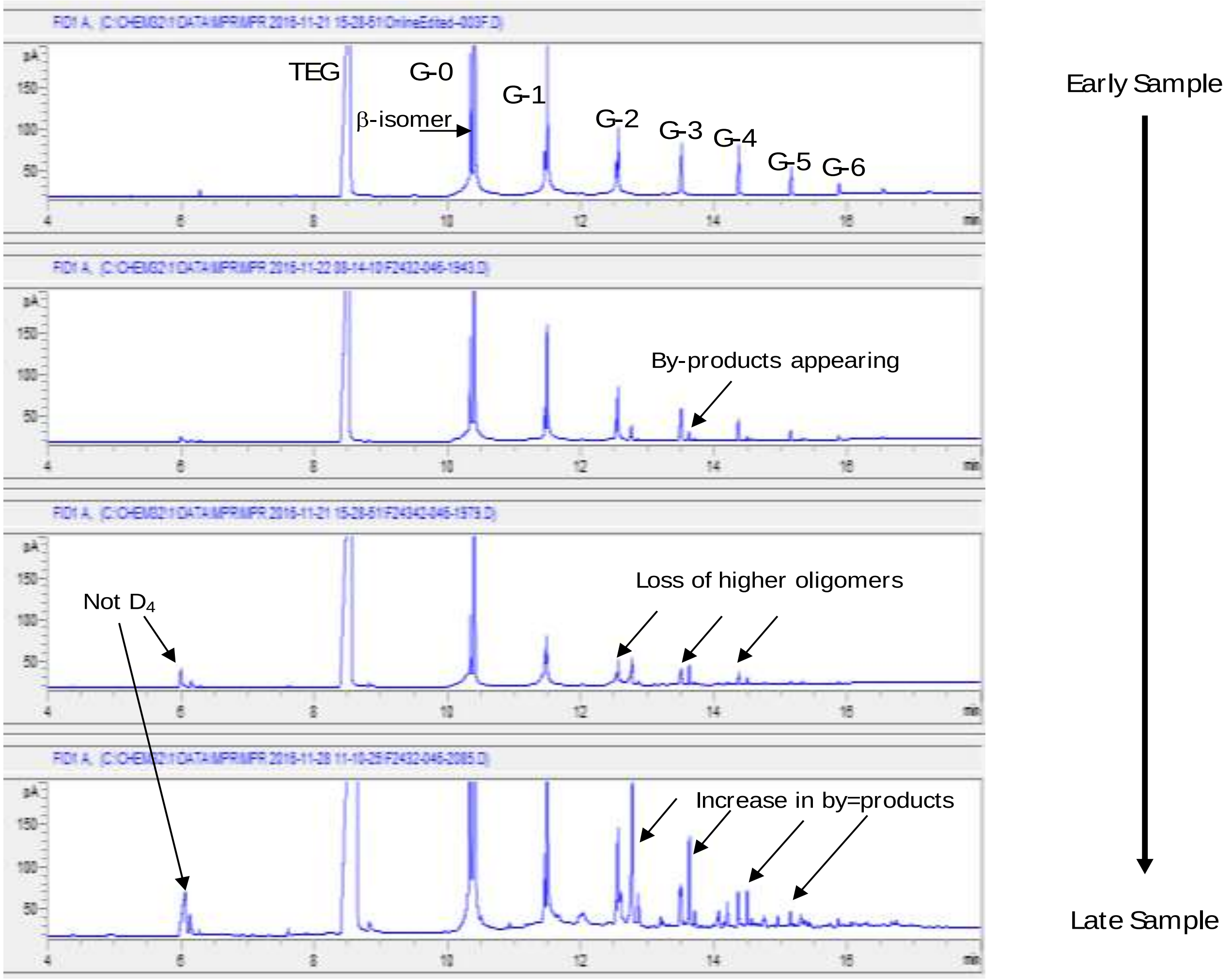


Figure 44. **CSTR Campaign:** GC chromatograms of aged absorber samples

As mentioned before, re-equilibration of the aminosilicones would generate cyclic silicones. It was clear from the decrease in the GAP-# that such cyclics had to be forming but their fate and location within the process were unknown. Several possible locations for these small molecules were possible. The first was to have them remain in the solvent mixture. This was ruled out because no evidence was seen in the GC traces above and, if these materials were resident in the absorber samples, the observed GAP # would have remained constant as there is no way to distinguish Si-methyl protons apart in the ^{1}H NMR.

An alternate location for the cyclics was in the condenser water samples. Since the cyclics are more volatile than the linear aminosilicones (174 and 210 °C respectively for D_4 and D_5 versus ~285 °C for GAP-1), they might be expected to be carried out with the exhaust gas and trapped in the water wash and/or condensers. Samples from both the 501 and 602 tanks were examined by GC as shown in **Figure 45**.

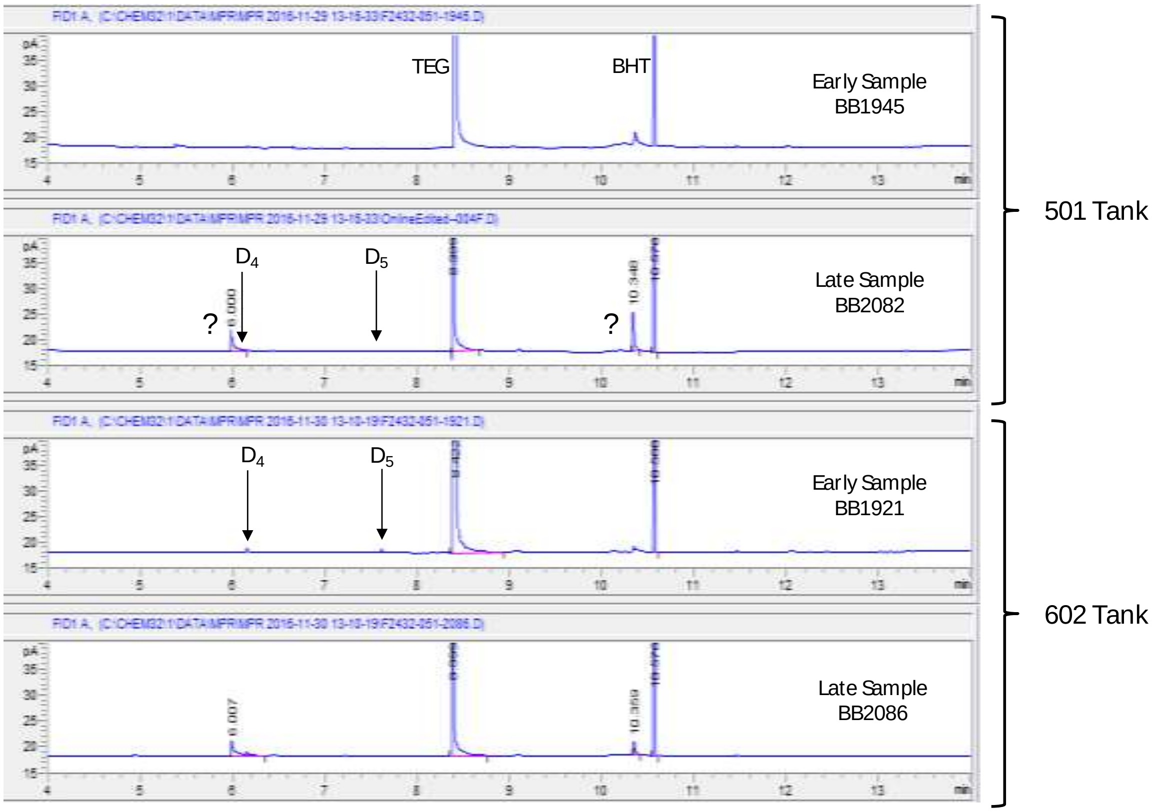


Figure 45. **CSTR Campaign:** GC chromatograms of water samples

It is evident that the major compound present in these samples is TEG. The BHT identified is from the antioxidant added to the THF solvent used to solubilize the water samples prior to injection. There are 2 unidentified peaks at 6.0 and 10.3 minutes but they do not correspond to the D_4 and D_5 cyclics. The early sample from the 602 tank does show very small traces of these cyclic silicones, but not in sufficient quantity to account for the GAP-# dropping from 0.96 to 0.6.

The water samples taken by NCCC and tested for amine are shown in **Table 11**. NCCC reports amine content as weight % as GAP-1. GE values match closely with those from NCCC. However, from the GC data in **Figure 44**, no GAP materials were present. This implies that some basic component is present in the water samples. Earlier work has shown that ammonia is produced during thermal cycling of the solvent, which could be the basic constituent of the aged solvent. If dissolved ammonia is present, then the wt.% as ammonia is approximately a factor of 10 lower than that for GAP-1.

Table 11. **CSTR Campaign:** Amine content in water samples

Sample	**Flue Gas Time (h)**	**Location**	**Wt.% Amine** (as GAP-1, NCCC)	**Wt.% Amine** (as GAP-1, GE)	**Wt.% Amine** (as NH_3, (GE)
BB1945	164	501 Tank	1.97	-	-
BB2082	505	501 Tank	4.83	4.61	0.49
BB1921	60	602 Tank	7.16	6.75	0.71
BB2086	505	602 Tank	3.04	2.81	0.30

While not as large a contributor to the loss of activity as urea formation, oxidation of GAP-1 was occurring. The myriad of decomposition products formed at low levels precluded any identification by NMR and the silicon-containing materials did not provide useful data via GC/MS analysis.

3.5.4. Gas Analysis

Gas adsorption samples were collected during the CSTR campaign as following: (i) from the water wash gas exhaust, (ii) ELPI aerosol measurements, and (iii) CO_2 quality sample as summarized in **Table 12**.

Table 12. **CSTR Campaign:** Gas quality samples collected from outlet of water wash

Date	L (lb/hr)	G (lb/hr)	CSTR T (deg F)	Solvent H2O (%)	Gas Adsorption	ELPI / Aerosol	CO2 Quality
10/4/2016	18000	2000	230	4.2-8.9%	X		
10/10/2016	18500	5000	255	3.4-3.7%	X		
10/11/2016	18500	5000	262	3.5-7%			X
10/21/2016	18500	3750	248	target 5%	X	X	

Gas adsorption samples were collected according to the following procedure. The water wash vapor effluent was passed through a condensing system. The condensate was collected and the vapor slip from the condenser was captured on gas adsorption tubes. Details of the gas adsorption tubes are shown in **Table 13**. At each sampling interval, two tubes of each type were sampled, and all tubes were shipped to GE for analysis.

The results of gas adsorption analysis are shown in **Table 14**. Nitrosamines that are not listed were not detected above the limit of quantification of 0.011ug/tube in any samples. The analysis for ethylene glycol, D4, D5, and D6 are not quantitative. These species were detected in all samples.

Four replicates of aerosol particulate concentration and size measurements were sampled. The results are summarized in **Figure 46**. Most of the particles detected were smaller than 0.006 microns, and all particles were smaller than 0.087 microns in diameter. Direct composition measurement of the aerosol particles is not available from this method.

Table 13. **CSTR Campaign:** Adsorbent tubes for water wash vapor sampling

Adsorbent type	Tube size (mm)	Vendor	Analysis Company	Analytes of interest
226-10-06	6x70	SKC, Inc.	Analytics Corp.	Ammonia
226-30-18	6x70	SKC, Inc.	Analytics Corp.	Methyl amine, Ethyl amine
226-119	6x100	SKC, Inc.	Analytics Corp.	Formaldehyde, Acetaldehyde
226-01	6x70	SKC, Inc.	Analytics Corp.	Ketones (Acetone)
32010001	N/A	Ellutia, Inc.	RJ Lee	Nitrosodimethylamine, Nitrosodiethylamine, Nitromethylethylamine, Nitrosodi-n-propylamine
Carbotrap 300 (GE-supplied)	6x178	Gerstel	GE	Aminosilicone, Carbamate, TEG, D4, D5, D6, Ethylene oxide, Ethylene glycol, Dimethyl aminopropyl silanol

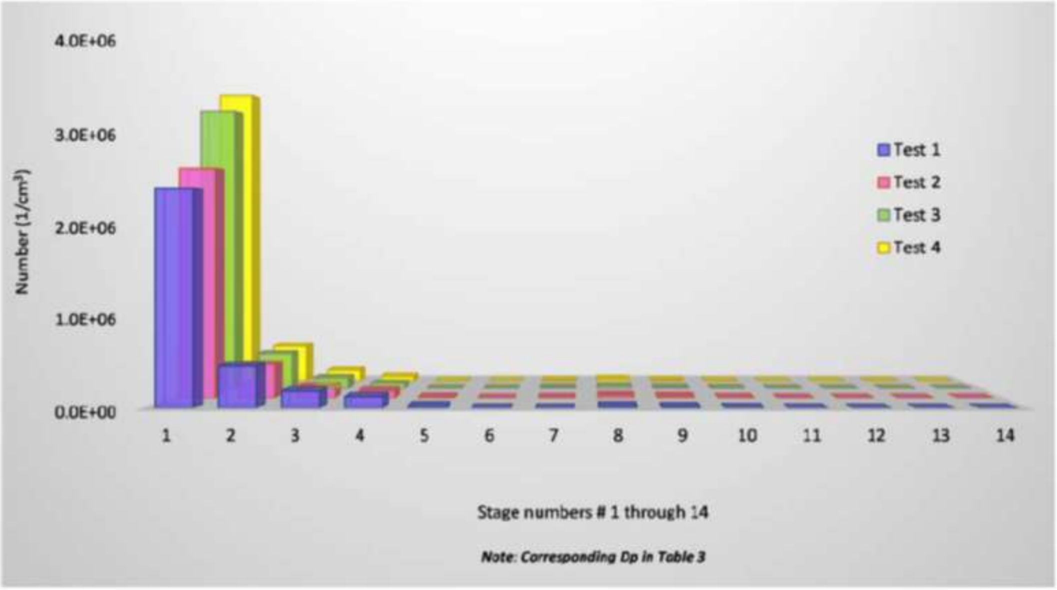


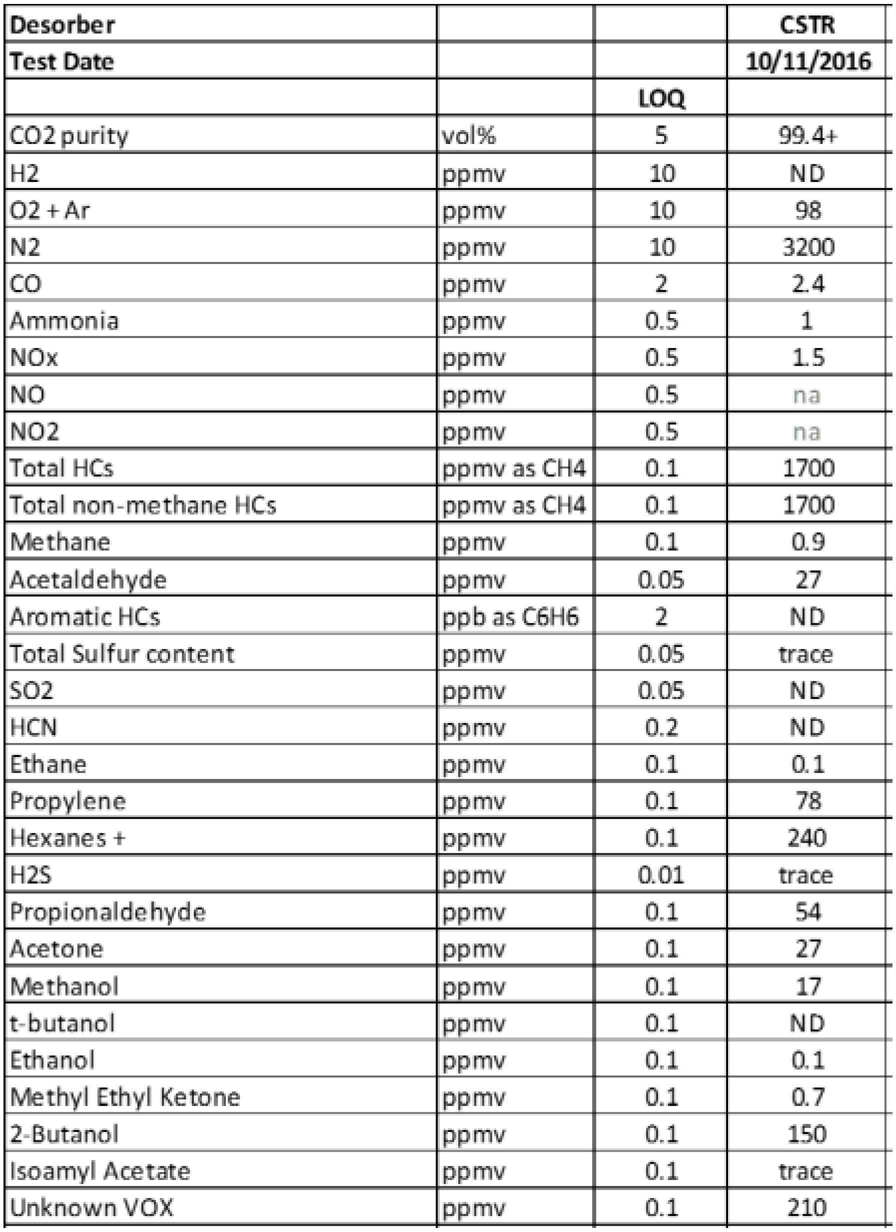
Figure 46. **CSTR Campaign:** ELPI aerosol particle count and size measurement

Table 14. **CSTR Campaign:** Gas adsorption analysis

Date	units	10/4/2016	10/10/2016	10/11/2016	10/21/2016
Formaldehyde	ppm	<0.0034	0.00543	N/A	0.00383
		<0.0034	0.00604	N/A	
Ammonia	ppm	437	38.1	N/A	42.1
		254	34	N/A	
Acetone	ppm	7.82	7.75	N/A	8.51
		9.42	8.33	N/A	
Ethylamine	ppm	<0.181	<0.181	N/A	<0.181
		<0.181	<0.181	N/A	<0.181
Methylamine	ppm	<0.262	<0.262	N/A	<0.262
		<0.262	<0.262	N/A	<0.262
N-nitrosodi-n-propylamine	ug/tube	0.059	<0.011	N/A	<0.011
		0.055	<0.011	N/A	
N-nitrosodimethylamine	ug/tube	<0.012	<0.012	N/A	0.018
		<0.012	<0.012	N/A	
Ethylene Glycol	Presence*	Present	Present	N/A	Present
		Present	Present	N/A	
D4	Presence*	Present	Present	N/A	Present
		Present	Present	N/A	
D5	Presence*	Present	Present	N/A	Present
		Present	Present	N/A	
D6	Presence*	Present	Present	N/A	Present
		Present	Present	N/A	

Finally, the CO_2 product stream was analyzed for one set of conditions during the CSTR campaign. A nonhazardous gas sampling kit supplied by Airborne Laboratories was used, and the samples were shipped to Airborne Labs for analysis. The results are listed in **Table 15** indicating that 99+% CO_2 product was achieved.

Table 15. **CSTR Campaign:** CO_2 quality samples



Desorber			CSTR
Test Date			10/11/2016
		LOQ	
CO2 purity	vol%	5	99.4+
H2	ppmv	10	ND
O2 + Ar	ppmv	10	98
N2	ppmv	10	3200
CO	ppmv	2	2.4
Ammonia	ppmv	0.5	1
NOx	ppmv	0.5	1.5
NO	ppmv	0.5	na
NO2	ppmv	0.5	na
Total HCs	ppmv as CH4	0.1	1700
Total non-methane HCs	ppmv as CH4	0.1	1700
Methane	ppmv	0.1	0.9
Acetaldehyde	ppmv	0.05	27
Aromatic HCs	ppb as C6H6	2	ND
Total Sulfur content	ppmv	0.05	trace
SO2	ppmv	0.05	ND
HCN	ppmv	0.2	ND
Ethane	ppmv	0.1	0.1
Propylene	ppmv	0.1	78
Hexanes +	ppmv	0.1	240
H2S	ppmv	0.01	trace
Propionaldehyde	ppmv	0.1	54
Acetone	ppmv	0.1	27
Methanol	ppmv	0.1	17
t-butanol	ppmv	0.1	ND
Ethanol	ppmv	0.1	0.1
Methyl Ethyl Ketone	ppmv	0.1	0.7
2-Butanol	ppmv	0.1	150
Isoamyl Acetate	ppmv	0.1	trace
Unknown VOX	ppmv	0.1	210

3.6. CSTR Campaign: Summary

(i) The CSTR desorber system was designed, fabricated and integrated with the pilot solvent test unit (PSTU), replacing the PSTU Steam Stripper Column at NCCC.

(ii) Solvent management and waste water special procedures were implemented to accommodate operation of the non-aqueous solvent in the PSTU.

(iii) Performance of the GAP-1_m/TEG solvent with the CSTR was demonstrated for over 500 hrs. while varying temperature of the desorption (230 – 265 ^oF), solvent circulation rate (GAP-1_m : CO_2 (molar) = 1.5 – 4), and flue gas flow rates (0.2 – 0.5 MW_e). Solvent carry-over in the CO_2 product was minimized by maintaining water content below 5 wt.%, and desorption pressure at 7 psig.

(iv) CO_2 capture efficiency was 95% at 0.25 MW_e (GAP-1_m : CO_2 = 4 (molar), 233 ^oF desorption), and 65% at 0.5 MW_e (GAP-1_m : CO_2 (molar) = 1.55, 248 ^oF).

(v) Solvent loss was dominated by thermal degradation of the rich solvent.

4. Steam Stripping Column (SSC) Campaign

4.1. Motivation

Initial design for the GAP-1_m/TEG process utilized a CSTR for CO_2 desorption based on the excellent thermal stability of the lean GAP-1_m/TEG solvent. However, later studies indicated that higher rate of thermal degradation of the CO_2 containing GAP-1_m/TEG occurred. In light of these discoveries, alternate designs for the regenerator in the aminosilicone based solvent process have been considered to reduce solvent loss due to thermal degradation.

The CSTR design has a number of advantages with respect to the aminosilicone-based solvent. Because the solvent is relatively non-volatile, the CSTR allows the CO_2 and any water to desorb in a single stage, with very little loss of solvent. The simplicity of this design decreases the required capital cost as the technology moves to commercial scales. It is also a design that allows for simple, robust process control. One area where the CSTR design is lacking, in comparison to more traditional distillation tower designs seen in aqueous solvent processes, is that there is no sweep gas. In the aqueous CO_2 capture process, water is vaporized in the reboiler of the distillation column, and this water vapor acts as a sweep gas, lowering the partial pressure of CO_2 in the gas phase, and therefore increasing the driving force for CO_2 desorption. By using a similar design with the aminosilicone-based solvent, a water vapor sweep gas could be used to increase the driving force for CO_2, resulting in a lean solvent with much lower concentrations of CO_2 than are possible with a CSTR. This, coupled with the data showing that water decreases the rate of thermal degradation, makes a distillation column-type regenerator using steam stripping a promising technology for the aminosilicone-based solvent process.

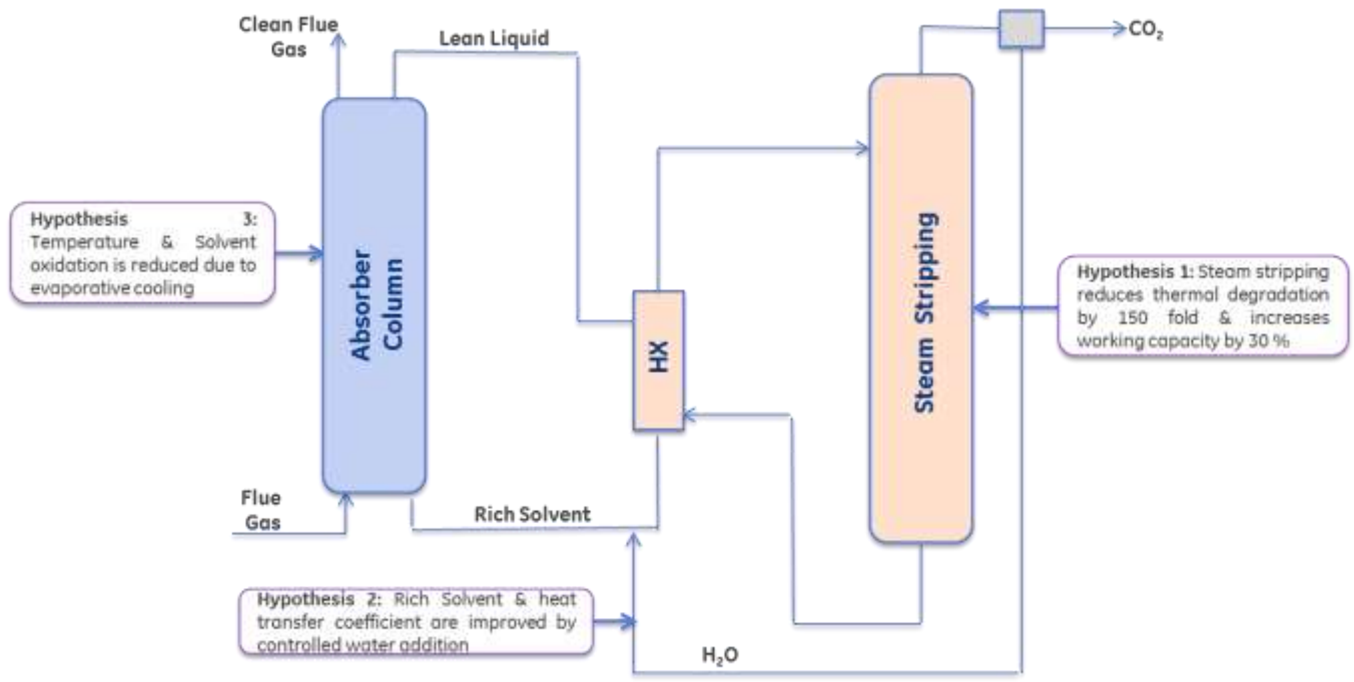
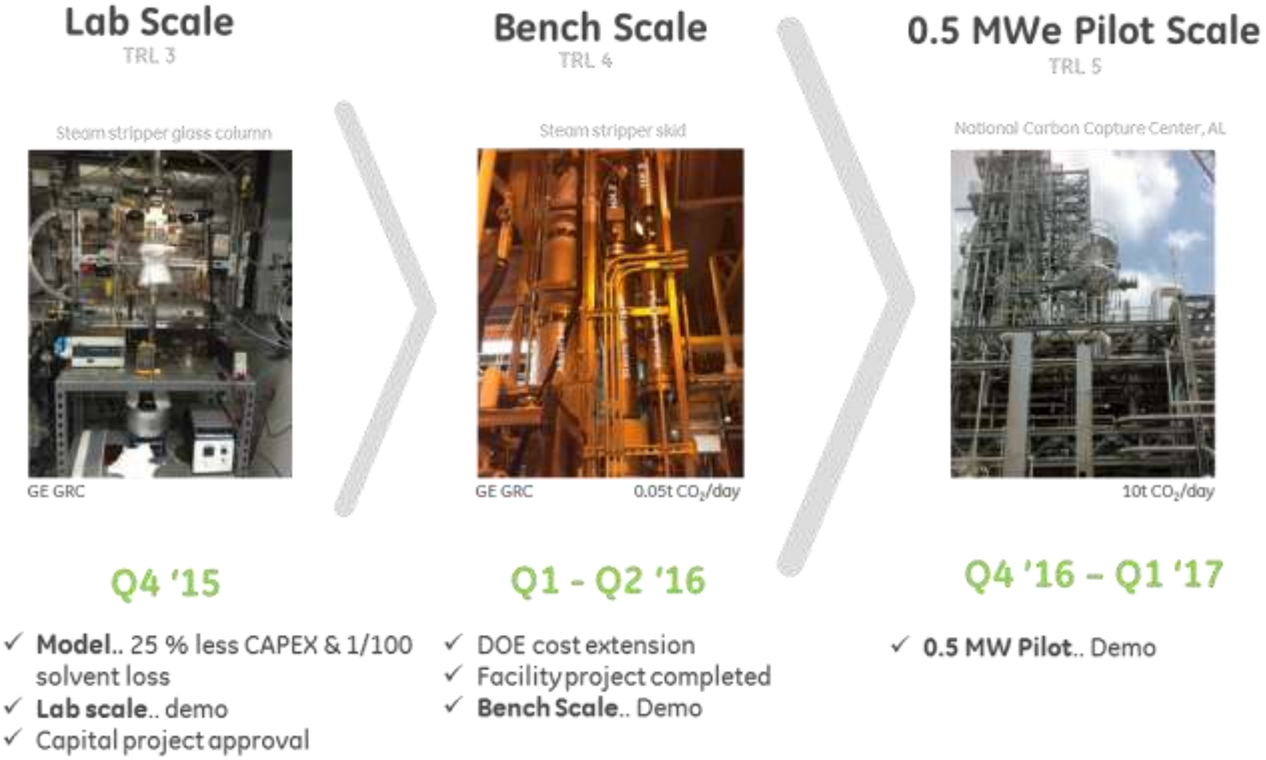


Figure 47. **Steam Stripping Process:** Solvent Management De-risk

Figure 47 describes the proposed steam stripping process. Controlled amounts of water (up to 20 wt.%) are added in the GAP-1_m/TEG working solution to induce steam stripping desorption, lower desorber temperature and hence reduce thermal degradation. Furthermore, controlled water addition is expected to improve heat and mass transfer process through reduction in solvent viscosity. Finally, temperature in the absorber will be lowered due to evaporative cooling, leading to decreased solvent oxidation rates.

Development of the steam stripping process was conducted in parallel to the CSTR campaign. The concept was first validated in a glass stripping column, followed by the demonstration in the bench scale system (2 kW$_e$) at GE GRC with simulated exhaust. Finally, the process was scaled-up at 0.5 MW$_e$ at NCCC, after the CSTR campaign was completed (**Figure 48**).



Lab Scale
TRL 3

Steam stripper glass column

GE GRC

Q4 '15

- ✓ **Model**.. 25 % less CAPEX & 1/100 solvent loss
- ✓ **Lab scale**.. demo
- ✓ Capital project approval

Bench Scale
TRL 4

Steam stripper skid

GE GRC 0.05t CO_2/day

Q1 - Q2 '16

- ✓ DOE cost extension
- ✓ Facility project completed
- ✓ **Bench Scale**.. Demo

0.5 MWe Pilot Scale
TRL 5

National Carbon Capture Center, AL

10t CO_2/day

Q4 '16 – Q1 '17

- ✓ **0.5 MW Pilot**.. Demo

Figure 48. **Steam Striper Process Development:** Timeline

4.2. SSC Campaign: Lab scale demonstration (Q4 2015)

Experiments have been performed with a lab-scale stripping column to demonstrate the concept of steam stripping with the aminosilicone-based solvent. **Figure 49** shows a picture of the experimental set-up. In these experiments, CO_2-rich solvent containing 10 wt.% H_2O is fed into the top of the column. As the solvent flows down the column, it is heated by steam generated in the reboiler. The CO_2 that is liberated from the solvent flows up the column with the steam. The solvent, which becomes progressively leaner and hotter as it flows down the column, ultimately flows into the reboiler, where it is heated to vaporize the water in the solvent. Lean solvent is removed from the column directly above the reboiler for composition testing. A condenser is at the top of the column to remove water from the CO_2 product gas. The condensate generated is collected for analysis.

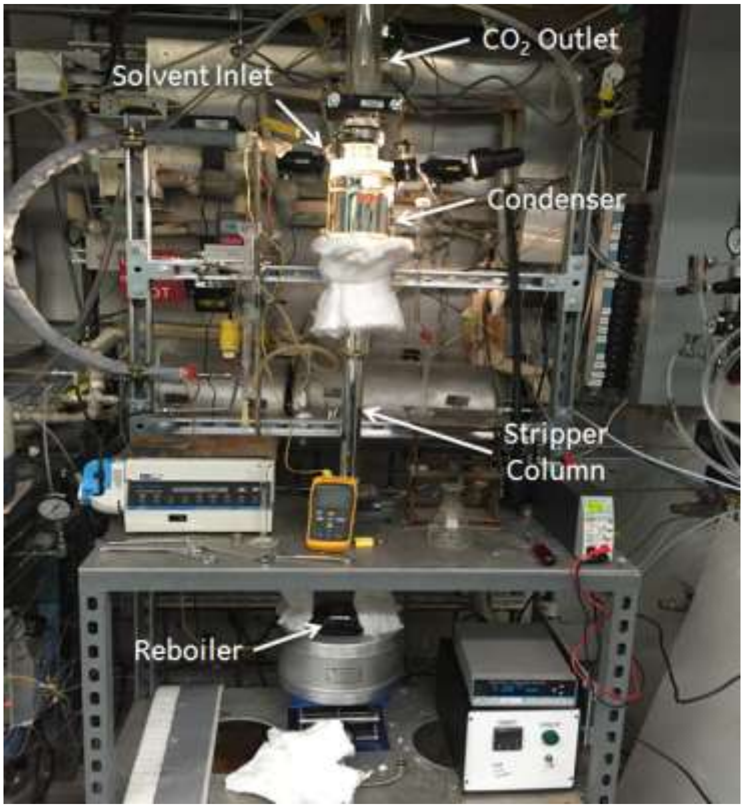


Figure 49. **Steam Stripping:** Lab scale stripping column

Because the solvent becomes progressively leaner as it flows down to the hotter regions of the column, the stripper column design ensures that only the leanest solvent contacts the highest temperatures. This decreases the rate of thermal degradation. Additionally, because the driving force for CO_2 desorption is increased by the presence of the steam, a lower maximum temperature is possible while achieving efficient removal of CO_2. **Figure 50** shows results for reboiler temperatures of 110 and 120 °C. Even at a reboiler temperature of 110 °C, 89% of the CO_2 fed into the column with the rich solvent is desorbed. This is significantly higher than can be achieved at the same temperature with a CSTR.

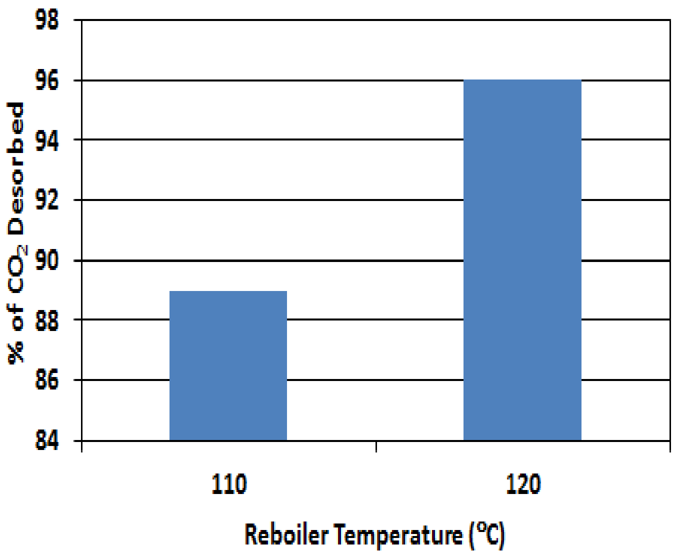


Figure 50. **Steam Stripping:** Lab scale demonstration

4.3. SSC Campaign: Bench scale demonstration (Q1-Q2 2016)

4.3.1. SSC Bench Scale: System Modification

CSTR bench scale system (2 kW_e) at GE GRC was retrofitted with a steam stripping column (SSC). The conceptual design of the retrofitted system is shown in **Figure 51**. For the normal operation of the SSC, three-way valve **T_1** is switched such that the rich solvent stream exiting the absorber column is redirected through the rich heat exchanger (**HX 1**), and SSC. Rich solvent flowing downwards through the steam stripping column is contacted with the steam generated in the reboiler / CSTR. CO_2 generated from the desorption of the rich solvent is passed through the partial condenser (**HX 2)**, and total condenser (**HX 3)**. Lean solvent stream collected in the CSTR / reboiler is cooled in the lean heat exchanger (**HX 4**) before being sent to the top of the absorber column. The added functionality allows sequential testing of CSTR and SSC to evaluate both desorption processes under similar process conditions.

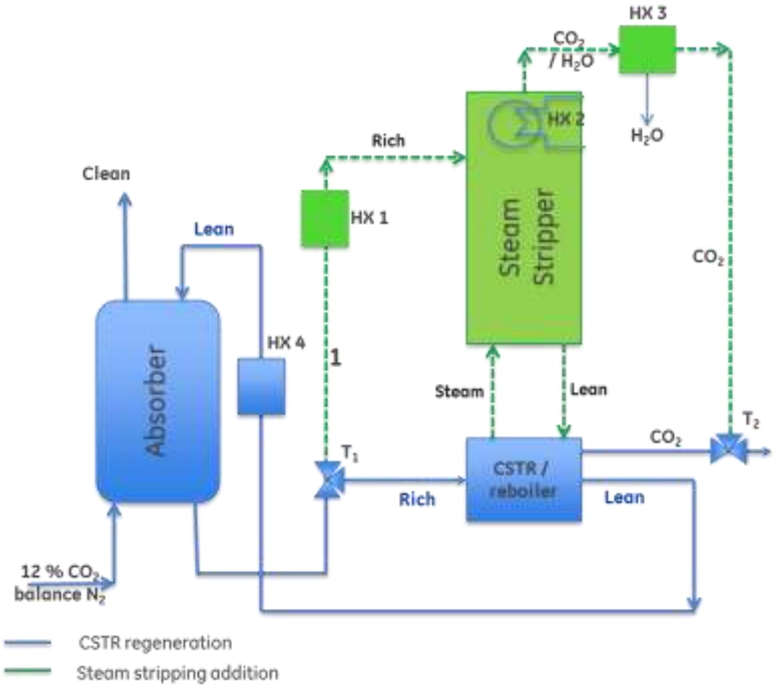


Figure 51. **Steam Stripping:** Bench Scale Conceptual Design

PI & D of the steam stripping column (SSC) is shown in **Figure 52**. Steam stripping column (6" (d) x 3' (H))) was manufactured by Atlantis Equipment Corporation, and was fitted with four thermocouples, and four sampling ports for monitoring temperature and concentration profiles within the column. Rich heat exchanger (**HX 1**), and the partial and total condensers (HX 2 and HX 3) were manufactured by YULA Corporation. All vessels were constructed of stainless steel, and rated for 300 Psi. Rich heat exchanger (**HX 1**) is heated with oil, while the **HX2** and **HX3** condensers are cooled with glycol solution. All process parameters (flow rates and temperatures, liquid level in the column / knock-out pot) are monitored and/or controlled by Cimplicity software. **Figure 53** shows the physical installation of the steam stripper, heat exchangers (HXs 2-3), reboiler vessel, and the 2" pipe connecting the bottom of the steam stripper column to the reboiler.

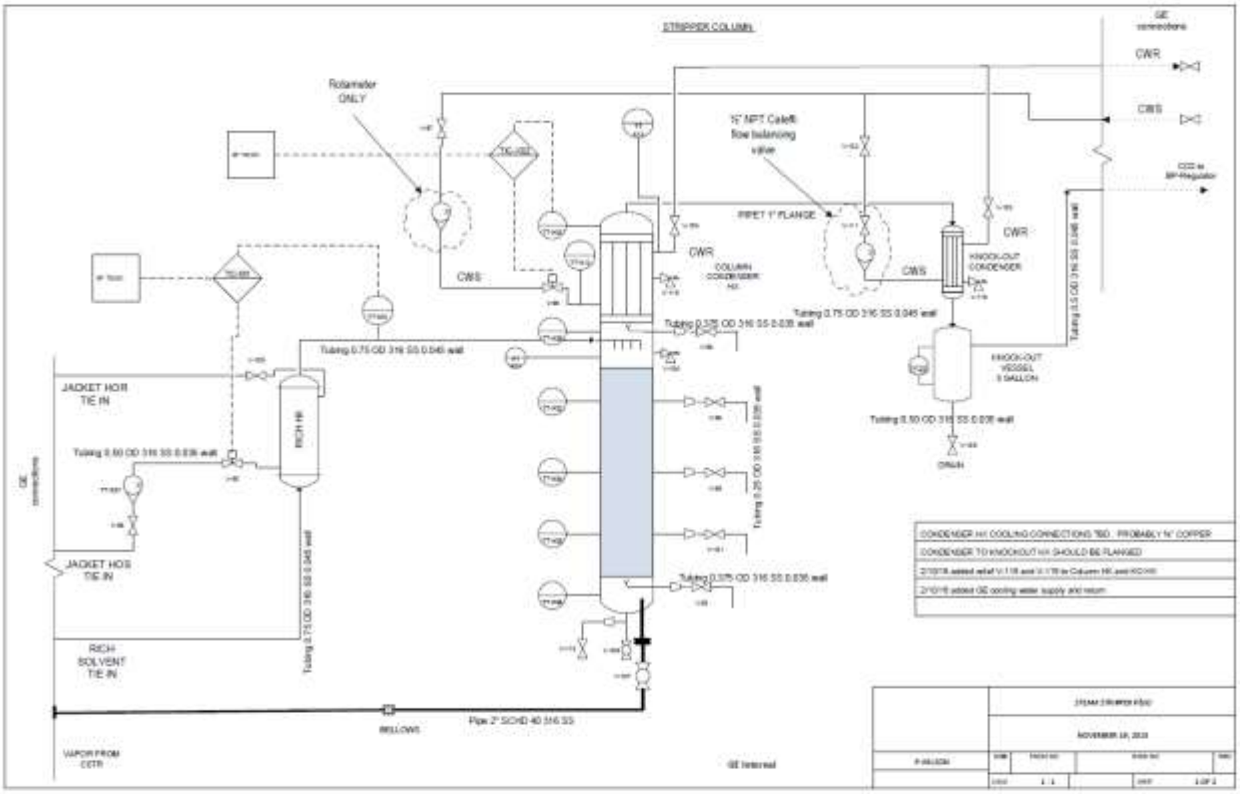


Figure 52. **Steam Stripping:** PI&D

Figure 53. Steam Stripping: Bench scale system ($2kW_e$) installed at GE GRC

4.3.2 SSC Bench Scale: Experimental Design

An experimental design was performed to evaluate the performance of the two desorption systems (i.e. CSTR and SSC) at 2KW$_e$ as a function of: (i) water content in the working solution, and (ii) GAP-1$_m$: CO_2 molar ratio. Maximum desorption temperature was kept at 108 °C (226 °F), and desorption pressure was kept at less than 1 PSIG. Performance of the GAP-1$_m$/TEG solvent was evaluated based on 4 criteria: % CO_2 capture, % SSC efficiency, hydrothermal stability and thermo-oxidative stability.

CO_2 capture was calculated based on the % carbamate measured by FTIR in the liquid samples collected at the bottom of the absorber and lean storage, respectively. Steam stripper efficiency was calculated based on the change in % carbamate in the liquid samples collected at the top and bottom of the column. Hydrothermal stability of the solvent was evaluated by quantifying degradation products via ^{1}H NMR and ^{29}Si NMR. Thermo-oxidation was evaluated by measuring % NH_3 in the clean stream simulated flue gas at the top of the absorber via gas FTIR. **Figure 54** highlights the main elements of the experimental design.

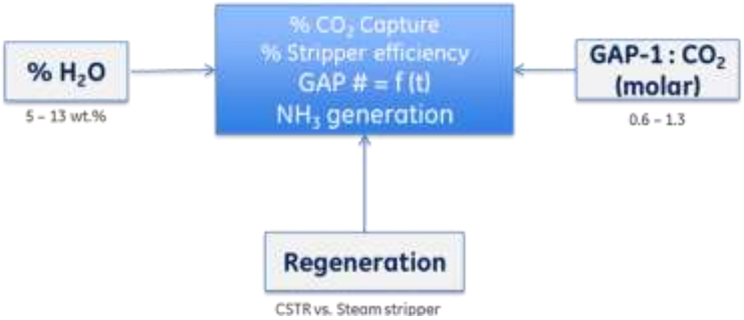


Figure 54. **Steam Stripping:** Experimental design
Effect of water, stoichiometry, and type of regeneration
Max T$_{desorption}$ = 108 °C (226 °F), P$_{desorption}$ < 1 Psig

% CO_2 Capture = f (H_2O%, and CSTR/SSC)

Performance of the 60 wt.% - 40 wt.% GAP-1_m - TEG was first evaluated as function of the desorber system (CSTR vs. steam stripper) while varying water content between 6 and 13 wt. %. A detailed description of the experiments is provided below. Performance of the system is compared in **Table 16**, **Figure 56** and **Figure 57**.

Desorption with CSTR: Experimental Procedure

Simulated exhaust gas (200 SLPM; 12 % CO_2, 5 % O_2, 1 ppm SO_2, balance N_2; 40 ^oC) was fed at the bottom of the absorber column. GAP-1_m /TEG (0.8 L / min, 40 ^oC) was fed at the top of the absorber column. This corresponds to a molar ratio GAP-1 : CO_2 = 1.3 : 1. Rich solvent, collected at the bottom of the absorber, was sent to the CSTR desorber. The temperature of the desorber was set at 108 ^oC, and the desorber pressure was 1 PSIG.

Desorption with SSC: Experimental Procedure

Simulated exhaust gas (200 SLPM; 12 % CO_2, 5 % O_2, 1 ppm SO_2, balance N_2; 40 ^oC) was fed at the bottom of the absorber column. GAP-1_m /TEG (0.8 L / min, 40 ^oC) was fed at the top of the absorber column. This corresponded to a molar ratio GAP-1 : CO_2 = 1.3 : 1. Rich solvent, collected at the bottom of the absorber, was sent to the steam stripper regenerator. The setpoint temperature of the solvent leaving the rich heat exchanger was set at 95°C; and the temperature of the reboiler was set at 108 ^oC. The reboiler pressure was 1 PSIG.

Performance of SSC and CSTR with controlled water addition was compared vs. the baseline case (CSTR with 2 % wt. water) in **Table 16**. The increase in water content from 3 wt. % to 10 wt. % (Table 1, Experiment 1 to Experiment 2) lowers the desorption/regenerator temperature from 125°C to 108° C. The lower desorption temperature renders lower heat-induced degradation of the GAP-1_m solvent. Moreover, the amount of absorption solvent required for a given amount of CO_2 capture can desirably be reduced by up to 30 %, as compared to baseline case, reducing the size of the CO_2 capture plant.

Table 16. SSC Bench Scale Demo: SSC vs. CSTR Performance

Experiments	**1***	**2**	**3**	**4**	**5**
% H_2O	3	10		13	
Regenerator	CSTR	CSTR	SSC	CSTR	SSC
GAP-1_m : CO_2 (molar)	1.8	1.3	1.3	1.3	1.3
Desorption Temperature, ^oC					
Steam stripper range	NA	NA	100 – 104	NA	100 - 104
Regenerator	125	108	108	108	108
% GAP-1 reacted					
Absorber, bottom	64	95	85	86	81
Steam Stripper, bottom	NA	NA	52	NA	27
Lean Storage	16	33	21	22	13
CO_2 Capture %	74	74	79	75	83

Lean solvent composition (dry-basis): 60 wt. % GAP-1 (Sivance) / 40 wt. % TEG. *Gas absorber inlet conditions:* 12 % CO_2, 5 % O_2, 1 ppm SO_2, (balance N_2); 40 ^oC. *Desorber pressure:* 1 Psig.

Performance of the CSTR vs. SSC is compared in **Figure 55** at varying water content. Performance of the two desorber systems was similar for 6 wt. % water. Higher water content (10 - 13 wt. %), and desorption in the steam stripper rendered increased % CO_2 capture (from 74 % to 83%), lower temperature of desorption (from 125 ^oC to 100-108 ^oC), and an increased solvent working capacity (30 % increase).

To better understand this behavior, temperature profiles in the SSC, and % SSC efficiency = f (water content) are shown in **Figure 56** and **Figure 57**, respectively. For working solutions with lower water content, there is limited steam circulation in the SSC as indicated by temperatures lower than 100 ^oC for the entire height of the column (6 wt. % water). In this case, most of the desorption is happening in the CSTR/reboiler (SSC efficiency ~ 10%). As water content in the working solution is increased to 10 and 13 wt. %, respectively, more steam is generated, and the efficiency of the stripping column increases to 58 % (10 wt. % H_2O) and 78% (13 wt. % H_2O), respectively. As expected, temperatures in the stripping column exceed 100 °C for most of the column height at water content above 10 wt. %. Performance of the CSTR vs. SSC is compared in **Figure 58** at varying GAP-1_m : CO_2 (molar) and 13 % wt. H_2O. % CO_2 capture efficiency is increased with solvent flowrates.

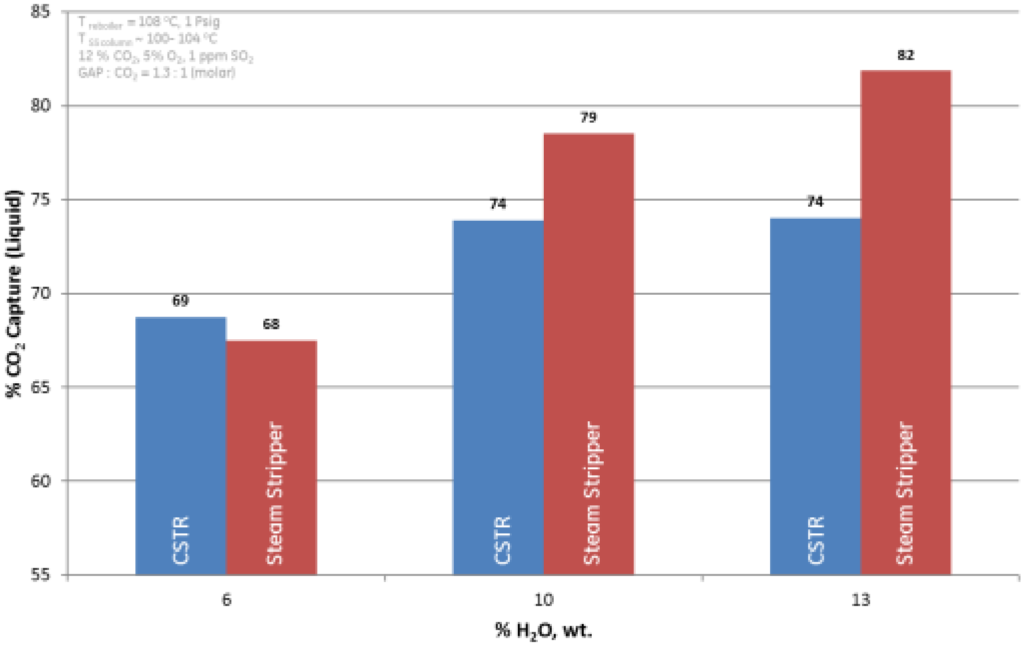


Figure 55. **SSC Bench Scale Demo:** % CO_2 Capture = f (H_2O%, desorption system)
Lean solvent composition (dry-basis): 60 wt. % GAP-1_m/ 40 wt. % TEG.
Gas absorber inlet conditions: 12 % CO_2, 5 % O_2, 1 ppm SO_2, (balance N_2); 40 °C. *Desorber pressure:* 1 Psig. T_{CSTR} = 108 °C, T_{SSC} = 100 – 104 °C. GAP -1_m : CO_2 (molar) = 1.3

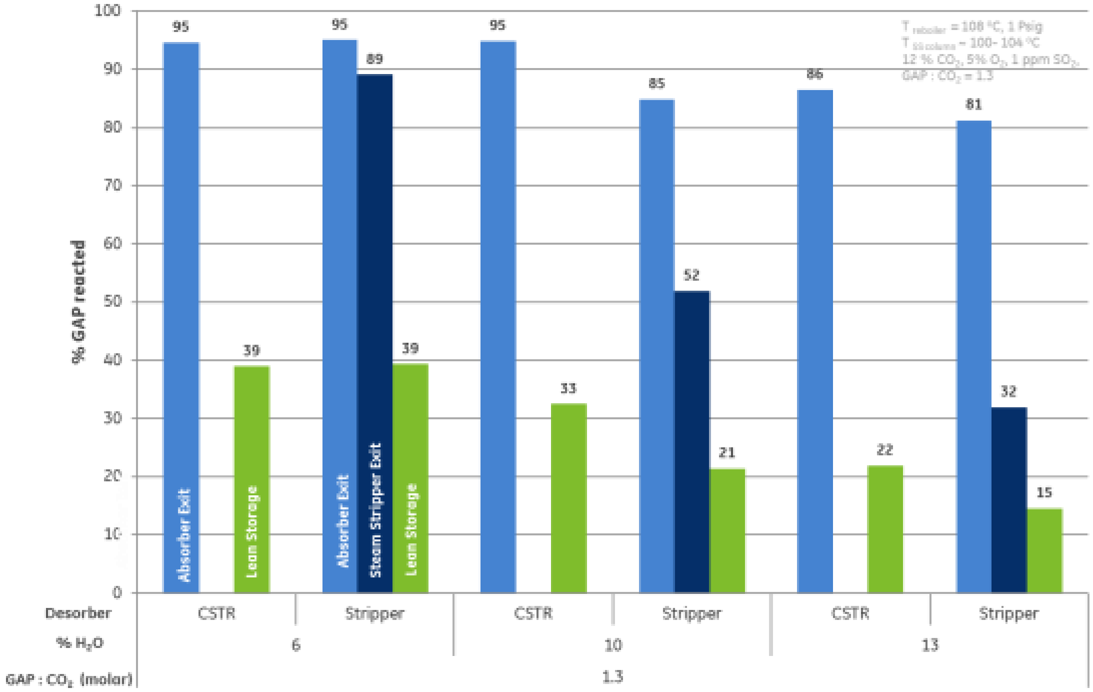


Figure 56. **SSC Bench Scale Demo:** % GAP carbamate (CSTR / SSC)
Conditions as in **Figure 55**

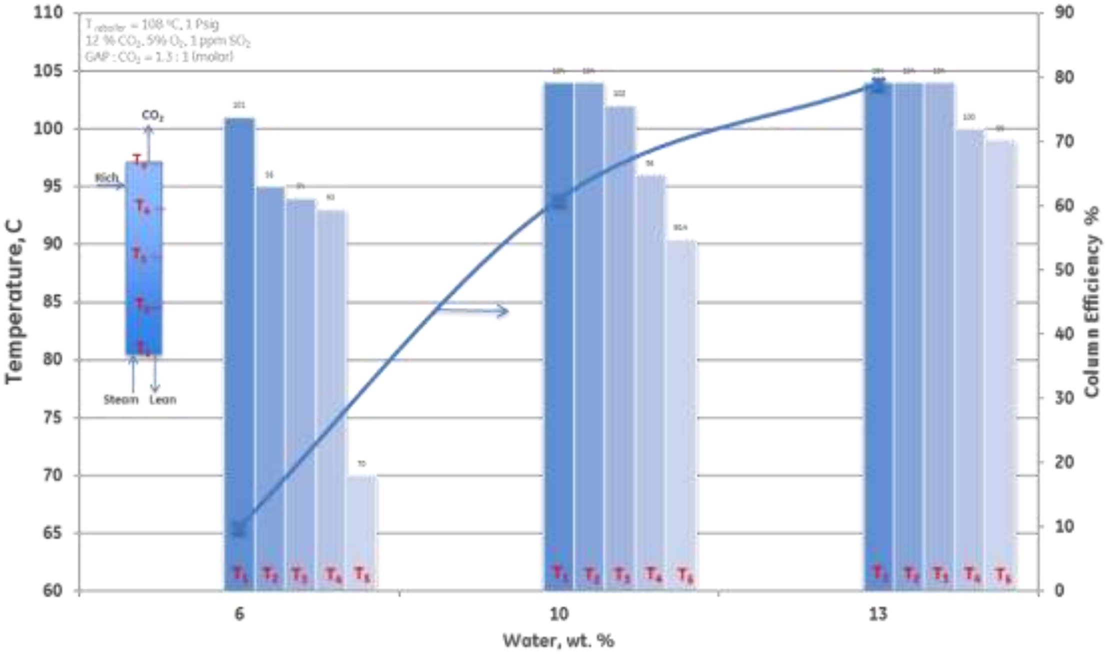


Figure 57. **SSC Bench Scale Demo:** SSC temperature profile
Conditions as in **Figure 55**

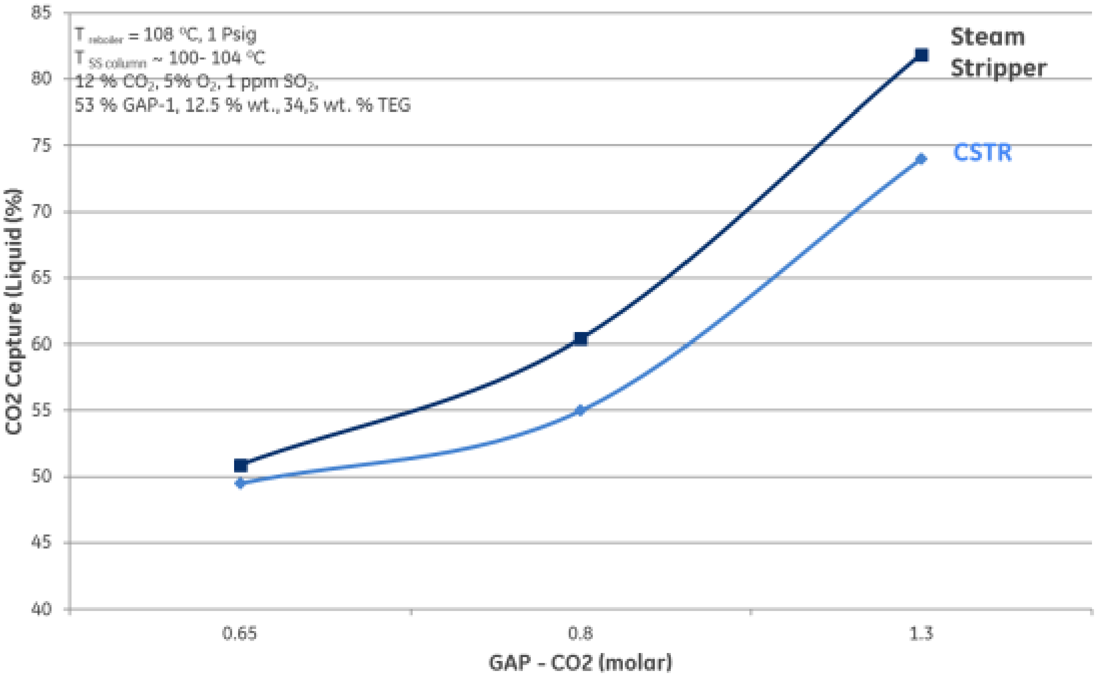
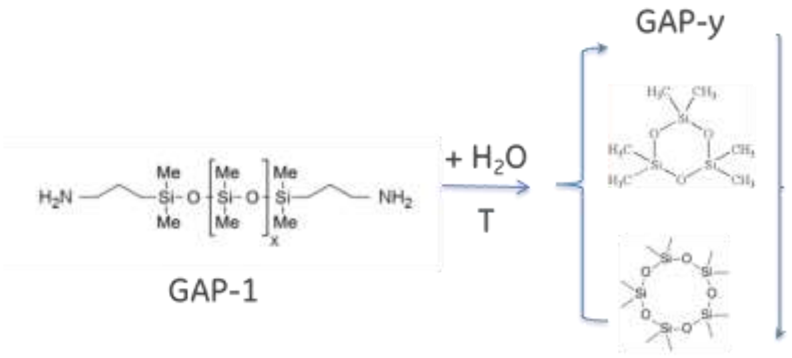


Figure 58. **SSC Bench Scale Demo:** CO_2 Capture Rate = f (GAP-1_m : CO_2 (molar))
Conditions as in **Figure 55**, 13 wt.% H_2O

4.3.3. SSC Bench Scale: Hydrothermal stability

Hydrothermal stability of the aminosilicone solvent was evaluated by following the evolution of GAP-X numbers, during the bench scale experiments. The overall hydrolytic reaction of GAP-X material is shown below:



Liquid samples collected periodically from the lean storage tank during the entire period of the campaign were analyzed by ^{1}H NMR. **Figure 59** shows the evolution of GAP-X number as a function of heating time. GAP-x number decreased from 0.75 (fresh solvent) to 0.6 after 20 hrs. of heating at temperatures between 105-115 ^{o}C.

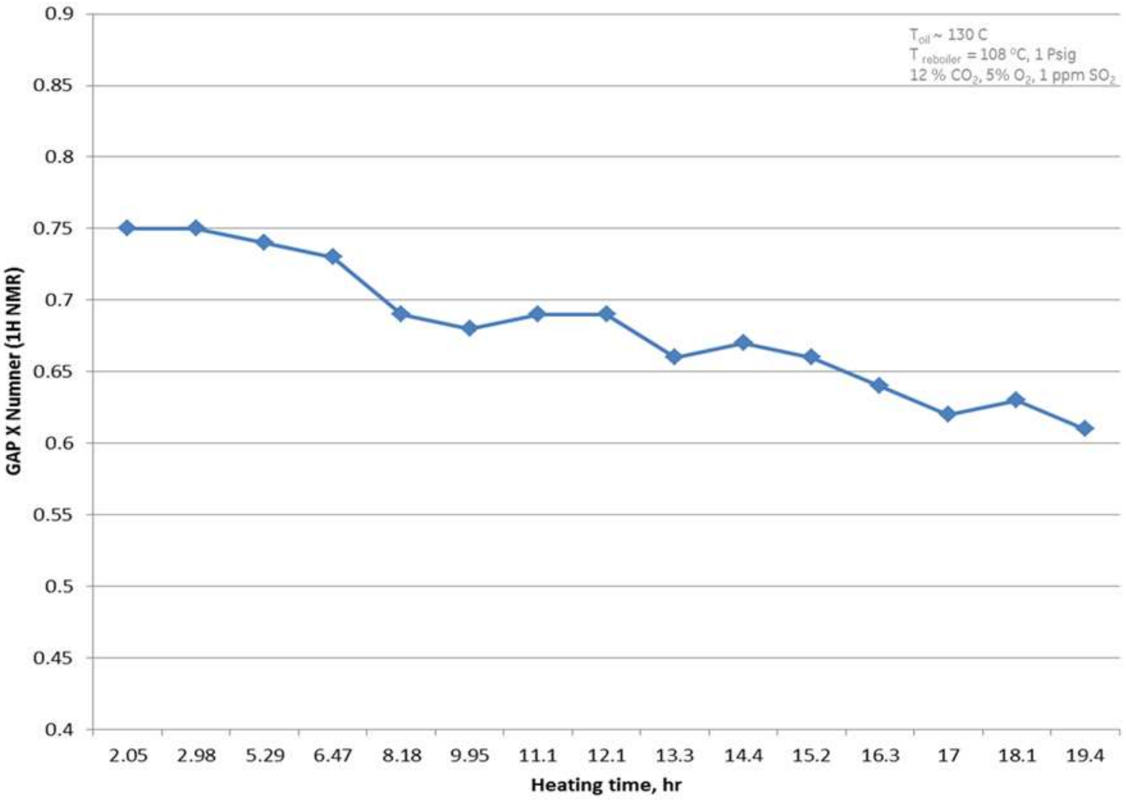


Figure 59. **SSC Bench Scale Demo:** *GAP Number = f (heating time)*
Conditions as in **Figure 55**, 13 wt.% H_2O

Product distribution of the hydrothermal degradation of the GAP-1_m solvent was evaluated by collecting and analyzing liquid samples from different locations of the process, as shown in **Figure 60**. **Table 17** shows phase composition determined by ^{1}H NMR.

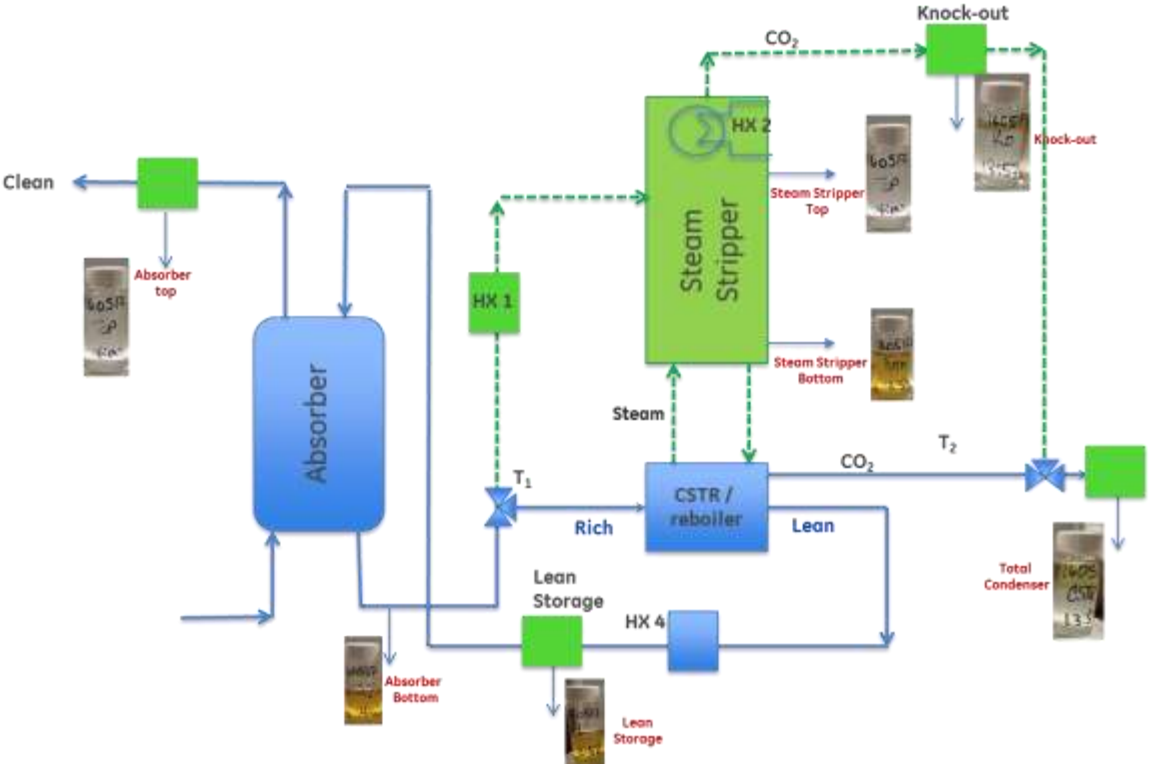


Figure 60. Hydrothermal stability: Sample collection

Table 17. **Hydrothermal Stability:** Product Composition (wt. %)

	Steam Stripper Top	Total Condenser (top layer)	Total Condenser (bottom layer)	Knock-out (bottom layer)	Knock-out (top layer)
Water	99.8	3.7	86	99.4	4
TEG	0.1	0.8	5.9	0.2	32.4
GAP-X	0.1	95.5	8.2	0.4	45.2

One phase, aqueous samples, were collected from the clean product stream (Absorber top sample), and the top of the steam stripper column (SSC top sample). These samples contain predominantly water (99+ wt.%) with traces of TEG and GAP-1_m degradation products (D_n, < 1 wt. %).

One phase, organic samples, were collected from the bottom of the steam stripper (SSC bottom sample), the bottom of the absorber (*Absorber bottom sample*), and the lean storage tank (Lean storage sample). These organic samples have the composition of the working solution (60 wt. % GAP-1_m, 40 wt. % TEG – dry basis). Two-phase, organic (top layer) – water (bottom layer), samples were collected from the knock-out condenser (*Knock-out sample*), and total condenser (Total Condenser sample).

4.3.4. SSC Bench Scale: Summary

- An experimental design was performed in the bench scale system ($2kW_e$) to evaluate the steam stripping desorption process vs CSTR while varying water content in the working solution, and amine to CO_2 stoichiometry. Temperature of the reboiler was kept constant at 108 °C and desorption pressure at 1 PSIG.

- Control water addition & SSC lowered desorption temperature with 20 °C and increased working capacity by 30 %.

- SSC efficiency was strongly correlated on the water content in the working solution. Most of the desorption occurred (> 75 %) in the SSC for water content > 10 wt. %. Performance of the SSC and CSTR were similar at low water content, as most of the desorption occurred in the reboiler.

- Hydrothermal stability: GAP number decreased from 0.75 to 0.6 in less than 20 hrs. of heating.

4.4. SSC 0.5 MW_e Pilot Scale (Q4 2016 – Q1 2017)

Testing the aminosilicone solvent utilizing the steam stripper column (SSC) at NCCC was conducted with the overall objective of reducing the thermal degradation of the solvent through decreased desorber temperature, and controlled water addition. The campaign was conducted in 3 phases: commissioning (Phase 1 – Nov. 2016), parametric study and optimization (Phase 2 – Dec. 2016), and solvent degradation and water loading optimization (Phase 3 – Feb. 2017).

Commissioning of the steam stripper column was conducted by gradually increasing the amount of water in the solvent (from 5 wt.% to 15 wt.%) while decreasing desorber temperature (from 255 °F to 235 °F) and pressure (from 7 Psig to 2 Psig). **Figure 61** describes the overall experimental design implemented in phase 1.

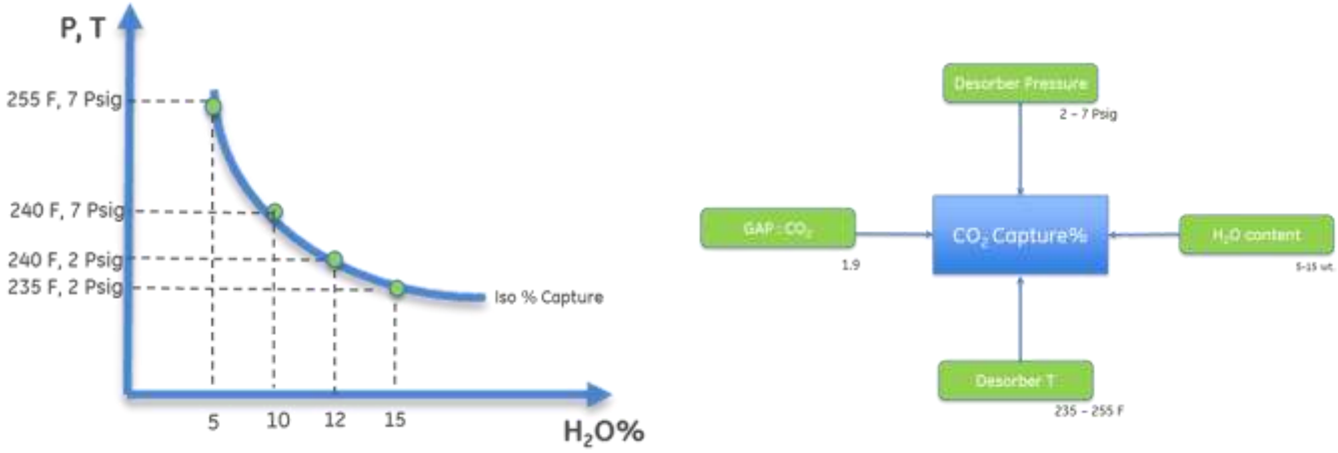


Figure 61. Steam Stripper Commissioning: Experimental Design

4.4.1. 0.5 MW_e SSC Phase 1: Commissioning (Nov. 2016)

Initial experiments were performed to evaluate performance of the regenerator column at increasing water content, while lowering desorber temperature and desorber pressure. The following sections describe the sequence of process conditions tested to evaluate the performance of the SSC with the non-aqueous aminosilicone solvent. **Table 18** summarizes the conditions utilized during the commissioning phase.

4.4.1.1 Experimental Conditions

Flue gas flowrate was maintained at 2,500 pph. Flue gas composition is listed in **Table 19**. The commissioning was conducted with the spent GAP-1_m/TEG solvent utilized in the CSTR campaign. Lean solvent working solution composition is listed in **Table 20**. Working solution flow rate was kept at 12,000 pph +/- 5%. GAP-1_m : CO_2 (molar) ratio was 1.8 +/- 10%. Amine content was 38 wt.% (dry basis).

Table 18. **SSC commissioning:** Process Conditions

Parameter	**1**	**2**	**3**	**4**
Flue Gas (FG) (lb./hr.)	2500	2500	2500	2500
Liquid (lb./hr.)	12000	12000	12000	12000
$T_{desorber}$ (°F)	255	240	240	235
$P_{desorber}$ (Psi)	7	7	2	2
H_2O (wt.%)	5	10	12.5	15
Water Management	Auto: 602 tank (1) to 401 tank (2)	*Manual*: 501 tank (3) to 401 tank Auto: 602 tank to 401 tank	*Manual*: 501 tank to 401 tank Auto: 602 tank to 401 tank	*Auto*: 501 tank to 401 tank Auto: 602 tank to 401 tank

(1)602 tank: mist separator tank; (2)401 tank: lean storage tank; (3)501 tank: water wash tank

Table 19. **SSC commissioning:** Flue Gas Composition

O2 (% vol, dry)		**CO2 (% vol, dry)**		**NO2 (ppm)**		**NO (ppm)**		**SO2 (ppm)**	
Average	Std. Dev	Average	Std. Dev	Average	Std. Dev	Average	Std. Dev	Average	Std. Dev
6.99	0.39	12.06	0.34	0.75	0.54	34.9	14.5	0.6	0.74

Table 20. **SSC commissioning:** Solvent composition

SAMPLE #	Description	Collection date	TOTAL AMINE wt. % (TITRATION)		TEG wt. % (GC)	WATER wt.%. (KARL FISHER)
			Wet basis	Dry basis		
BB02122	Absorber IN	11/2/16 17:00	35.4	39.3	33.3	10.1
BB02124	Absorber IN	11/3/16 8:30	34.3	38.3	33.5	10.5
BB02132	Absorber IN	11/4/16 8:45	33.6	38.4	33.3	12.5
BB02135	Absorber IN	11/4/16 14:50	32.3	38.3	32.8	15.6

***Condition 1**: 5 % H_2O, 7 Psig and 255 ^oF Desorption*

The starting conditions were similar to the ones used in the CSTR campaign: 5 % H_2O, 255 ^oF desorber temperature, and 7 Psig desorber pressure. CO_2 capture efficiency, measured based on the gas phase analysis, was 80%. Temperature profile in the regenerator column is shown in **Figure 62**, indicating that only the bottom 10% of the regenerator column was under the steam conditions. Regenerator liquid level was constant at 60% indicating normal operation of the column with the non-aqueous aminosilicone solvent. Limited or no carry-over was recorded in the total condenser or 602 mist separator. Absorber temperature did not exceed 160 F. Temperature increase in the three absorber beds was as following: 30 ^oF (top bed), 10 ^oF (2nd bed) and 7 ^oF (3rd bed) indicating that most of the absorption occurred in the 1st bed of the column.

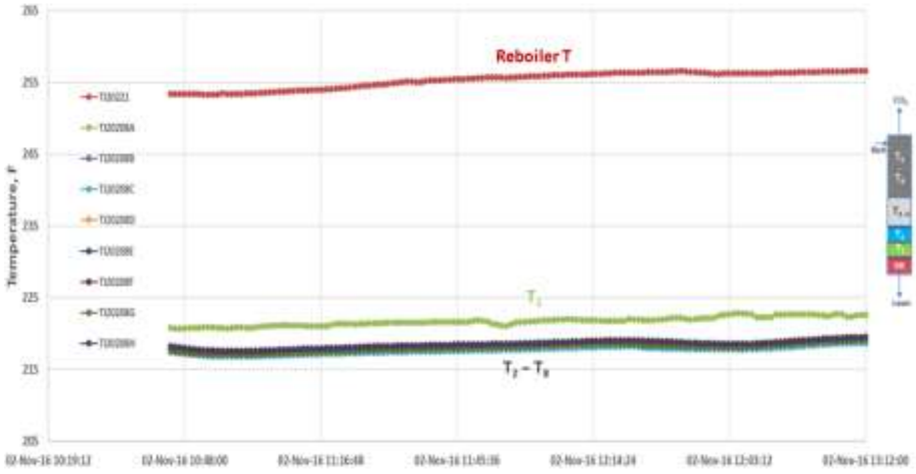


Figure 62. **SSC Commissioning:** Desorber T Profile for Condition 1
5 % H_2O, 7 Psig, 255 ^oF desorber temperature, FG = 2,500 lb./hr.; Liquid = 12,000 lb./hr.;

***Condition 2**: 10 wt. % H_2O, 7 Psig and 240 ^oF Desorption*

Water level in the working solution was increased from 5 wt. % (condition 1) to 10 wt.% by adding 90 gallons of water from 602 tank (mist separator) to lean storage tank (401). During the run, water was continuously transferred from 602 tank to 401 tank to keep the liquid level in lean storage tank, 401 at 30% fill. Desorber temperature was dropped to 240 ^{o}F. All the other process conditions were kept as for condition 1.

CO_2 capture efficiency, measured based on the gas phase analysis, was 77%. Only the bottom 15% of the regenerator column was under the steam conditions. Regenerator liquid level was constant at 60% indicating normal operation of the column with the non-aqueous aminosilicone solvent. Limited or no carry-over was recorded in the total condenser or 602 separator. Absorber temperature did not exceed 160 ^{o}F. Temperature increase in the three absorber beds was as following: 37 ^{o}F (top bed), 12 ^{o}F (2nd bed) and 9 ^{o}F (3rd bed). % CO_2 in the rich and lean working solutions were 3.2 wt. % and 0.98 wt.%, respectively.

***Condition 3**: 12.5 wt. % H_2O, 2 Psig and 240 ^{o}F Desorption*

Water level in the working solution was increased from 10 wt. % (condition 2) to 12.5 wt.% by adding 30 gallons of water from 501 tank (water wash tank) to the lean storage tank (401). During the run, water was continuously transferred from 602 tank to 401 tank to keep its liquid level at 30% fill. Desorber temperature was maintained at 240 ^{o}F. Desorber pressure was lowered to 2 Psig. All the other process conditions were kept the same as for condition 1.

CO_2 capture efficiency, measured based on the gas phase analysis, was 90%. Only the bottom 15% of the regenerator column was under the steam conditions. Increased water content and reduced desorber pressure rendered higher temperature in the bottom of the regenerator column due to higher steam circulation (**Figure 63**). Regenerator liquid level was constant at 60% indicating normal operation of the column. Limited or no carry-over was recorded in the total condenser or 602 separator. Max absorber temperature was 162 ^{o}F (top bed). Temperature increase in the three absorber beds was as following: 42 ^{o}F (top bed), 19 ^{o}F (2nd bed) and 9 ^{o}F (3rd bed). % CO_2 in the rich and lean working solutions were 3.2 wt. % and 0.45 wt.%, respectively.

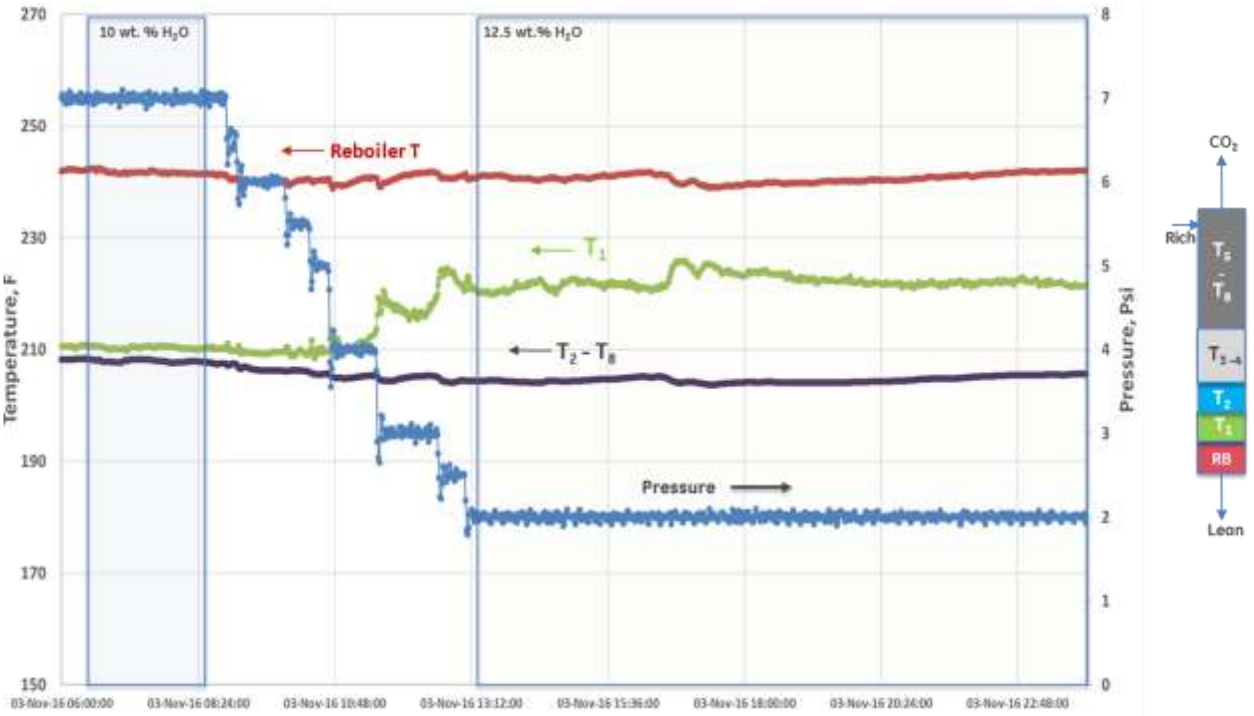


Figure 63. **SSC Commissioning:** Desorber T Profile for Condition 3
Process conditions listed in **Table 18**

***Condition 4**: 15 wt. % H_2O, 2 Psig and 235 ^oF Desorption*

Water level in the working solution was increased from 12.5 wt. % (condition 3) to 15 wt.% by adding additional 50 gallons of water from 501 tank (water wash tank) to the lean storage tank (401). During the run, automatic water control was implemented by controlling liquid level in the 401 lean storage through water addition from the water wash tank (501). Desorber temperature was lowered to 235 ^oF. Desorber pressure was maintained at 2 Psig. All the other process conditions were kept the same as for condition 1.

CO_2 capture efficiency, measured based on the gas phase analysis, was 90%. Increased water content rendered higher temperature in the bottom of the regenerator column due to higher steam circulation (**Figure 64**). Limited or no carry-over was recorded in the total condenser or 602 mist separator. Maximum absorber temperature was 162 ^oF (top bed). Temperature increase in the 3 absorber beds was as following: 50 °F (top bed), 19 °F (2nd bed) and 8 °F (3rd bed). % CO_2 in rich and lean working solutions was 3.2 wt. % and 0.15 wt.%, respectively.

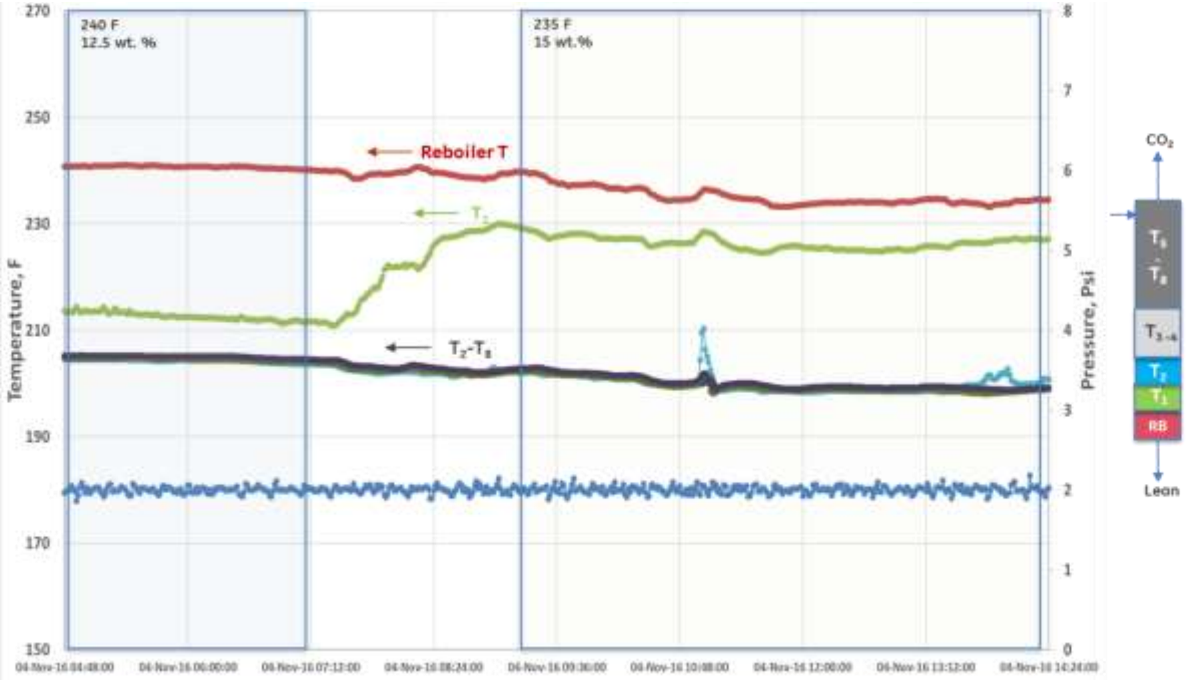


Figure 64. **SSC Commissioning:** Desorber T Profile for Condition 3
Process conditions listed in **Table 18**

4.4.1.2 SSC Performance = f (% water, desorption pressure and temperature)

Performances of the SSC and CSTR are similar at 5 wt. % H_2O (73% (CSTR) vs. 79% (SSC), **Figure 65**). The steam circulation in the regenerator is limited to the bottom of the column, and most of the desorption happens in one stage (i.e. in the reboiler) as in case of the CSTR. CO_2 capture reached 90% efficiency while increasing water content from 5 wt.% to 15 wt.%, decreasing desorber pressure from 7 Psig to 2 Psig, even though the desorber temperature was lowered from 255 °F to 235 °F. This trend can be attributed to the increased steam circulation in the regenerator column that lowers the partial pressure of CO_2, and drives the desorption equilibrium towards leaner working solution.

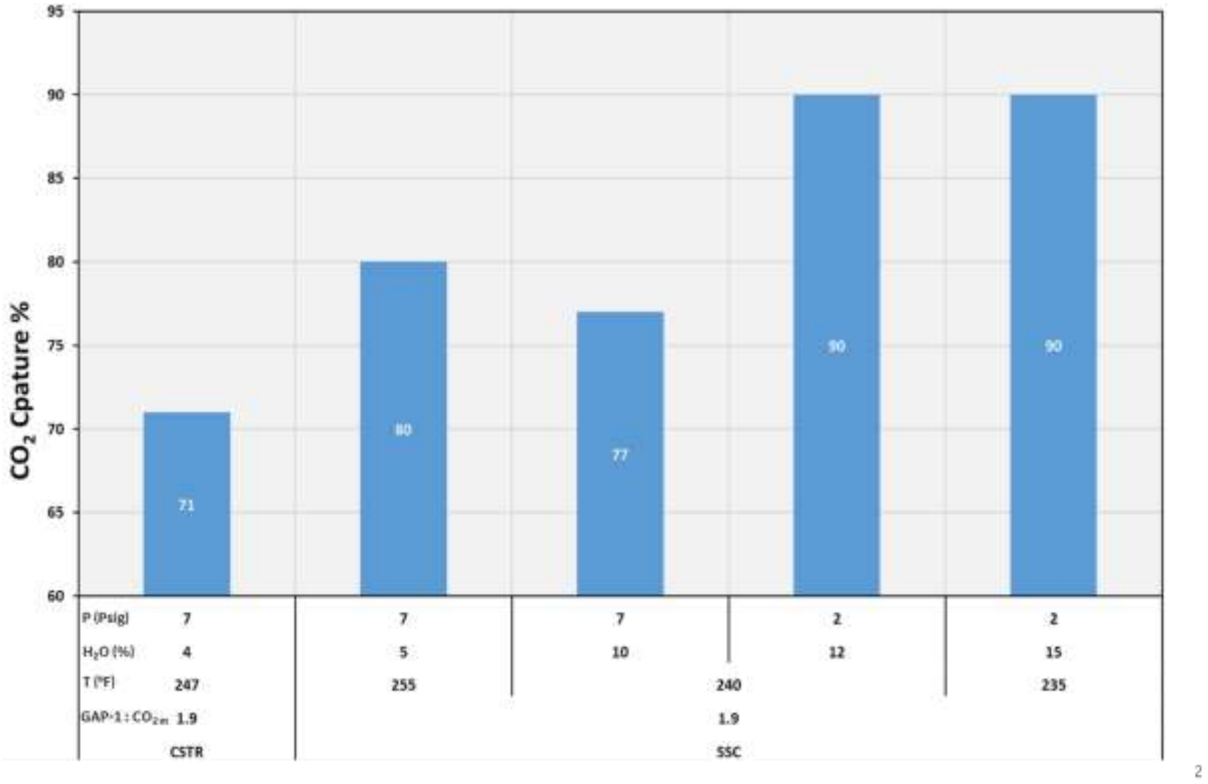


Figure 65. **SSC Commissioning:** CO_2 Capture Efficiency =f (CSTR vs. SSC)
Process conditions listed in **Table 18**

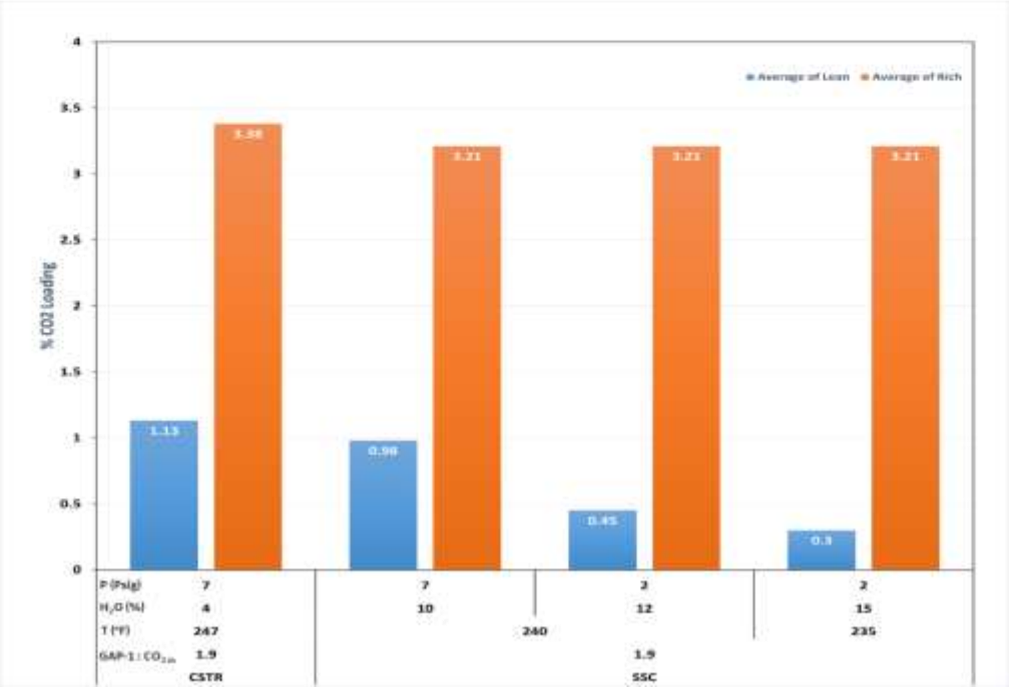


Figure 66. **SSC Commissioning:** CO_2 Capture Efficiency =f (CSTR vs. SSC)
Process conditions listed in **Table 18**

Figure 66 compares % CO_2 in the lean and rich solutions while increasing water content and reducing desorber pressure and temperature. Higher water content and lower desorber pressure decreased the %CO_2 in the lean solvent to 0.3 wt.% (15 wt.% H_2O, 2 Psig and 235 ^oF, SSC) due to a more efficient desorption process.

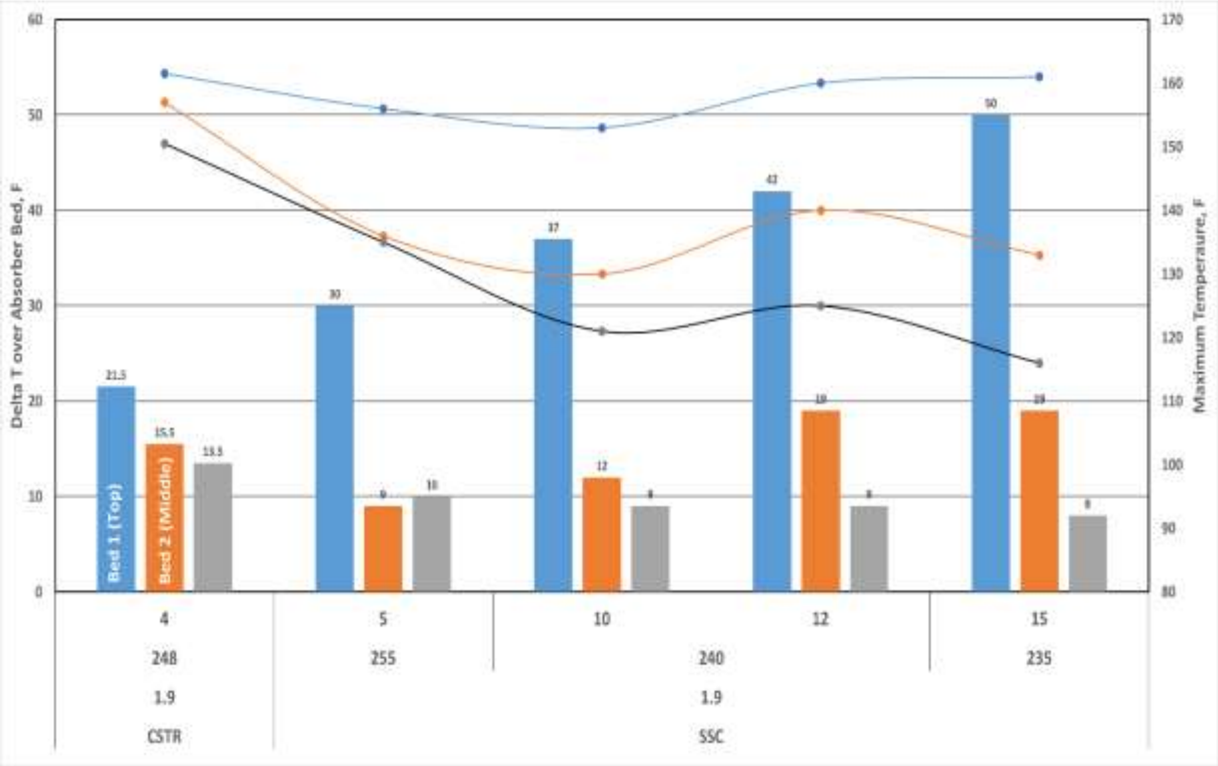


Figure 67. **SSC Commissioning:** Absorber temperature =f (CSTR vs. SSC)
Process conditions listed in **Table 18**

Distribution of the CO_2 absorption in the absorber beds, and maximum temperature in each of the beds were greatly influenced by the water loading in the working solution, and desorber conditions, as shown in **Figure 67**. High water content and low pressure desorption led to higher exotherms in the top bed: 30 ^oF (255 ^oF desorption, 5 wt.%, 7 Psig) < 37 ^oF (240 ^oF desorption, 10 wt. %, 7 Psig) < 42 ^oF (240 ^oF desorption, 12 wt. %, 2 Psig) < 50 ^oF (235 ^oF desorption, 15 wt.%, 2 Psig). Under these conditions, the desorption process in SSC is more efficient, yielding a much leaner solvent. This leads to a more efficient absorption process and more heat generation in the top bed. Lower temperature increase in the bottom beds is indicating that the absorber is oversized for the conditions tested.

Maximum temperature in the bottom absorber bed is lowered by the increased water content in the working solution: 135 ^oF (5 wt. % H_2O) > 121 ^oF (10 wt.% H_2O) > 116 ^oF (15 wt.% H_2O). This effect could be attributed to the endothermic process of water evaporation from the working solution into flue gas. The phenomenon is beneficial as it can reduce the cooling duty of the absorber.

4.4.1.3. SSC performance: 2 kW_e (bench scale, GRC) vs. 0.25 MW_e (pilot, NCCC)

Performance of the GAP-1_m/TEG with SSC was compared at two different scales: 0.25 MW_e (NCCC pilot) and 2 kW_e (GE GRC). Under similar conditions (240 ^oF and 2 Psig desorption, 13 wt.% H_2O), CO_2 capture performance at both scales was between 85 – 90% (**Table 21**). Comparing the temperature profile in the SSC between the 2 scales (**Figure 68**) indicates that only 10% of the column is under the steam conditions at 0.25 MW_e. Absorber temperature profiles are shown in **Figure 69**. Maximum absorber temperature at 2 kW_e scale was 70 ^oC with no intercooling.

Table 21. **Performance of the SSC:** 2 kW_e vs. 0.25 MW_e

Conditions	Bench Scale (2 kW_e)	NCCC (0.25 MW_e)
Run	07072016	11042016
H_2O wt. %	13.5	12.5
T (F)	239	240
GAP : CO_2 (molar)	1.37	1.92 (total) 1.34 (active)
$P_{desorber,}$ (Psig)	3 - 4	2
CO_2% Rich SSC Lean Storage	 6.5 2.9 1.4	 3.2 0.45
CO_2 Capture %	84-86	89-91

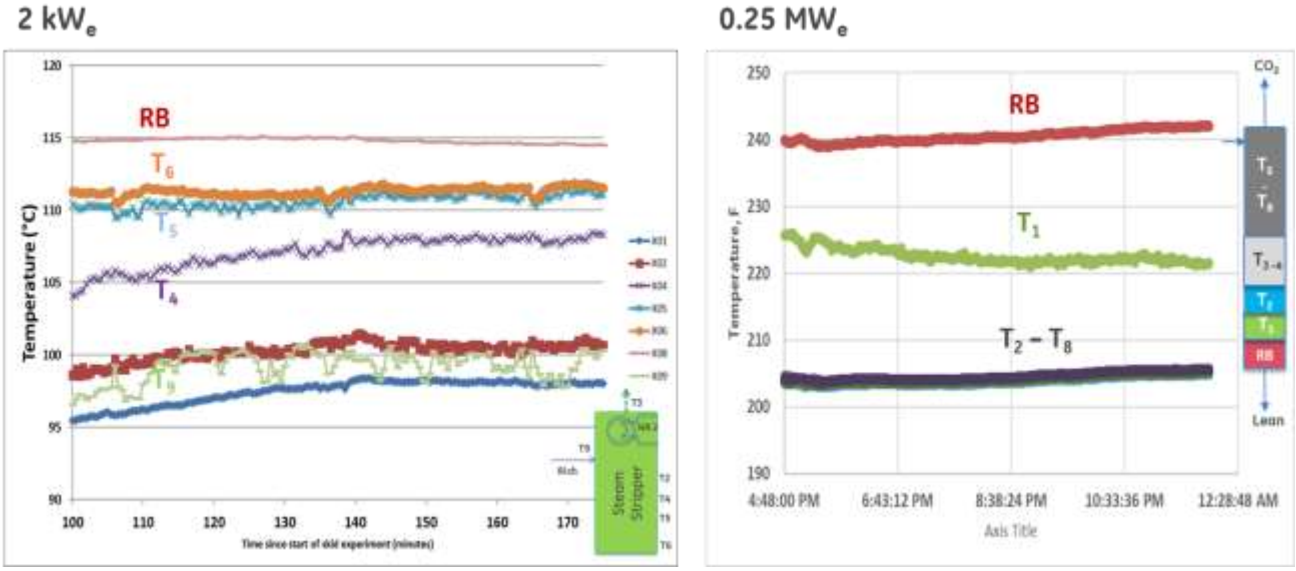


Figure 68. **SSC temperature profile:** Bench scale (2 kW_e) vs. Pilot Scale (0.25 MW_e)

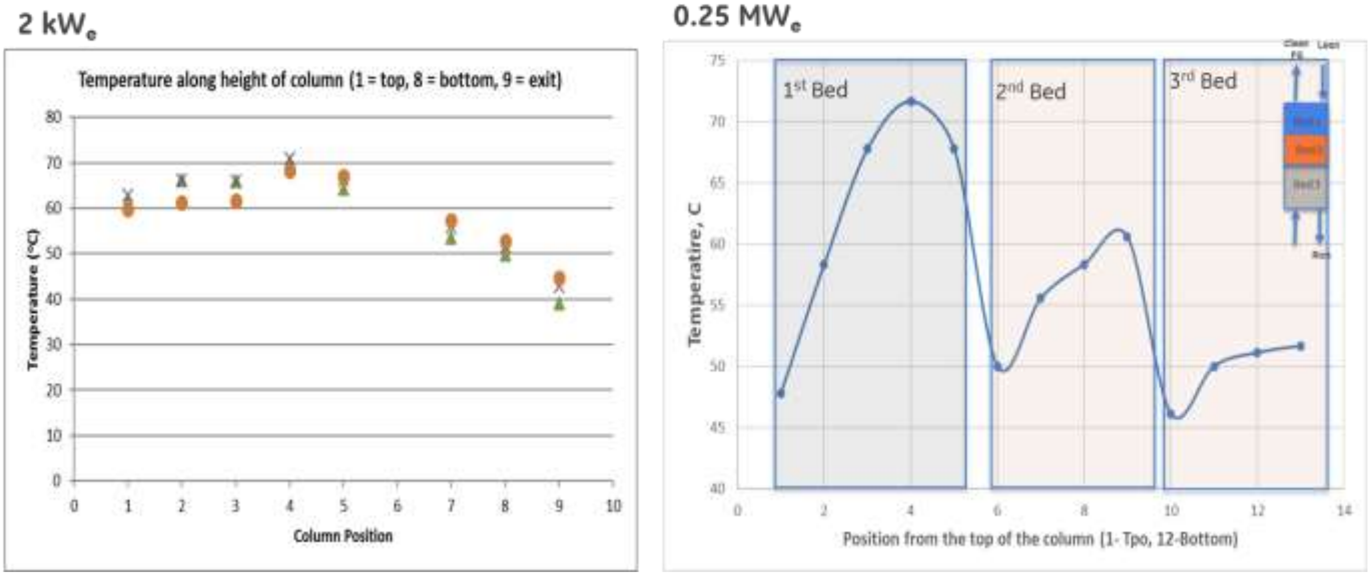


Figure 69. **Absorber temperature profiles:** Bench scale (2 kW, no inter-stage cooling) vs. Pilot Scale (0.25 MW_e, 2 inter-stage cooling)

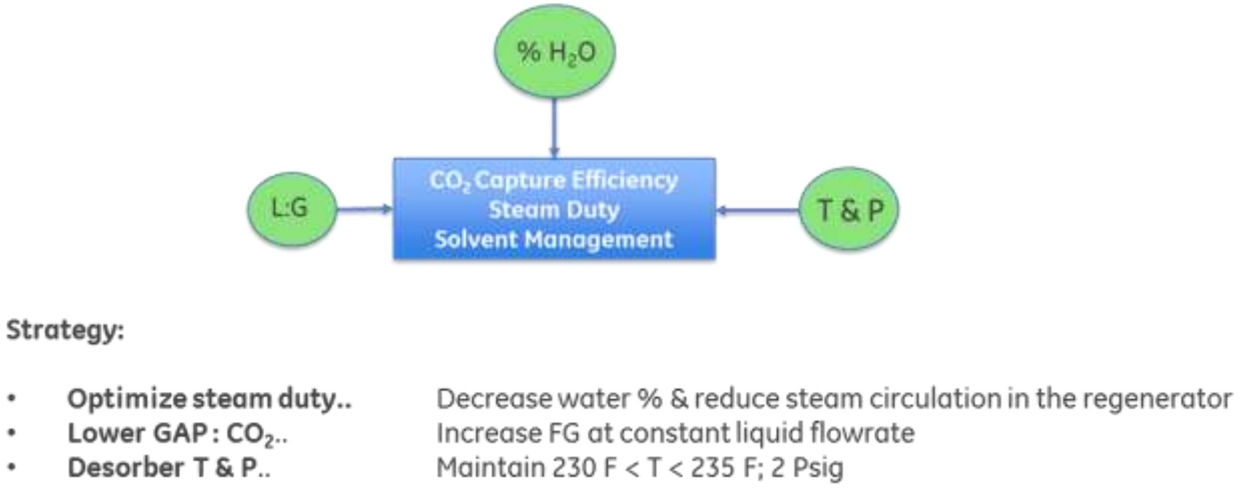
4.4.1.4. 0.5 MW_e SSC Commissioning: Summary

1. Steam stripping column at NCCC was successfully commissioned with GAP-1_m/TEG-1 solvent. No solvent carry-over was observed at water content < 15 wt.%, and low desorption pressure operation. Automatic water management was demonstrated by maintaining liquid level in the lean storage tank (401) through automatic transfer from the water wash tank (501). Stable low pressure desorption was demonstrated.

2. The following performance was demonstrated (0.25 MW_e) with the steam stripper column:
   a. 90 % Capture efficiency was demonstrated at 240 ^oF (12 % H_2O) and 235 ^oF (15+% H_2O)
   b. Absorber temperature was decreased by up to 20 ^oF upon increasing water content to 15 wt.%
   c. Steam circulation in the regenerator column was improved by decreasing desorber pressure, and increasing water content (12-15 wt.% H_2O)

4.4.2. 0.5 MW_e SSC Campaign Phase 2: Optimization

Phase 2 of the SSC campaign at NCCC was conducted to optimize performance of the GAP-1_m/TEG at 0.5 MW_e scale (**Figure 70**). First, the molar ratio GAP-1_m : CO_2 was lowered by increasing the flue gas flow rate from 2500 lb./hr. (0.25 MW_e) to 5000 lb./hr. (0.5 MW_e), while keeping liquid flow rate constant at 13,000 lb./hr. Next, steam duty was optimized at 0.5 MW_e by lowering the water content in the working solution while maintaining CO_2 capture efficiency between 87 - 93 %. Desorber temperature and pressure were maintained below 235 ^oF and 2 Psig, respectively, to minimize solvent thermal degradation. **Table 22** and **Table 23** list the process conditions and flue gas composition utilized during the campaign.



Strategy:

• **Optimize steam duty..**	Decrease water % & reduce steam circulation in the regenerator
• **Lower GAP : CO_2..**	Increase FG at constant liquid flowrate
• **Desorber T & P..**	Maintain 230 F < T < 235 F; 2 Psig

Figure 70. **SSC campaign (Phase 2):** Solvent Circulation and Steam Duty Optimization

Table 22. **SSC campaign (Phase 2):** Process conditions

Condition	**5**	**6**	**7**	**8**	**9**	**10**
Objective	Solvent circulation flow rate			0.5 MWe Demo	Steam Optimization	Pressure Effect
Flue Gas (FG) (lb./hr.)	2500	3750	5000	5000	5000	5000
Liquid (lb./hr.)	12000	12000	12000	13000	15000	15000
$T_{desorber}$ (F)	230	235	235	235	235	235
$P_{desorber}$ (Psi)	2	2	2	2	2	5

Water Management: automatic water addition from water wash tank (501) to lean storage tank (401).

Table 23. **SSC campaign (Phase 2):** Flue gas conditions

	NO	**O_2**	**CO_2**	**NO_2**	**T**
	ppm	% vol.	% vol	ppm	F
Avg	34.1	6.6	12.5	0.6	135.
Stdev.	7.9	0.8	0.6	0.2	2.8

Table 24. **SSC campaign (Phase 2):** Solvent Composition

Sample	**Total Amine wt.%**		**CO_2 wt.%**	**TEG**	**Water**
	wet	dry	wt.%	wt. %	wt.%
Initial	45.8	57	0.69	30.3	19.8
Condition 5	45.5	57	1.14	31.2	20.2
Condition 6	47.4	58	0.87	32.2	17.9
Condition 7	45.9	59	0.37	31.2	21.9
Condition 8	45.3	59	1.3	33.6	23.4
Condition 9	48.2	59.2	1.3	33.8	18.9
Condition 10	47.2	58.3	2.2	33.7	19

4.4.2.1. 0.5 MW_e SSC Campaign (Phase 2): Solvent circulation

Effect of the amine to CO_2 stoichiometry on the fresh GAP-1_m/TEG performance was evaluated by increasing the flue gas flow rate from 2500 lb./hr. (0.25 MW_e) to 5000 lb./hr. (0.5 MW_e) while all the other process parameters were kept constant (Conditions 5-7). Optimization of the regenerator column was performed with fresh GAP-1 / TEG working solution. Solvent properties are listed in **Table *24***. Water content in the working solution was maintained between 18-20 wt.% by controlling liquid level in the lean storage tank (401) through automatic water addition from the water wash tank (501), and mist separator tank (602). **Figure 71** shows liquid level in the lean storage tank (401), water wash tank (501) and mist separator tank (602) for conditions 5-7.

Effect of the liquid flow rate on CO_2 capture efficiency is shown in **Figure 72**. CO_2 capture efficiency reached 100% at GAP-1_m : CO_2 molar ratios between 1.3 to 2 (Condition 5 and 6). Under CO_2 excess (GAP-1_m:CO_2 = 0.9 (molar), condition 7), CO_2 capture efficiency reached 87%, demonstrating stoichiometric capture efficiency under low temperature desorption conditions.

Performance of the 3-bed, inter-staged absorber was influenced by the amine to CO_2 stoichiometry. Maximum temperature in the absorber beds, and temperature increase in each of the beds are listed in **Table 25**. Under a large excess of solvent (Condition 5, GAP-1_m : CO_2 = 2 (molar), 100% Capture Efficiency), most of the absorption happened in the bottom, and middle beds, respectively. Little or no absorption occurred in the top bed (2 ^oC temperature increase), due to near zero CO_2 inlet concentration in this bed. Lowering the amine : CO_2 molar ratio from 2 to 1.3 and 0.9, respectively changed the reaction distribution in the absorber beds. CO_2 absorption was equally distributed among the 3 beds under condition 6, as inferred from the temperature increase in the individual sections of the absorber (42 ^oF (top) > 24 ^oF (middle) > 26 ^oF (bottom)). Under excess of CO_2 (GAP-1_m : CO_2 =0.9 (molar)), most of the absorption occurred in the top bed (temperature increase: 46 ^oF (top) > 15 ^oF (middle) > 15 ^oF (bottom).

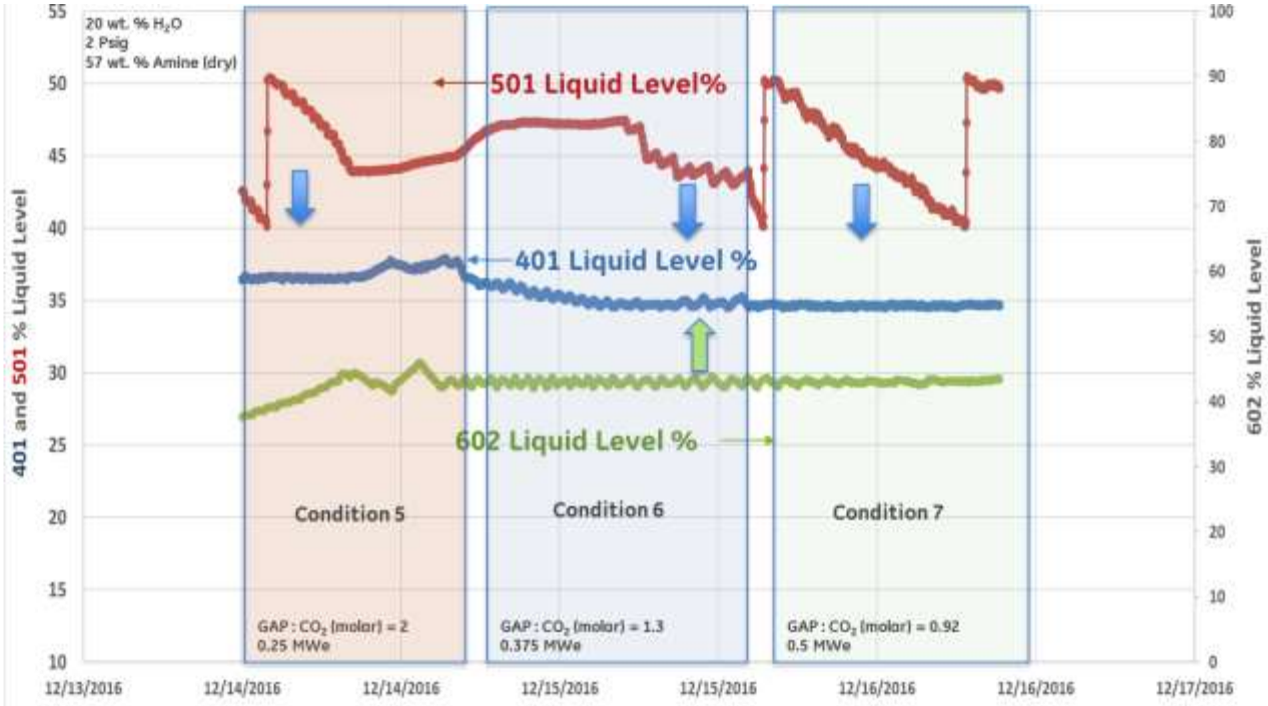


Figure 71. **SSC campaign (Phase 2 – solvent circulation):** Water management
Automatic water transfer from water wash tank (501), and mist separator tank (602) to lean storage tank (401). **Table 22** lists process conditions for Conditions 5-7.

Table 25. SCC campaign (Phase 2): Absorber performance = f (solvent circulation)

		Condition 5	**Condition 6**	**Condition 7**
P	Psig	2	2	2
T	ºF	230	235	235
GAP-1_m : CO_2	molar	2	1.3	0.9
CO_2 Capture	%	100	100	87
Bed 1 (top)	T_{max} (F)	118	156	160
	Delta T (F)	2	42	46
Bed 2 (middle)	T_{max} (F)	118	165	130
	Delta T (F)	24	24	15
Bed 3 (bottom)	T_{max} (F)	141	150	115
	Delta T (F)	32	26	15

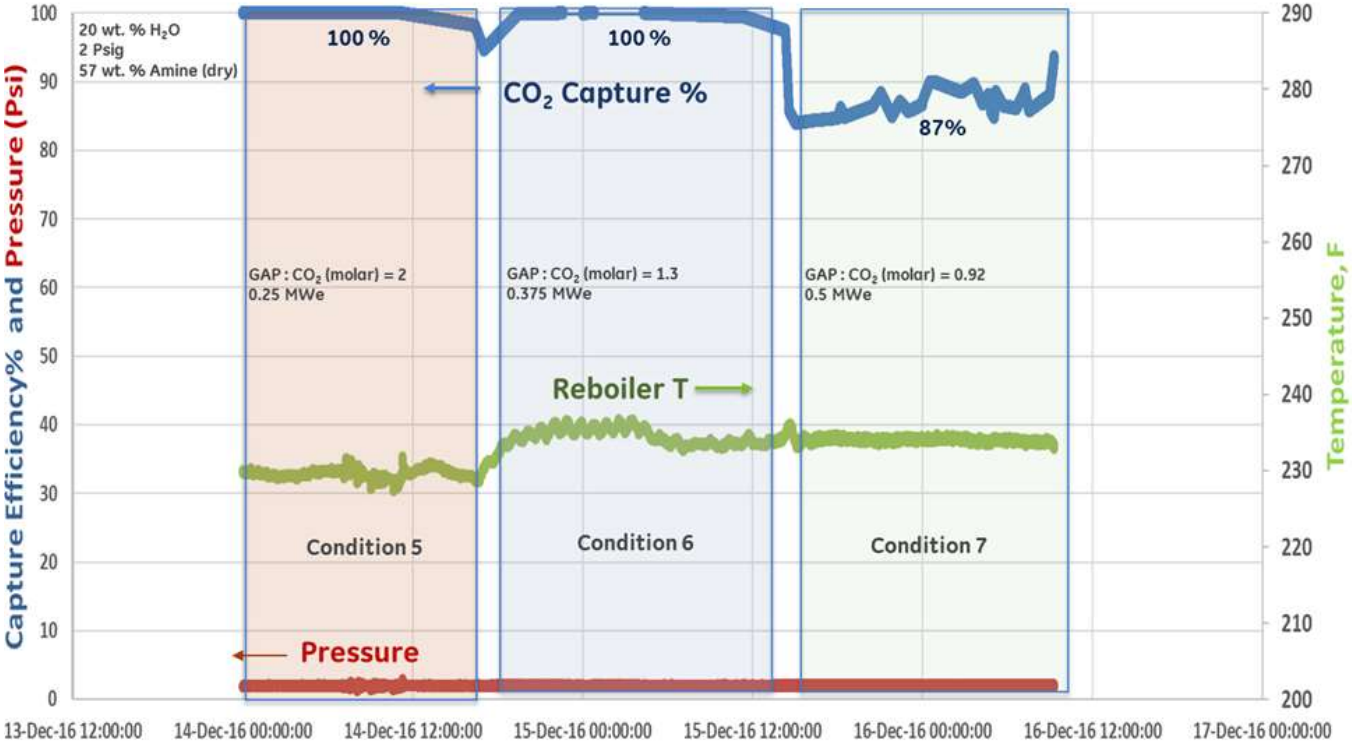


Figure 72. **SSC campaign (Phase 2 - solvent circulation):** CO_2 Capture Efficiency
Table 22 lists process conditions for Conditions 5-7.

Regenerator temperature profile for Conditions 5 is shown in **Figure 73** indicating that 90% of the regenerator column was under steam conditions. Water carry-over from the regenerator column was collected in the total condenser and/or mist separator (602). The condensate was periodically transfferend back to the lean storage tank (401) to control the liquid level in the mist separator tank (602) at 43% fill. Finally, amine to CO_2 stoichimetry had little or no effect on the specific steam utilization (0.48 - 0.5 lb CO_2/ lb steam, **Figure 74**), as long as the water content of the working solution was maintained constant (~ 20 wt.%).

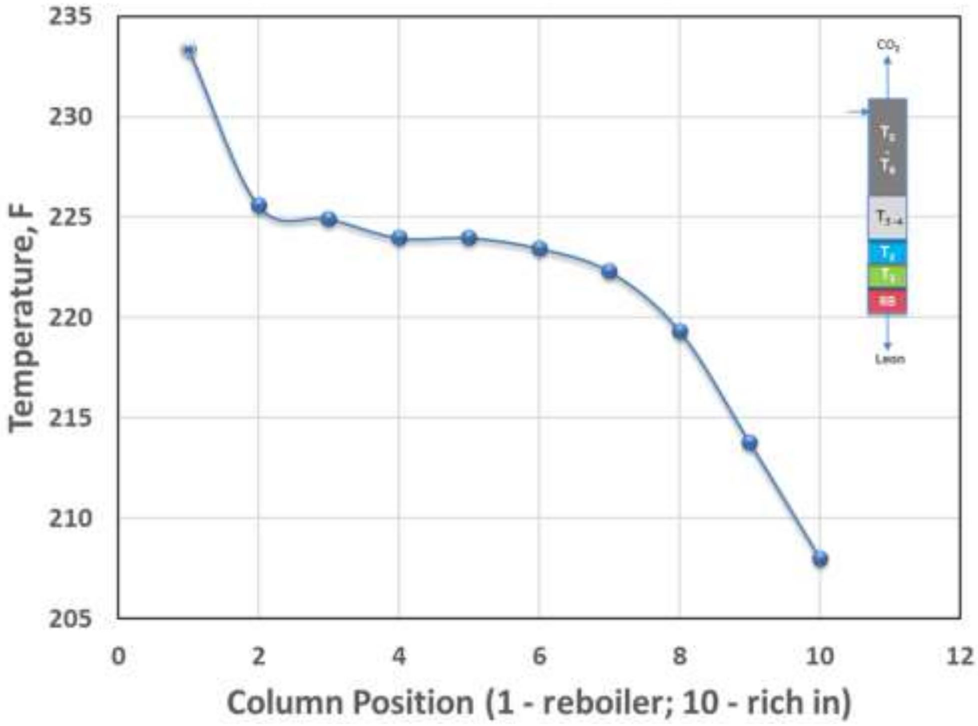


Figure 73. **SSC campaign (Phase 2– solvent circulation):** SSC temperature profile **Table 22** lists process conditions for Conditions 5.

In summary, stoichiometric capture was demonstrated with the regenerator column for the GAP-1_m/TEG working solution (20 wt. % H_2O) at 0.5 MW_e, 2 Psig and 235 ^oF desorption. Absorber operation was greatly influenced by the CO_2 to amine stoichiometry. Under amine excess, most of the absorption occurred in the bottom bed and capture efficiency reached 100%. Finally, specific steam utilization (lb. CO_2 / lb. steam) was constant (0.48 - 0.52) as a function of the amine to CO_2 stoichiometry.

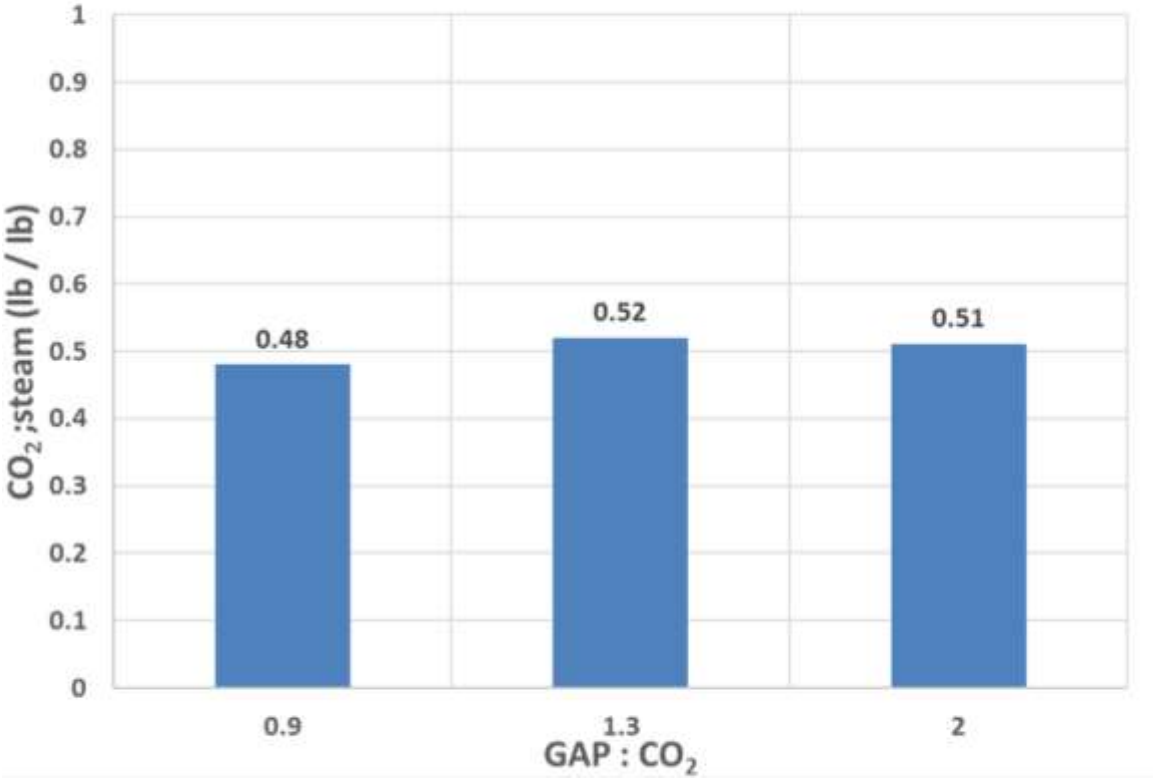


Figure 74. **SSC campaign (Phase 2– solvent circulation):** Specific steam utilization **Table 22** lists process conditions for Conditions 5-7.

4.4.2.2. 0.5 MW_e SSC Campaign (Phase 2): 0.5 MW_e Demo

Performance of the SSC with GAP-1_m/TEG solvent was demonstrated at 0.5 MW_e for 84 hrs. Process conditions are listed in **Table 22** (Condition 8). GAP-1_m : CO_2 molar ratio was maintained at 1.1. Desorption conditions were kept constant at 235 ^oF and 2 Psig, respectively. Solvent composition is listed in **Table 24** (condition 8).

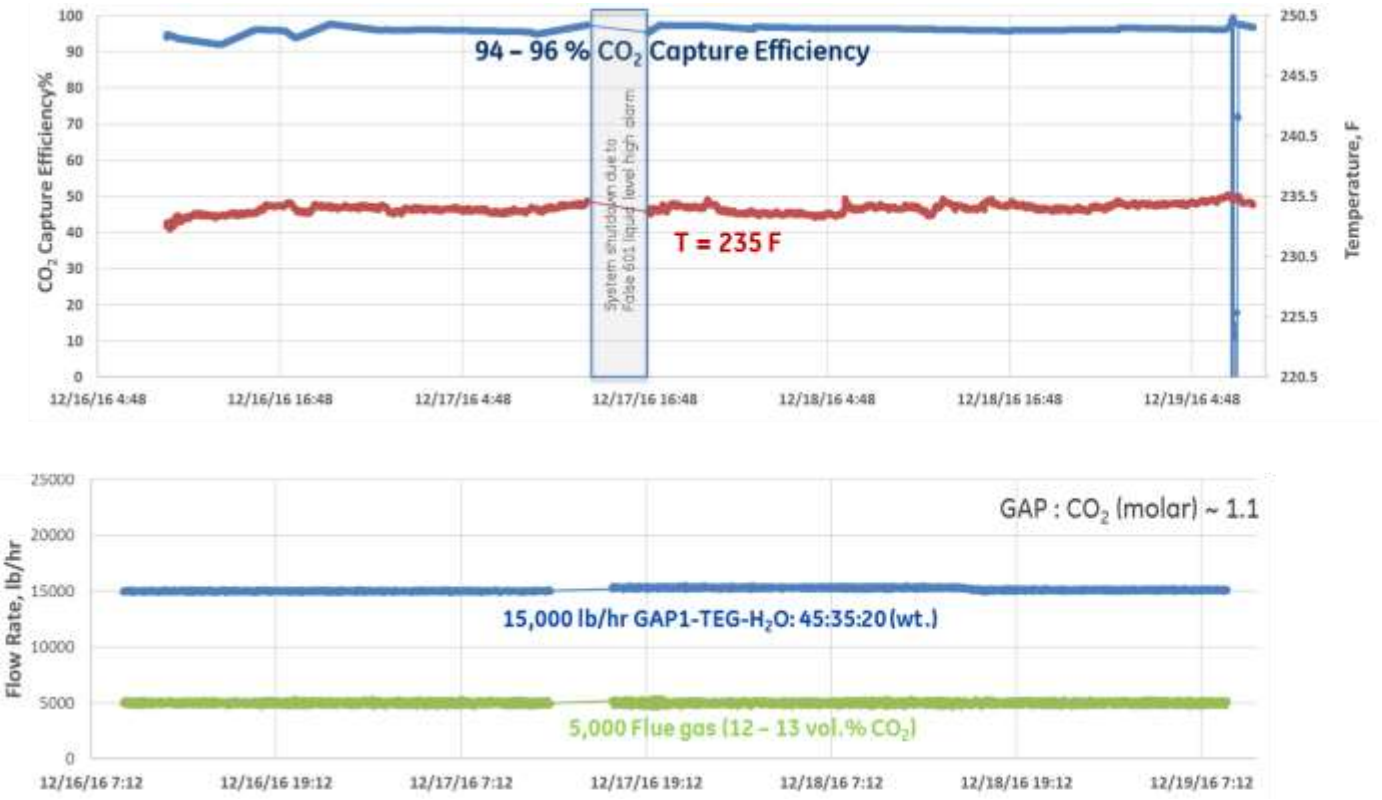


Figure 75. **SSC campaign (Phase 2 - 0.5 MW$_e$ Demo):** CO_2 capture efficiency
Table 22 lists process conditions for Conditions 8.

Performance of the SSC at 0.5 MW$_e$ is shown in **Figure 75**. The system was shut down for 2 hours due to a false liquid level high alarm. CO_2 capture efficiency reached 94 - 96 % based on the gas phase analysis.

Absorber temperature profile is shown in **Figure 76**. Temperature increase in the three absorber beds varied as following: 55 ^oF (top bed) > 22 ^oF (middle bed) > 16 ^oF (bottom bed). Temperature reached a maximum of 163 ^oF in the top bed. Most of the absorption occurred in the top bed, indicating that the size of the absorber and the location of the inter-stage cooler could be further optimized to reduce the footprint, and the maximum temperature in the absorber. Reducing absorber temperature is an effective way to minimize the oxidative degradation of the solvent, as indicated by separate bench scale experiments.

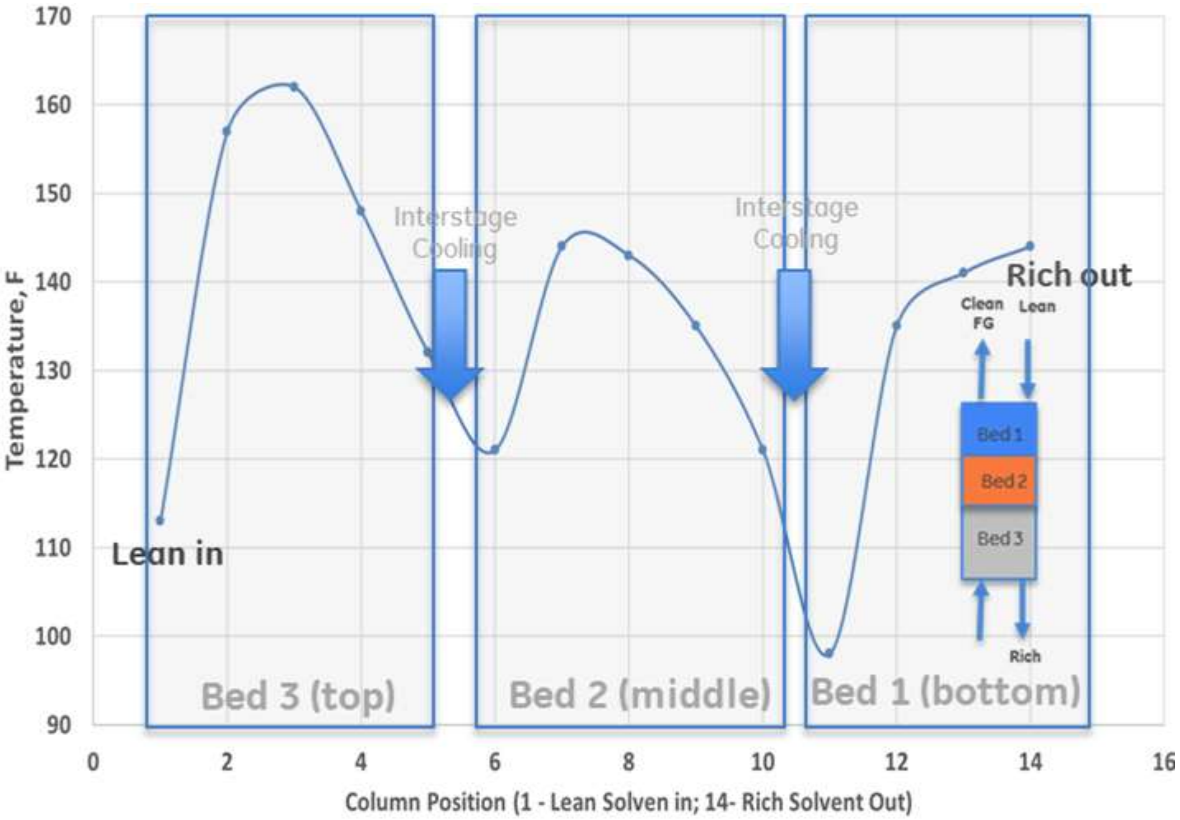


Figure 76. **SSC campaign (Phase 2 - 0.5 MW_e Demo):** Absorber temperature profile

Table 22 lists process conditions for Conditions 8.

Regenerator temperature profile was similar to the one shown in **Figure 73**. 90% of the regenerator column was under steam conditions. Water content in the working solution was maintained constant at 20 wt. % by utilizing the strategy highlighted for conditions 5-7. Water was continuously transferred from the water wash tank (501) and mist separator (602) to the lean storage tank (401). In the last 12 hours of the test, no condensate was transferred from the 602 to 401 tank due to a frozen valve. **(Figure 77)** This led to the increase of the liquid level in 602 tank from 43% to 58%, and water content in the working solution increased from 20.4 wt.% to 23.8 wt.%. At 23.8 wt.% water, the rich solvent sample was bi-phasic: lower phase contained mostly water and TEG (5 wt. % GAP-1_m carbamate, 50 wt. % H_2O, 45 wt. % TEG, by ^1H NMR) while the upper phase had similar composition to the initial working solution (54 wt.% GAP-1_m carbamate, 33 wt.% TEG, and 13 wt. % water, by ^1H NMR). The corresponding lean solvent sample containing 23.8 wt. % H_2O was homogeneous. Finally, all the other samples with lower water content (< 20 wt.%) were homogeneous regardless of the CO_2 content.

Figure 77. **SSC campaign (Phase 2 - 0.5 MW_e Demo):** Water management
Table 22 lists process conditions for Conditions 8.

Specific steam utilization was between 0.45 – 0.5 (lb. CO_2 / lb. steam) (**Figure 78**). Steam conditions were as following: 43 Psig and 335 °F. CO_2 capture efficiency exceeded 95% for most of the run. Under these conditions, 90 % of the column was under steam conditions indicating that steam input can be further optimized. On the other hand, the specific steam utilization of the SSC was almost half when compared to CSTR desorber due to the increased water content in the working solution.

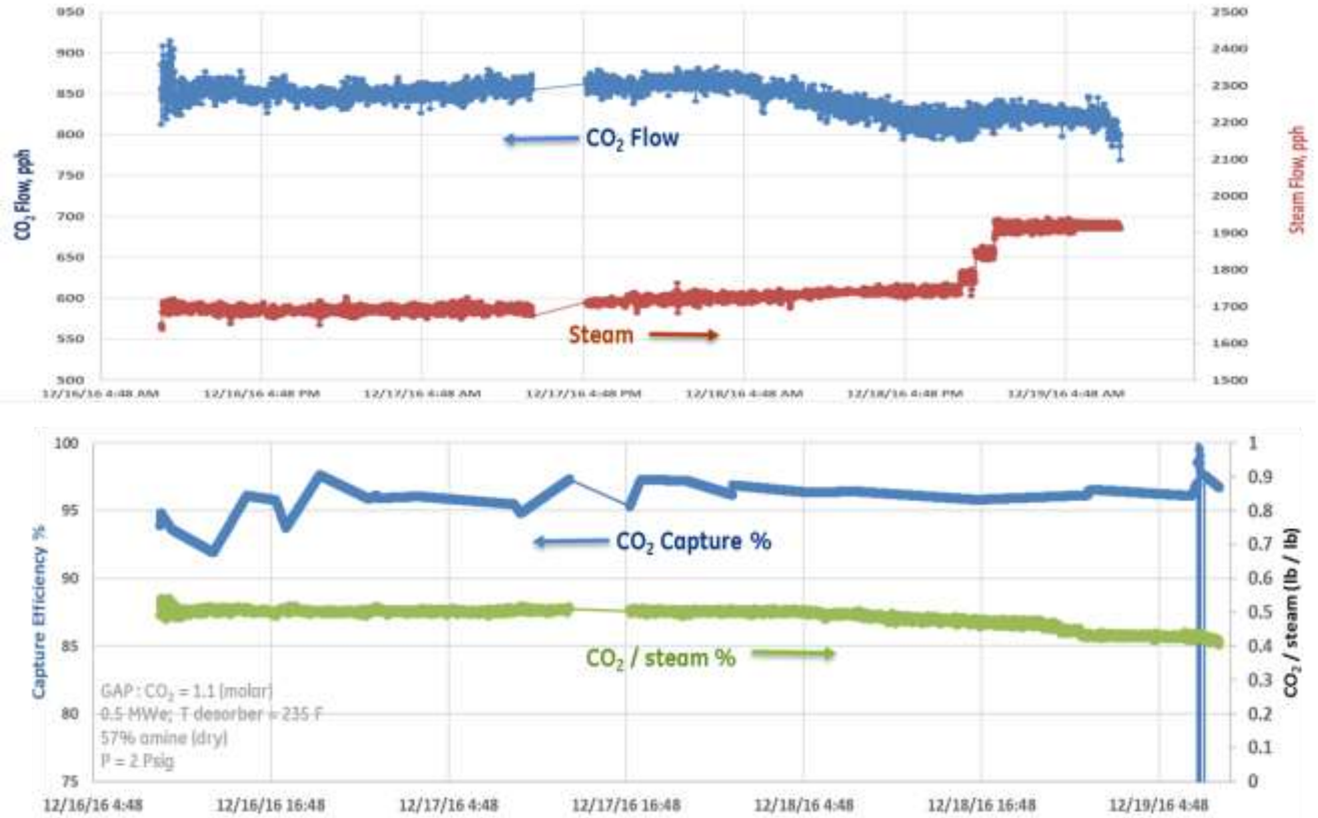


Figure 78. **SSC campaign (Phase 2 - 0.5 MW$_e$ Demo):** Specific steam utilization
Table 22 lists process conditions for Conditions 8.

Most of the process variability during the 0.5 MW$_e$ demo run was caused by the change in the power load of the power plant. Nominally, the plant operated at 800 MW. Under these conditions, average flue gas temperature was 127 ^{o}F, CO$_2$ concentration averaged around 12.8 % vol, average temperature in the bottom absorber bed was 124.4 ^{o}F, and top bed regenerator temperature was 215 ^{o}F **(Table 26)**. After 50 hrs. into the demo run, the power plant power load was downgraded to 650 MW to adjust for lower demand. This change led to a decrease in average flue gas temperature (from 127 ^{o}F to 122 ^{o}F), absorber temperature (bottom bed, 125 ^{o}F to 102 ^{o}F) and regenerator temperature (upper bed, 216 ^{o}F to 211 ^{o}F). **Figure 79** describes the time traces for all these parameters during the 0.5 MW$_e$ SSC demo. The process was robust with respect to the variability caused by the power load, as the CO$_2$ capture efficiency remained above 95% for most of the run.

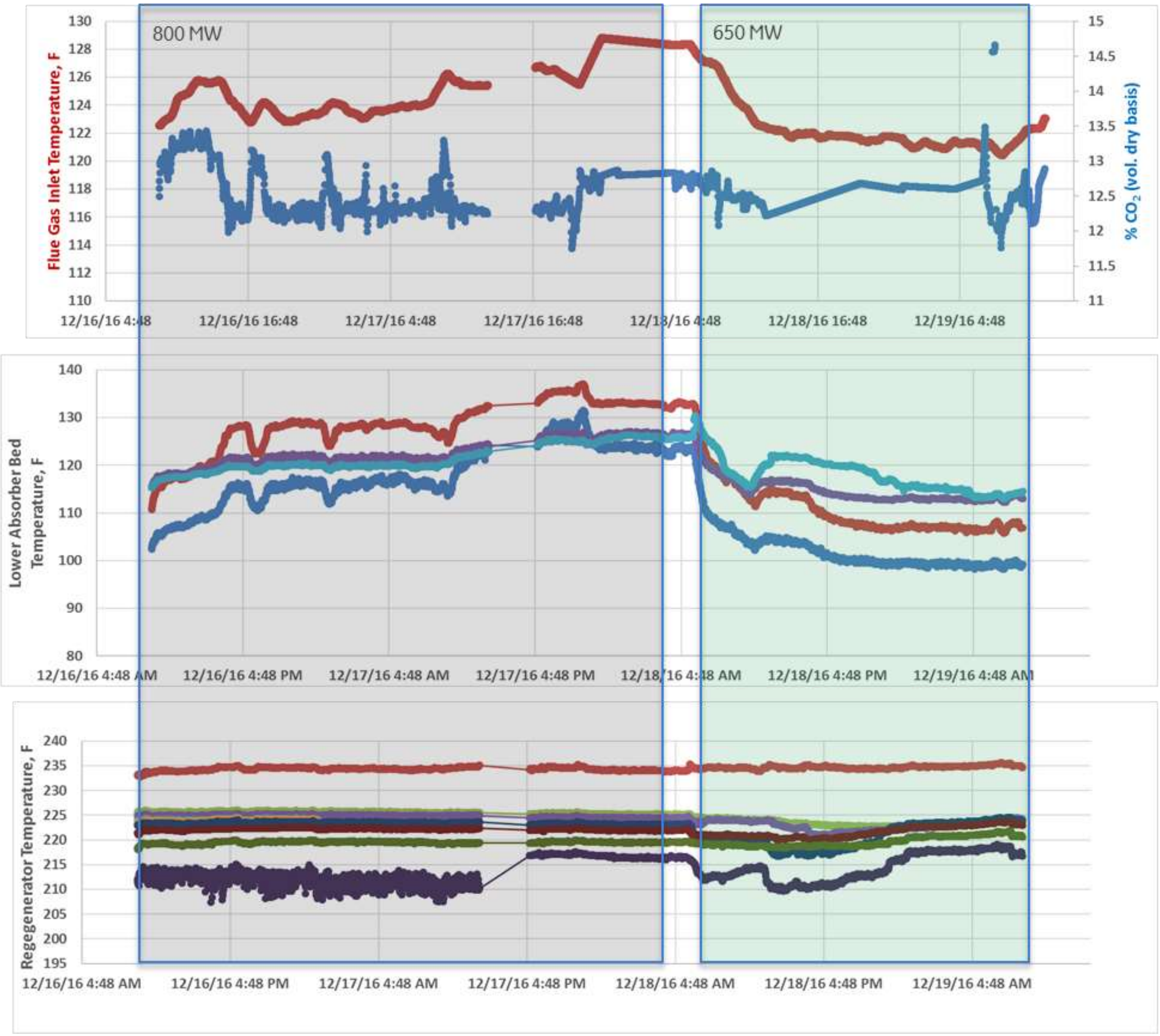


Figure 79. **SSC campaign (Phase 2 – 0.5 MW$_e$ Demo):** Input process variability

Table 22 lists process conditions for Conditions 8.

Table 26. **SCC campaign (Phase 2):** Input process variability (0.5 MW_e)

Load	Flue Gas Temperature		CO_2		Absorber T (Lower Bed)		Regenerator T (Top Bed)	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
	F	F	% vol.	% vol	F	F	F	F
800 MW	127.3	0.3	12.8	0.1	124.4	2.6	215.7	2.2
650 MW	121.9	0.2	12.5	0.0	101.7	4.0	211.0	1.6

In summary, we demonstrated sustained performance of the GAP-1_m/TEG working solution with the SSC at 0.5 MW_e for over 80 hrs. of operation. Under near stoichiometry (GAP-1_m : $CO_{2\ molar}$ = 1.1), CO_2 capture efficiency reached 95%. Maximum absorber temperature was 162 °F (top bed). Temperature increase in the absorber beds varied as following: Top (55 °F) > Middle (22 °F) > Bottom (16 °F). 90 % of the steam stripper column was under steam conditions. Specific steam utilization was between 0.45 – 0.5 (lb. CO_2 / lb. steam). Water content was kept between 20 -24 wt.% through automatic control of the liquid level in the lean storage tank (401). CO_2 capture process was robust as a function of the input variability caused by the power plant load.

4.4.2.3. 0.5 MW_e SSC Campaign (Phase 2): Steam input and Water loading

Performance of the GAP-1_m/TEG working solution with the SSC at 0.5 MW_e was evaluated with a non-optimized steam input and water content. As discussed in the previous sections, controlled amounts of water in the GAP-1_m/TEG working solution were found to be an effective way to enable steam stripping, to lower desorption temperature, and hence reduce thermal degradation. Steam stripping also increased working capacity by 30 % due to more efficient desorption. Controlled water addition had additional benefit of reducing the viscosity of the working solution, making both the absorption and desorption steps more efficient. On the other hand, increased water levels in the working solution increased the steam duty of the regeneration process. Hence, in the next set of conditions during Phase 2, we further optimized the operation of the SSC by reducing the water content and steam input while keeping the CO_2 capture efficiency at 90%.

Figure 80 describes the steps taken to reduce the water content in the working solution from 23.8 wt. % (end of Condition 8) to 18 wt.% (Condition 9). During the partial dehydration step, the water transfer from the water wash tank (501) to lean lean storage tank (401) was stopped, and the liquid level in the 401 tank was set at 30.5 %. 1% percent drop in the liquid level of the 401 tank corresponds to a 1.5 wt. % decrease in the water content. At 0.5 MW_e, the rate of partial de-hydration was 1.75 wt. H_2O solvent/hr. Once the desired water content was reached (18 wt.%, Condition 9), liquid level control in 401 tank was switched back to automatic. During condition 9, water was automatically transferred from the water wash tank (501) and the mist separator (602) to the lean storage tank (401). Water level in the working solution was maintained at 18 wt. % while running condition 9.

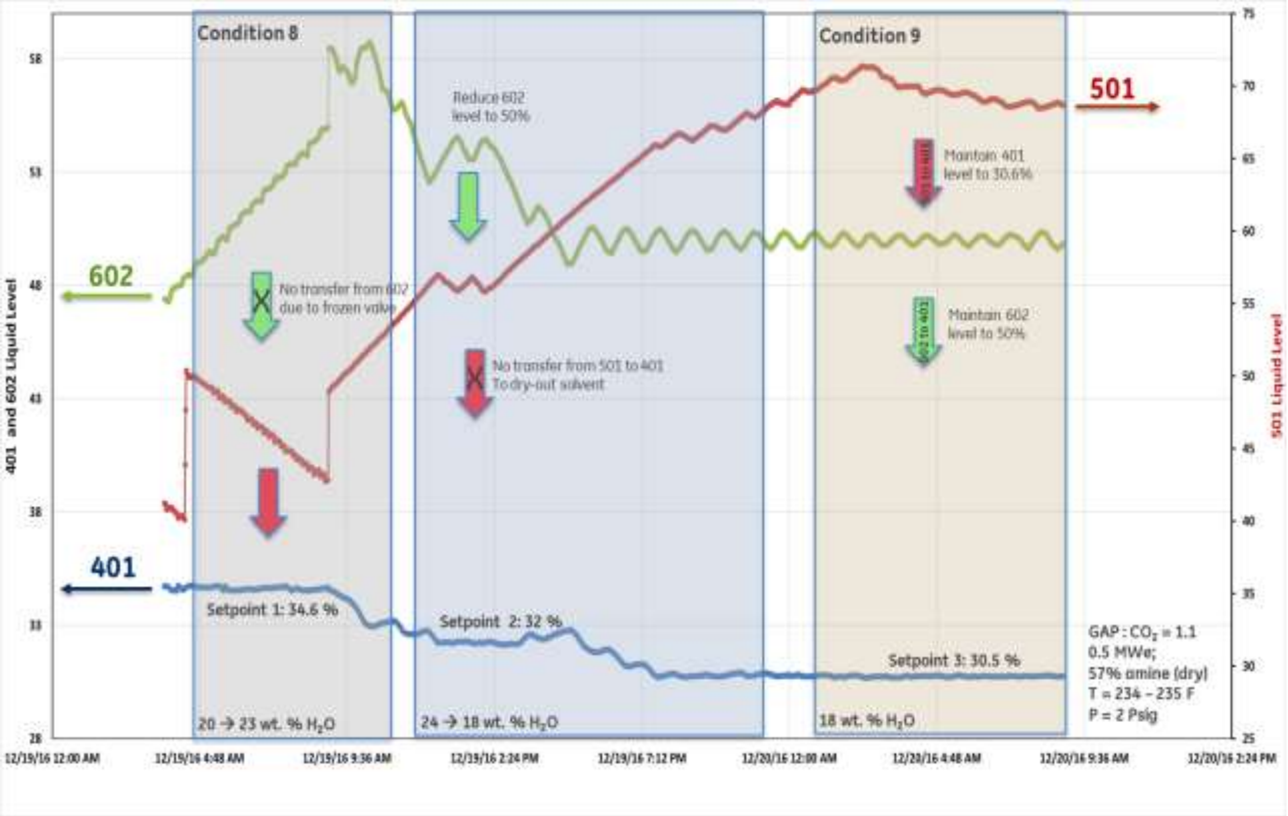


Figure 80. **SSC campaign (Phase 2 - % H_2O Optimization):** Water Management
Table 22 lists process conditions for Conditions 8 and 9.
Tank 501 - water wash tank; **Tank 602** - mist separator (602); **Tank 401** - Lean storage tank.

As part of the optimization, steam input was lowered from 1,900 lb./hr. (Condition 8) to 1,300 lb./hr. (Condition 9). Furthermore, water content was dropped from 23.8 wt.% (Condition 8) to 18 wt. % (Condition 9). CO_2 capture efficiency was maintained between 87 – 90%. (**Figure 81**) Reduced water content, and optimized steam input increased the specific steam utilization (CO_2/steam) from 0.45 to 0.58, while maintaining the CO_2 capture efficiency at 90%.

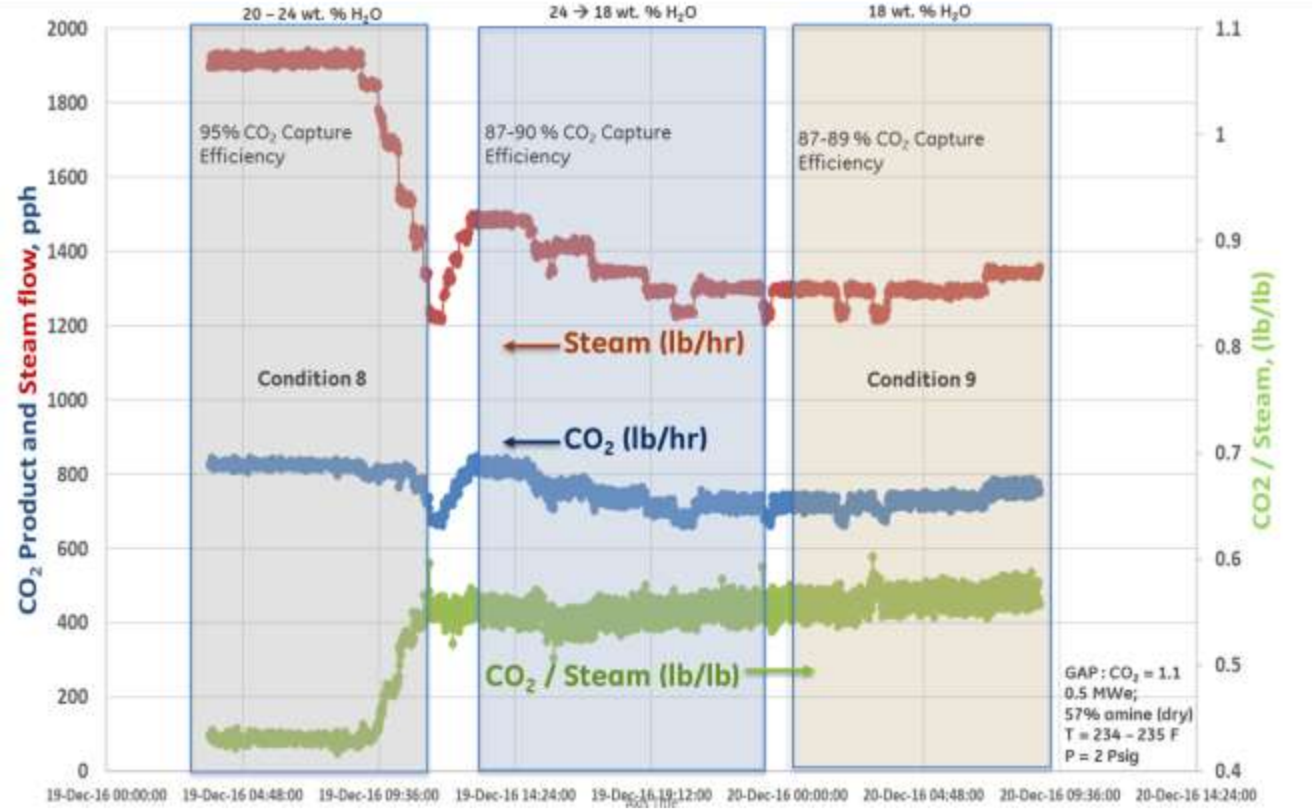


Figure 81. **SSC campaign (Phase 2 - % H_2O Optimization):** Specific steam utilization
Table 22 lists process conditions for Conditions 8 and 9.

Lower steam input and water content in the working solution decreased the steam circulation in the steam stripper column (**Figure 82**)**.** Under Condition 9, only one third of the regenerator column was under steam conditions, indicating the column is oversized. Optimized conditions reduced also the water carry-over in the total condenser. Most of the steam was condensed in the middle section of the column before reaching the total overhead condenser. (**Figure 83**

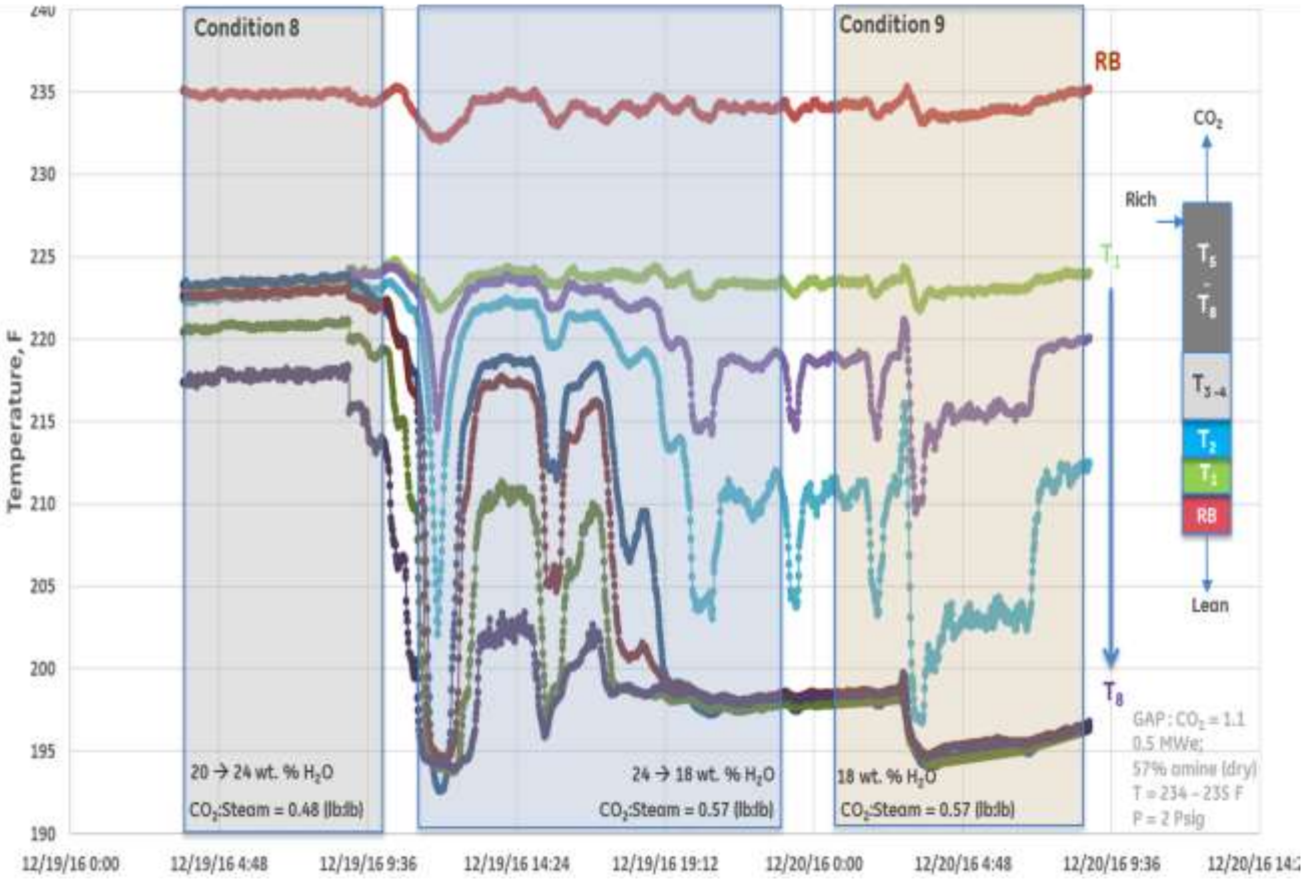


Figure 82. **SSC campaign (Phase 2 - % H_2O Optimization):** SSC temperature profile **Table 22** lists process conditions for Conditions 8 and 9.

In summary, we optimized operation of the SSC by lowering water content in the working solution (from 23 to 18 wt. %) and steam input (1900 lb./hr. to 1,300 lb./hr.) while maintaining CO_2 capture efficiency at 90%. Specific steam utilization was increased by 25 %. Limited water carry-over from the regenerator column occurred under the optimized conditions.

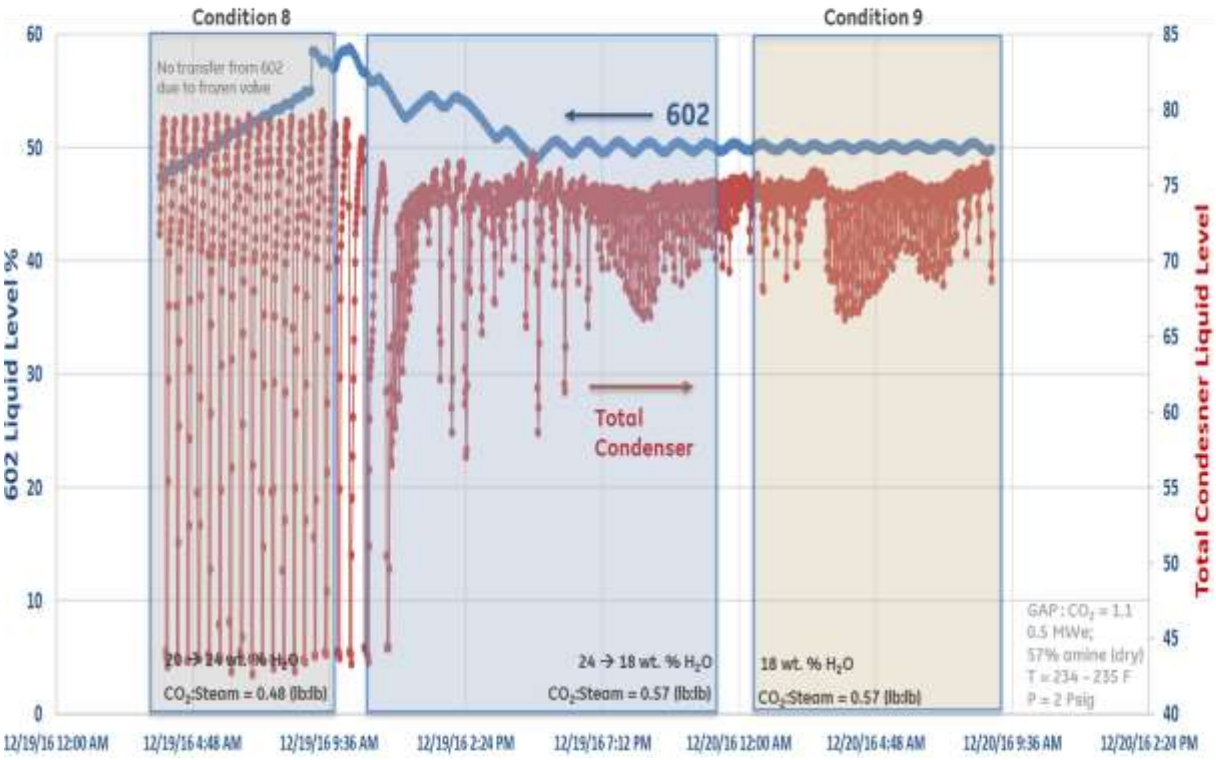


Figure 83. **SSC campaign (Phase 2 - % H_2O Optimization):** Total condenser and mist separator liquid level

Table 22 lists process conditions for Conditions 8 and 9.

4.4.2.4. 0.5 MW_e SSC Campaign (Phase 2): Desorption pressure

Increasing desorption pressure from 2 Psig to 5 Psig had a significant effect on the performance of the GAP-1_m/TEG solvent with SSC. Overall process conditions, and solvent composition are listed in **Table 22** and **Table 24**, respectively. CO_2 capture efficiency dropped from 88% (2 Psig, Condition 9) to 70% (5 Psig, Condition 10) upon pressure increase (**Figure 84**). This significant drop in capture efficiency could be traced back to the effect of pressure on the steam circulation in the steam stripper column (**Figure 85**). One third of the SSC was under steam conditions at 2 Psig desorption (T_1 – T_4 > 200 °F). Increased desorption pressure led to a reduced steam circulation in the column, and only 10% of the SSC was under steam conditions (i.e. T_1 > 200 °F, T_i < 200 °F, i = 2-8). Accordingly, CO_2 loading of the lean solvent leaving the SSC increased from 1.3 wt.% at 2 Psig (Condition 9) to 2.3 wt. % at 5 Psig (Condition 10). Finally, when the flue gas was shut down and solvent was leaned-out, the entire column was under steam conditions (i.e. T_1 – T_8 ~ 230 °F) as all heat input was utilized for steam generation in the SSC.

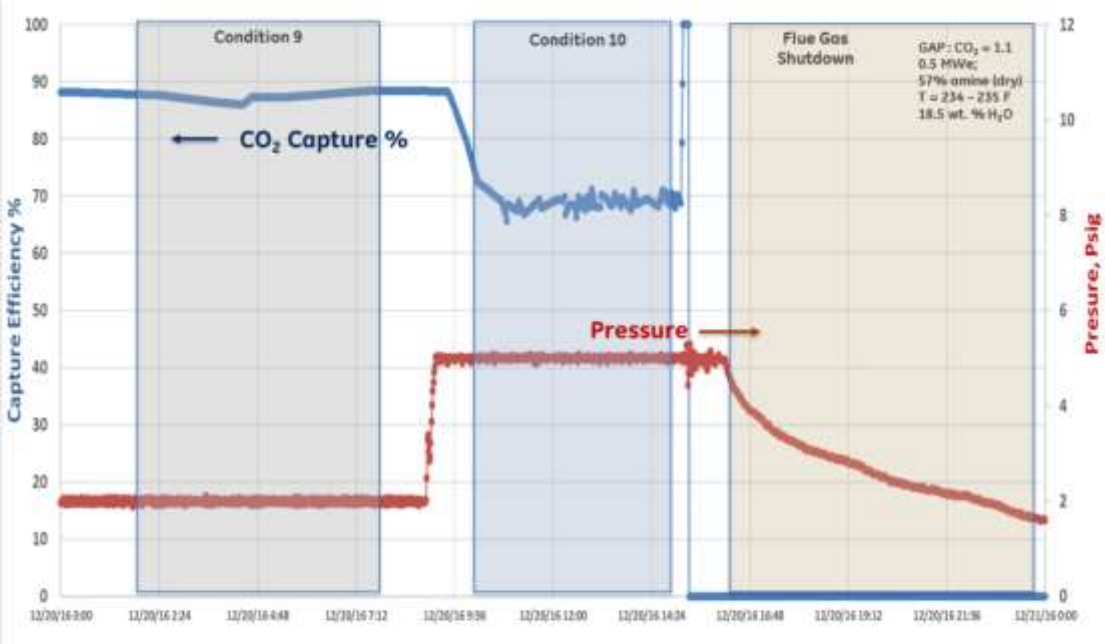


Figure 84. **SSC campaign (Phase 2 – Pressure effect):** CO_2 capture efficiency
Table 22 lists process conditions for Conditions 9 and 10.

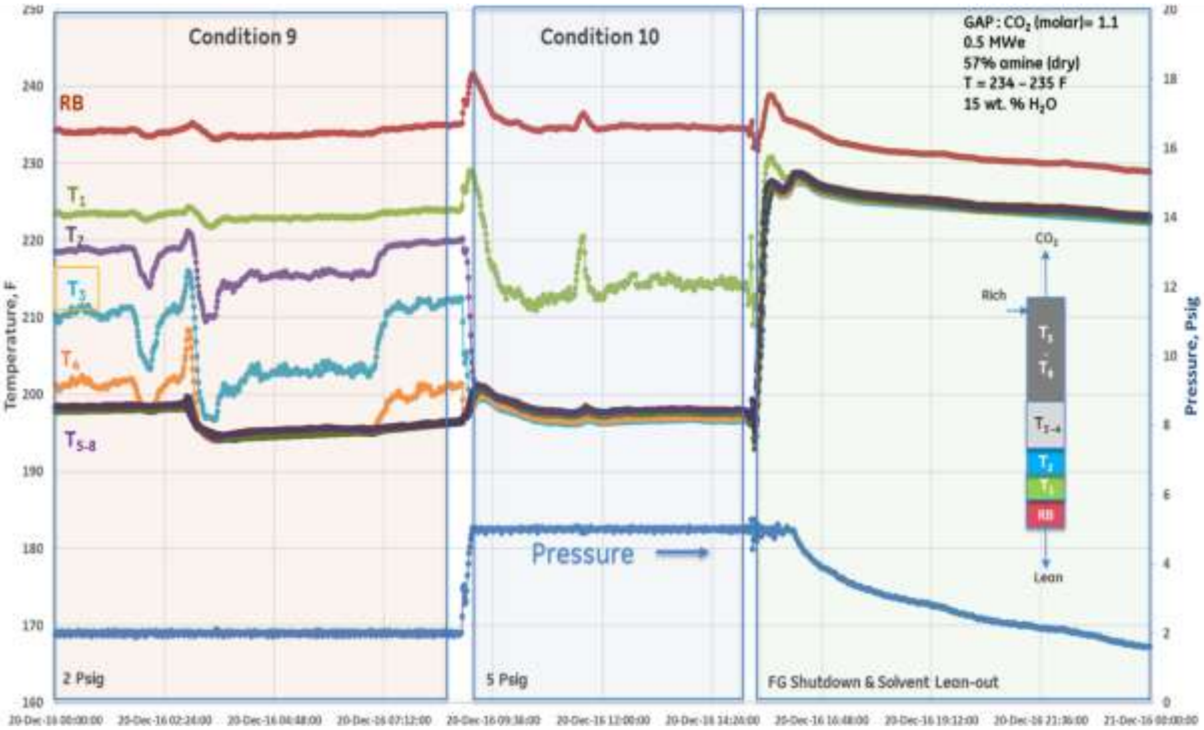


Figure 85. **SSC campaign (Phase 2 – Pressure effect):** SSC temperature profile

Table 22 lists process conditions for Conditions 9 and 10.

Increased desorber pressure lowered CO_2 product flow rate from 750 pph (2 Psig, Condition 9) to 550 pph (5 Psig, Condition 10). Steam input dropped proportionally from 1300 pph (Condition 9) to 1000 pph (Condition 10). Hence, specific steam utilization remained constant (0.55 lb. CO_2 / lb. steam) as a function of pressure, even though steam circulation in the regenerator column was lower at 5 Psig (**Figure 86**). Finally, temperature across the absorber beds was slightly lower (5 ^oF) at 5 Psig, due to overall decreased absorption efficiency (**Figure 87**).

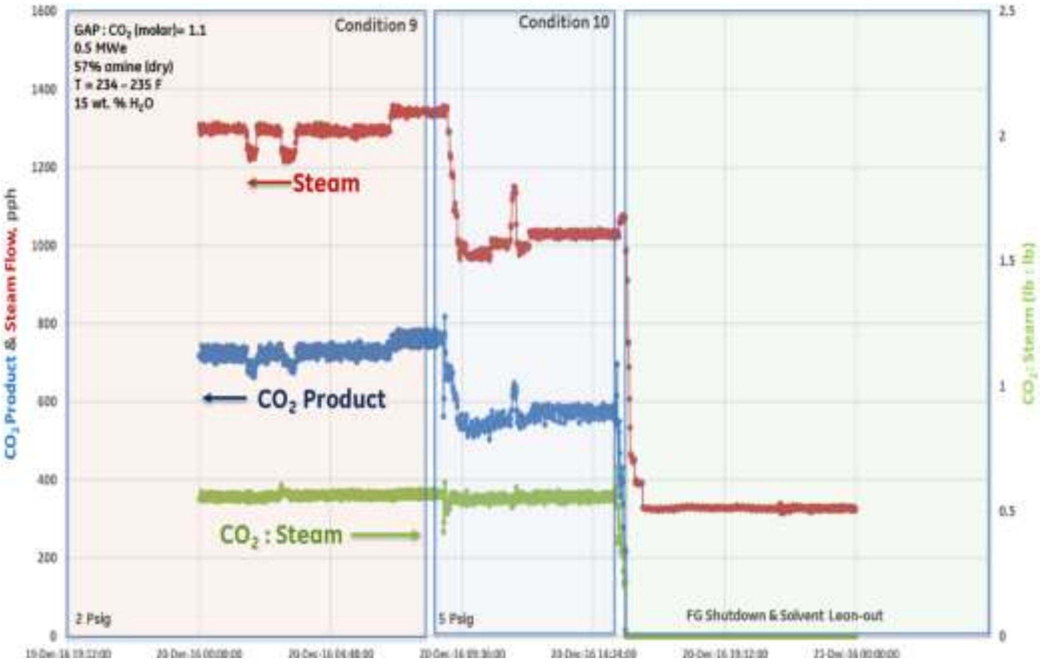


Figure 86. **SSC campaign (Phase 2 – Pressure effect):** Specific steam utilization

Table 22 lists process conditions for Conditions 9 and 10.

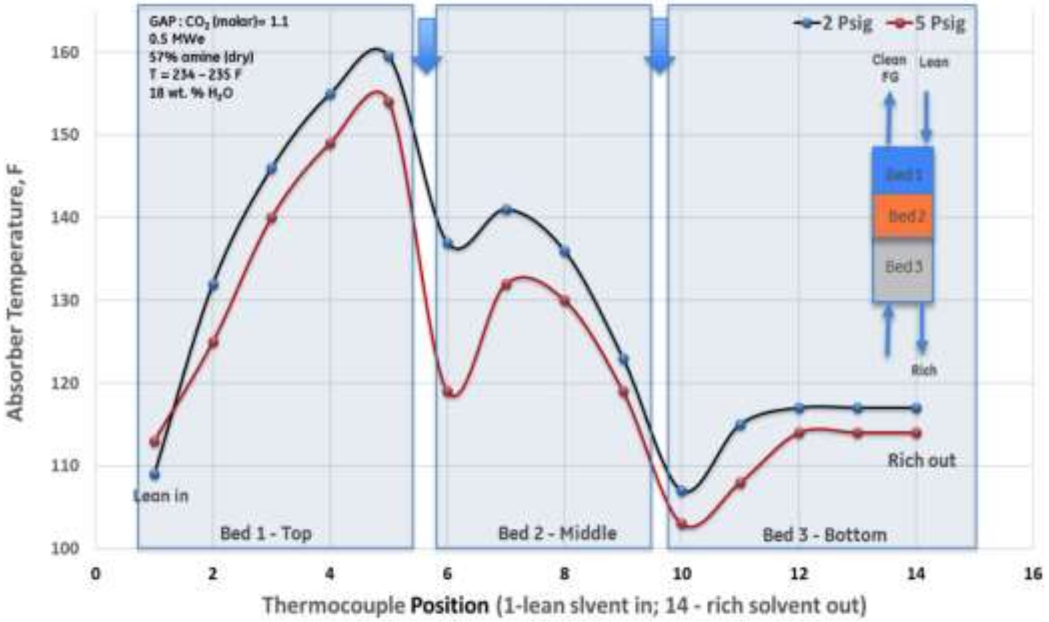


Figure 87. **SSC campaign (Phase 2 – Pressure effect):** Absorber performance

Table 22 lists process conditions for Conditions 9 and 10.

4.4.2.5. 0.5 MW_e SSC Campaign (Phase 2): Summary

Solvent Circulation Effect

Effect of solvent circulation (L : G) was evaluated at constant water content (20 wt.% H_2O), 2 Psig and 235 ^oF desorption conditions. Stoichiometric capture was demonstrated at 0.5 MW_e. Maximum working capacity was 6.1 wt. % (dry basis). Under GAP-1_m excess, most of the absorption occurred in the bottom bed of the absorber. Specific steam utilization (lb. CO_2 / lb. steam) was constant (0.48 - 0.52) as a function of the amine to CO_2 stoichiometry.

0.5 MW_e Demo

Performance of the aminosilicone solvent was demonstrated at 0.5 MW_e with the SSC for 84 hrs. Capture efficiency reached 95 – 97% under stoichiometric conditions (GAP-1_m : CO_2 (molar) ~ 1.1), 235 ^oF and 2 Psig desorption conditions. Active working capacity was 6.1 wt.% (dry basis).

Steam / water optimization

Specific steam utilization was increased by 25 % by lowering water content to 18 wt.% at 90% capture. Under optimized conditions, only 30% of the regenerator column was under the steam conditions, with limited solvent/water carry-over in the overhead total condenser.

Pressure Effect

CO_2 capture efficiency dropped from 90% to 70% upon increasing desorption pressure from 2 to 5 Psig while maintaining amine to CO_2 stoichiometry. At elevated pressures, only 10% of the regenerator column was under steam conditions.

4.4.3. 0.5 MW_e SSC Campaign (Phase 3): Solvent Degradation

Phase 3 of the NCCC steam stripper column campaign was conducted to further optimize performance of the aminosilicone solvent at 0.5 MW_e scale and evaluate solvent degradation (**Figure 88**). First, water content in the working solution was varied between 14 wt. % and 37 wt. % while maintaining molar ratio GAP-1_m : CO_2 between 1.1 to 1.3 and steam input at 1,500 pph. Desorber pressure was kept at 2 Psig, while temperature did not exceed 235 °F, to minimize the solvent thermal degradation. **Table 27** and **Table 28** list the process conditions and flue gas composition utilized during the campaign.

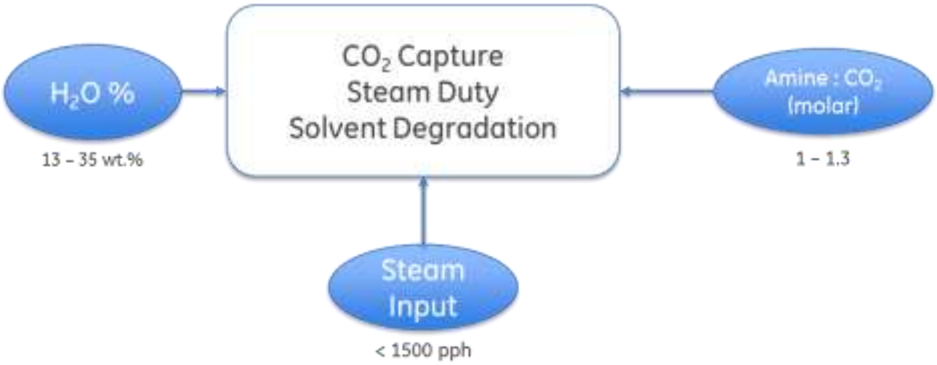


Figure 88. **SSC campaign (Phase 3):** Optimization of H_2O% and probe solvent degradation

Table 27. SSC campaign (Phase 3): Process conditions

Condition	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Objective	Water content & steam optimization						Solvent Circulation
Flue Gas (FG) (lb/hr)	5000	5000	5000	5000	5000	5000	5000
Liquid (lb./hr.)	15000	15000	15000	15000	15000	15000	16500
$T_{desorber}$ (F)	226	228	234	234	234	234	234
$P_{desorber}$ (Psi)	2	2	2	2	2	2	2
Water (wt.%)	37	30	23	19	14	17.5	17.5

Water Management: automatic water addition from water wash tank (501) to lean storage tank (401).

Table 28. SSC campaign (Phase 3): Flue gas conditions

	NO	**O_2**	**CO_2**	**NO_2**	**T**
	ppm	vol.%	vol.%	ppm	F
Avg	37.1	6.45	12.78	0.82	138.1
Stdev.	6.9	0.85	0.52	0.2	2.35

Table 29. SSC campaign (Phase 3): Lean solvent composition

Sample	**Total Amine wt.%**		**CO_2 wt.%**	**TEG**	**Water**
	wet	dry	wt.%	wt. %	wt.%
Initial	45.8	57	0.69	30.3	19.8
Condition 11	33	52	0.87	26.3	36.7
Condition 12	37	52	1.14	30.6	29.7
Condition 13	39.4	51	3.82	33.8	22.7
Condition 14	47.2	58.4	1.35	36.8	19.3
Condition 15	50.2	58.3	2.26	33.8	13.9
Condition 16	50.5	60.1	1.55	33	17.5
Condition 17	50.5	60.1	1.55	33	17.5

4.4.3.1. 0.5 MW$_e$ SSC Campaign (Phase 3): Effect of water loading

Performance of the GAP-1$_m$/TEG working solution with SSC at 0.5 MW$_e$ was further evaluated as a function of a wider range of water loadings in the working solution while probing longer term solvent degradation. Water content was decreased from 37 wt. % (Condition 11, **Table 27 and Table 29**) to 14 wt.% (Condition 15, **Table 27 and Table 29**) by gradually lowering the set point of the liquid level in the lean storage tank (401) while automatically transferring water from the water wash tank (501) and the mist separator tank (602) (**Figure 89**). Rich working solutions were bi-phasic for water content higher than 20 wt. %. SSC operated normally even under high level of water (30 – 35 wt.%). Solvent carry-over was minimized due to a larger disengagement volume of the regenerator. SSC design allowed more flexibility with respect to the water content in the working solution compared to the CSTR.

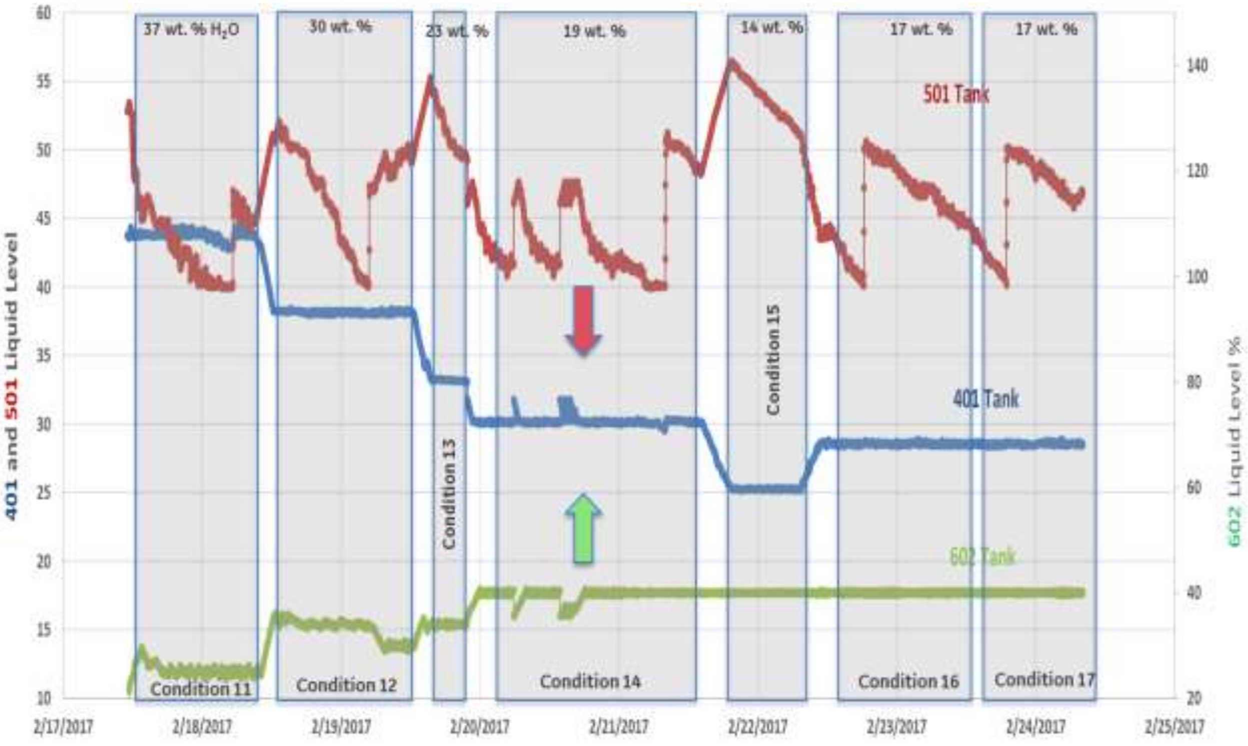


Figure 89. **SSC campaign (Phase 3 – water loading):** Water management
Table 27 lists process conditions for Conditions 11 - 17.

Figure 90 shows the CO_2 capture efficiency plot as a function of the water content in the working solution while maintaining steam input at a maximum of 1500 pph. At the high levels of water (30 wt. % and 37 wt. %), a larger portion of the steam input is utilized for boiling water, and therefore the reboiler temperature did not exceed 227 °F. CO_2 capture efficiency was 78% and 84%, respectively. Upon drying the solvent, reboiler temperature increased to 235 °F, and CO_2 capture efficiency reached a maximum of 88-89% for 17 – 19 wt. % H_2O. At the lowest water content (14 wt.%, Condition 15), CO_2 capture efficiency did not exceed 70%.

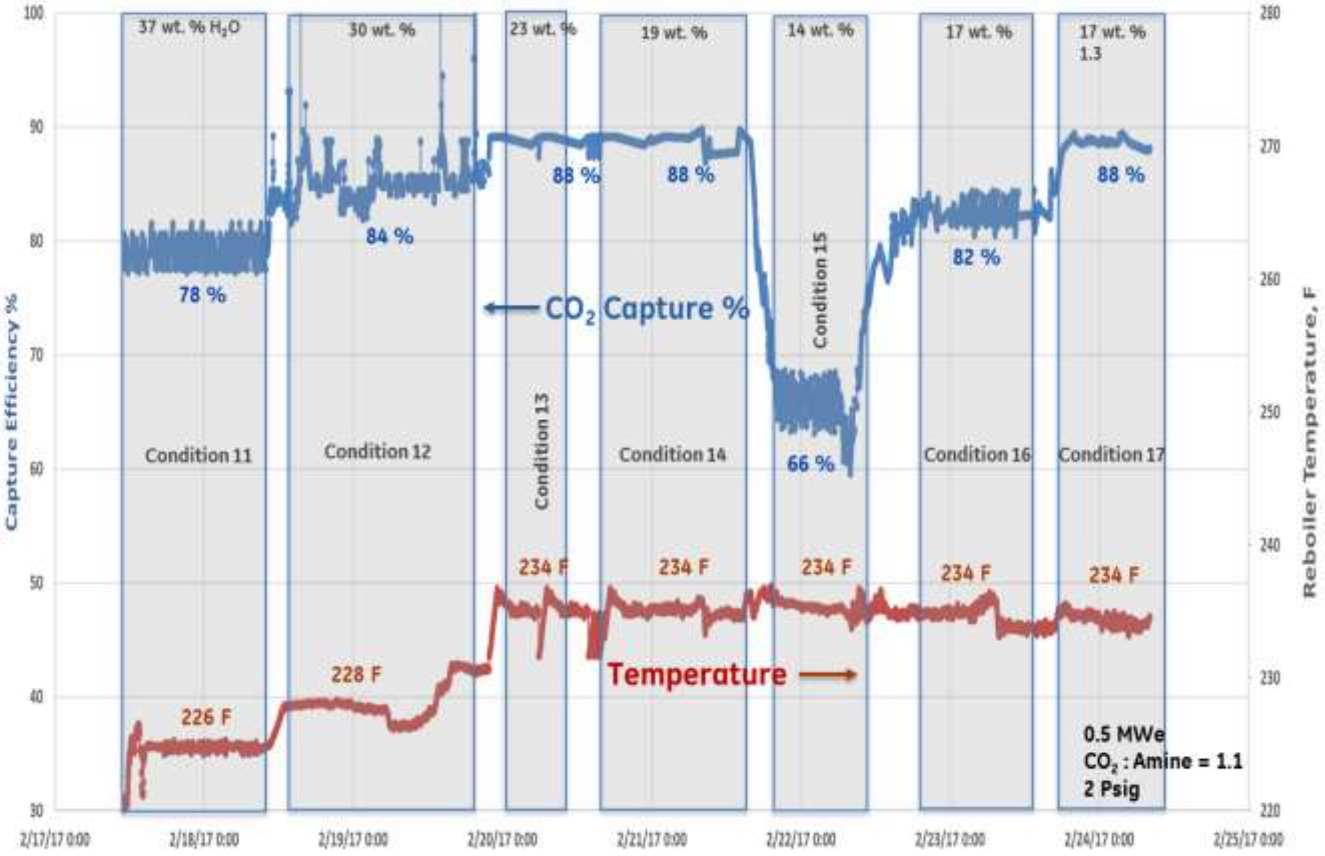


Figure 90. **SCC campaign (Phase 3):** CO_2 Capture efficiency

Table 27 lists process conditions for Conditions 11 - 17

The effects of water loading on the CO_2 capture efficiency can be rationalized based on the performance of both the absorber and steam stripper columns. **Figure 91** shows the temperature profile in the SSC. Upon decreasing water content, only a fraction of the regenerator column is under the steam conditions. Only the 1st stage from the bottom is under the steam conditions at lower water content, leading to a non-ideal desorption process and lower CO_2 capture efficiency. The optimum conditions are reached at 18-20 % wt. H_2O, when 30% of the column (stages 1-4) is under the steam conditions, and water / solvent carry-over in the overhead is minimized.

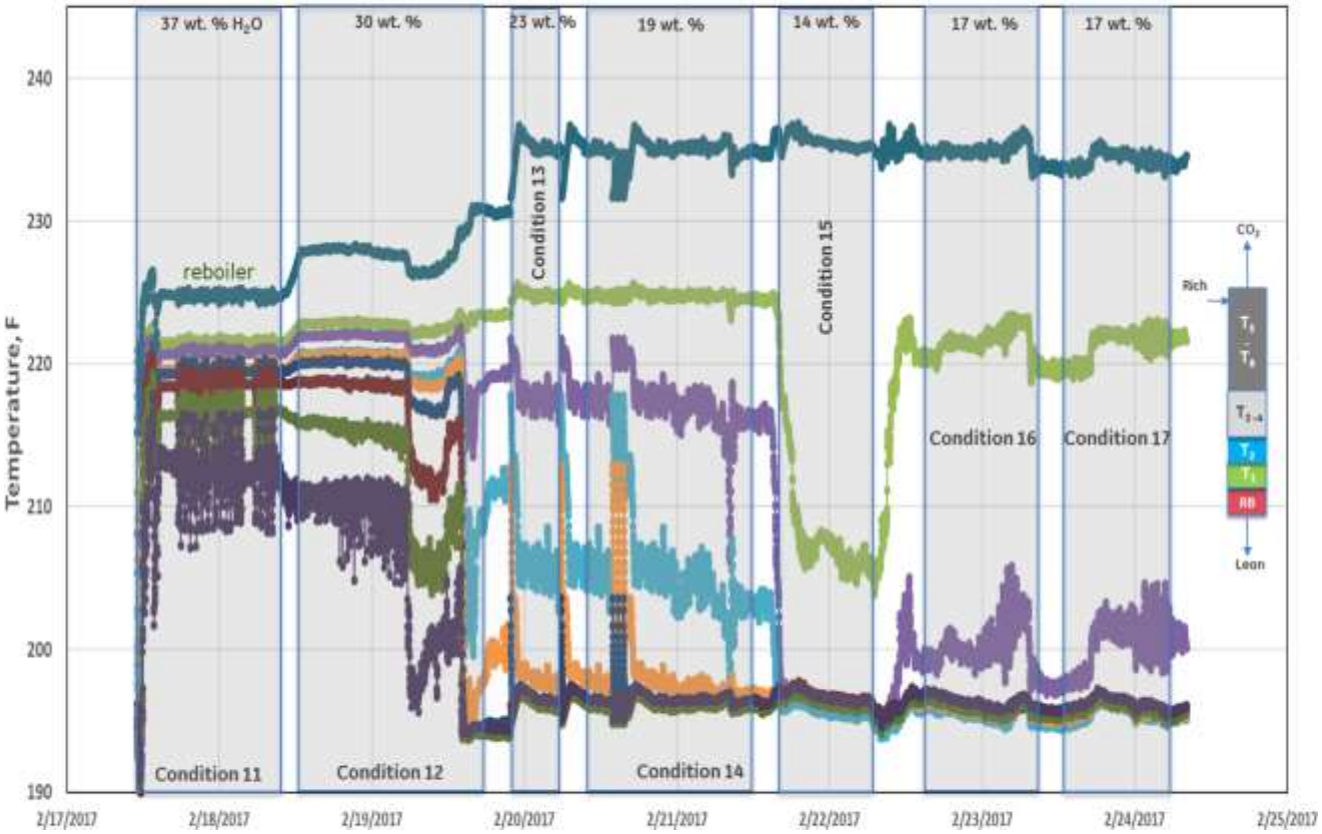


Figure 91. **SCC campaign (Phase 3):** SSC performance

Table 27 lists process conditions for Conditions 11 - 17

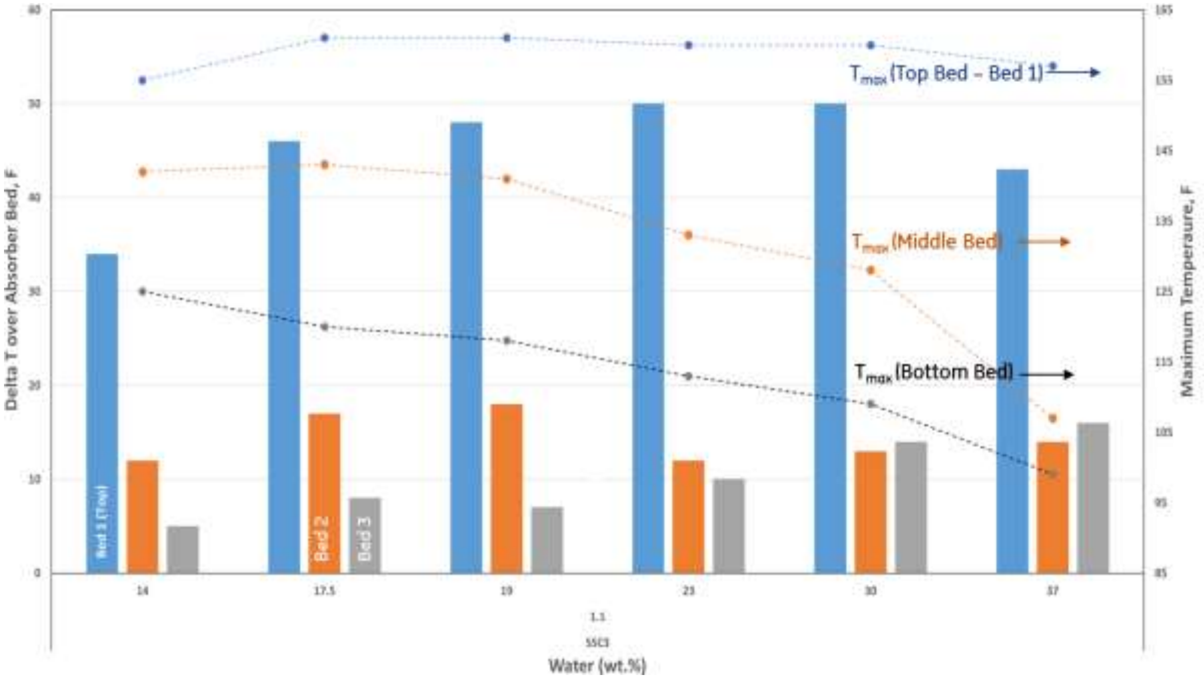


Figure 92. **SCC campaign (Phase 3):** Absorber performance
Table 27 lists process conditions for Conditions 11 - 17

Temperature increase and the maximum temperature in the absorber beds as a function of water loading are shown in **Figure 92**. Maximum absorber temperature in the bottom and middle beds decreased while water content was increased from 14 to 37 wt.%. In the lower bed, the maximum temperature decreased from 125 °F (14 wt. % H_2O) to 97 °F (37 wt.% H_2O) due to evaporative cooling of water from the liquid to gas phase. At the same time, the top bed was the hottest part of the column (155 – 160 °F) indicating that this was the location where most of the absorption occurred.

Finally, **Figure 93** shows the effect of water loading on the specific steam utilization and CO_2 capture efficiency. At 30+ wt.% H_2O, steam utilization is the lowest (CO_2 : Steam = 0.45), as a large extent of steam input is utilized to vaporize the excess water carried-over in the total condenser and mist separator tank. At the lowest water content (14 wt.%), the CO_2 capture efficiency is below 70% due to the insufficient steam circulation in the regenerator column. The water loading for which both the specific steam utilization and CO_2 capture are optimized is reached at 18-20 wt.%. Under these conditions, the regenerator column is operated efficiently with a minimum water / solvent carry-over.

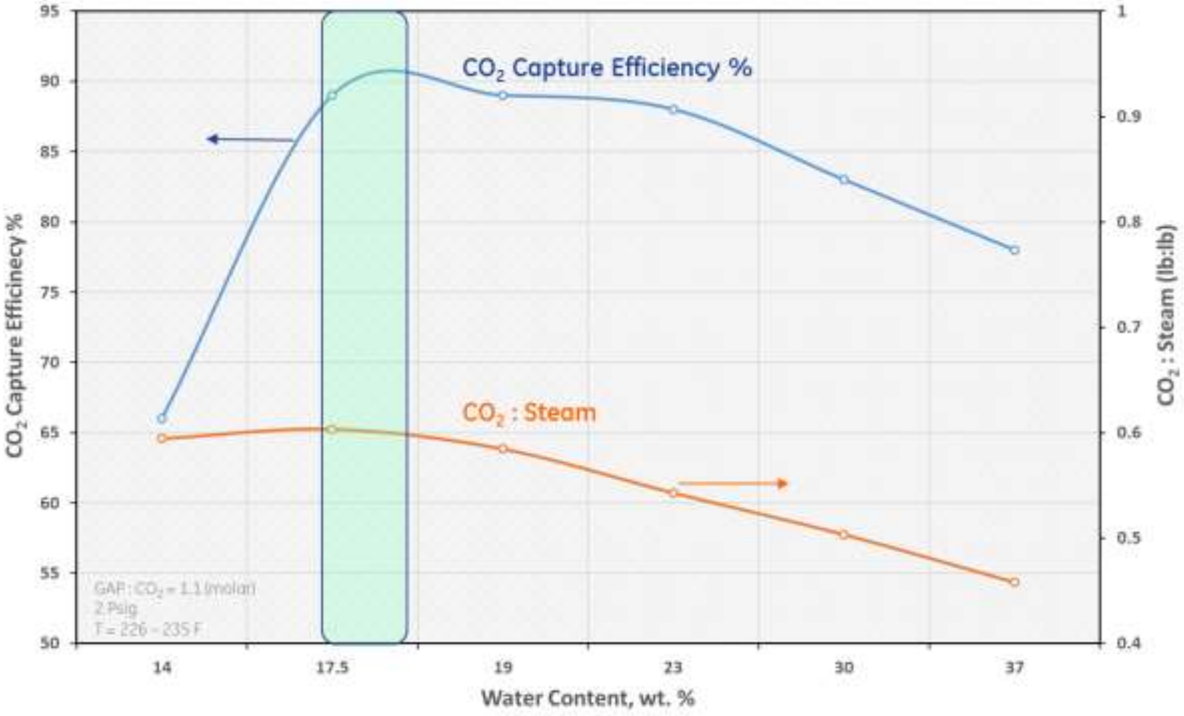


Figure 93. **SCC campaign (Phase 3):** Steam utilization and CO_2 capture efficiency
Table 27 lists process conditions for Conditions 11 - 17

4.4.3.2. 0.5 MW_e SSC Campaign (Phase 3): Solvent degradation

A variety of analyses were conducted to determine how GAP-1_m/TEG solvent mixture performed and changed during both CSTR and SSC campaigns. Solvent performance and degradation during the SSC campaign was monitored based on the following measurements: (i) amine content of the working solution, (ii) ^1H NMR and (iii) CO_2 uptake experiments. They provided information on the GAP # of the aminosilicone, mass balance of the components, and urea formation.

Figure 94 shows the absorber samples taken during the SSC campaign. The initial solvent was dark amber because a substantial amount of solvent mixture from the previous CSTR campaign was still in the system. Not enough fresh solvent was available to completely refill the system so a mixture of old and new was used for the SSC campaign. However, the color did not change over time.

Figure 94. **Solvent Degradation (SSC Campaign):** Absorber samples = f (time)
The dark amber initial color is indicating that the starting solvent of the SSC campaign had been slightly contaminated with used solvent from the CSTR campaign.

Active amine functionality in the GAP-1_m/TEG working solution was monitored during both the CSTR and SSC campaigns. For the CSTR campaign, reboiler temperature varied between 230 °F to 265 °F to maintain CO_2 capture efficiency between 70% - 90%. Water loading was less than 5 wt.%, and desorber pressure was kept at 7 Psig to avoid solvent carry-over. Total run time was more than 360 hours at temperature, before a make-up solvent was added. For the SSC campaign, temperature of the desorber was maintained below 235 °F, while water content varied between 14 to 37 wt.%, and desorption pressure varied between 2 – 5 Psig. Under these conditions, CO_2 capture efficiency varied between 66% – 95%. Total run time for the SSC campaign was 360 hrs.

Figure 95 describes the amine content (dry basis) of the GAP-1_m / TEG working solution as a function of time, and desorber temperature for both CSTR and SSC desorbers. The rate of amine degradation strongly depends on the desorption temperature for the CSTR. The rate of degradation was 0.45 wt.% amine / day at temperatures below 240 °F, and accelerated to 1.65 wt.% amine / day upon increasing desorption temperature to 265 °F. In the case of SSC, amine content oscillated between 57.5 – 60 wt.% for over 350 hrs. of operation, with the amine degradation measured below 0.05 wt.% / day. This result agrees with our previous accelerated degradation studies indicating that a water loading of more than 10 wt.%, and desorption temperatures lower than 240 °F decreased the rate of degradation of the rich solvent by two orders of magnitude.

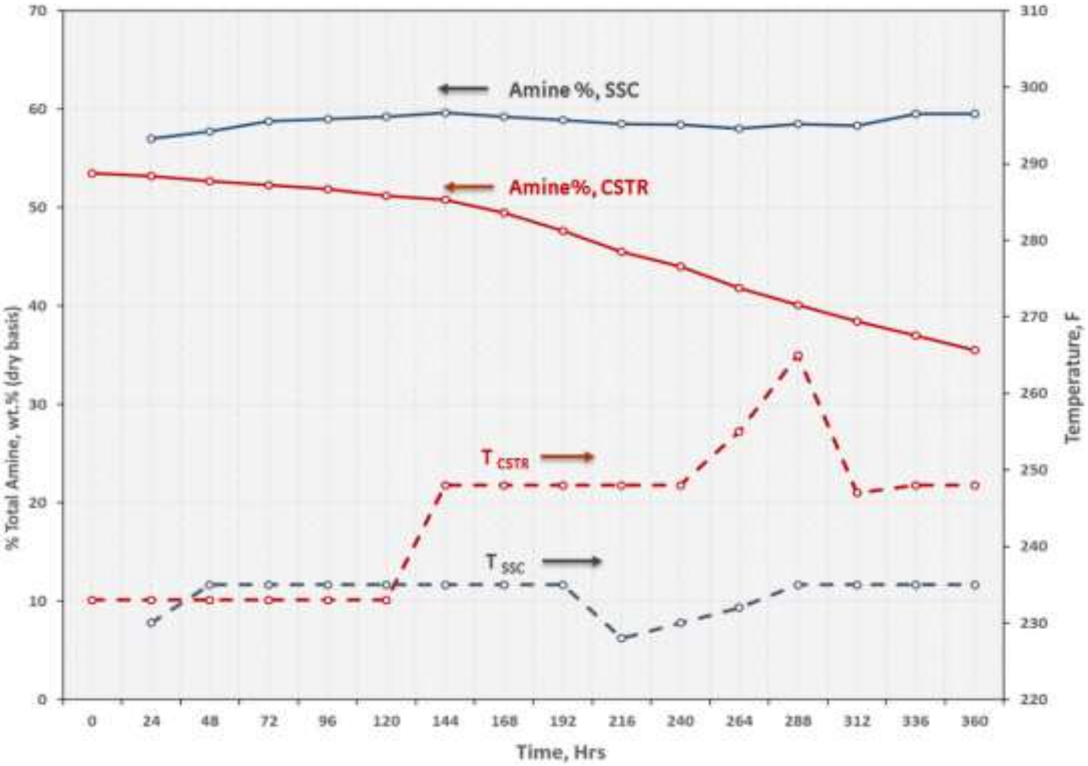


Figure 95. **Solvent Degradation**: CSTR vs. SSC

SSC: $T_{desorber}$ = 230–235 °F; P = 2 Psig; 0.25–0.5 MWe, 14-35 wt.% H_2O

CSTR: $T_{desorber}$ = 230 – 248 °F; P = 7 Psig; 0.25 – 0.5 MWe, 3-5 wt. % H_2O

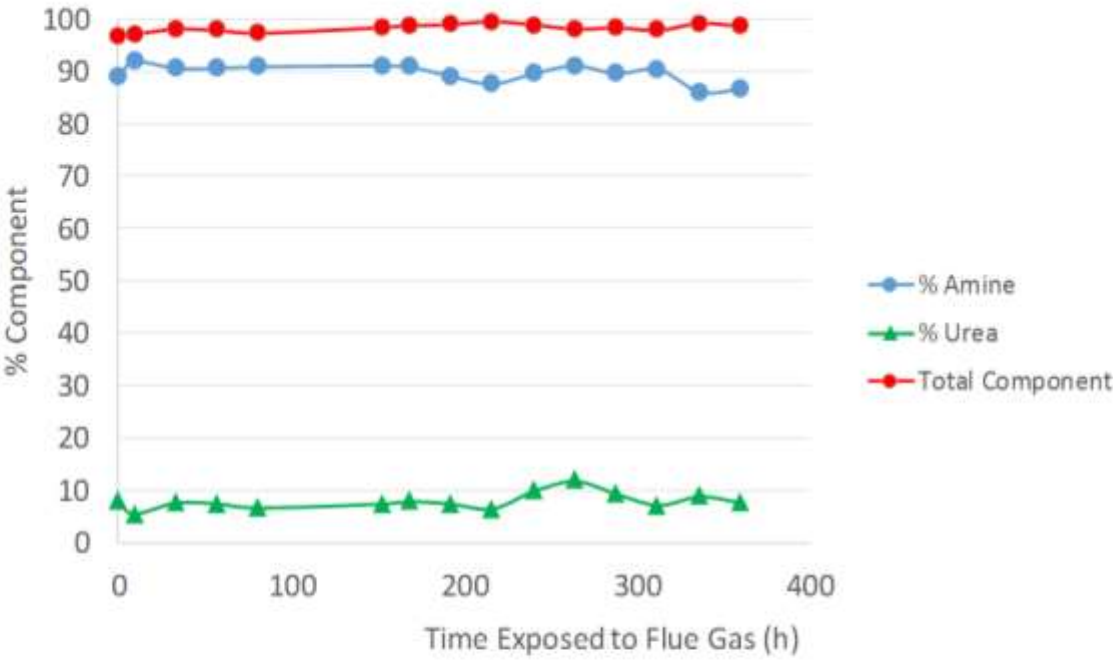


Figure 96. **Solvent Degradation (SSC Campaign):** Urea content by ^{1}H NMR
Process conditions listed in **Table 18**, **Table 22**, and **Table 27**. The non-zero initial value for urea % is indicating that the starting solvent of the SSC campaign had been slightly contaminated with used solvent from the CSTR campaign.

^{1}H NMR analysis of the aged samples allowed the quantification of both active amine and urea content of the solvent. As **Figure 96** shows, there was very little change in the amine content of the solvent and that the urea level also remained low. An average of ~8-9% urea was maintained during operation and it is likely that very little formed during the SSC campaign because there was ~ 9% present in the starting solvent left from the CSTR campaign as noted above. Greater than 98% of the mass was accounted for from the sum of both the amine and the urea components of the solvent. This indicated that there were no significant side-reactions or losses of material that were unaccounted for.

Hydrothermal equilibration process was also evaluated based on the ^{1}H NMR analysis. GAP-# was calculated based on the ratio of the methylene group adjacent to the Si atom relative to the total number of methyl groups on silicon. The original GAP-1_m/TEG solvent started with a GAP-# of 0.96 indicating that it was very close to the desired starting # of 1. **Figure 97** shows that this value steadily decreased with time. This was expected as a re-equilibration reaction can occur under basic conditions and with heat and water present. This re-equilibration reaction not only generates an aminosilicone with a smaller average GAP-# but also results in the formation of cyclic silicones such as D_4 and D_5. The largest change was in the first 200 hours of operation with the GAP # dropping from 0.96 to 0.41. This is in marked contrast to that seen with the CSTR which showed a GAP # of 0.62 after the same time. The SSC was anticipated to give a higher rate of re-equilibration than the CSTR because of the greater abundance of water present in the system. It appeared that a steady state was being approached with regard to the GAP # after ~ 300 hours with a value of 0.3 being reached.

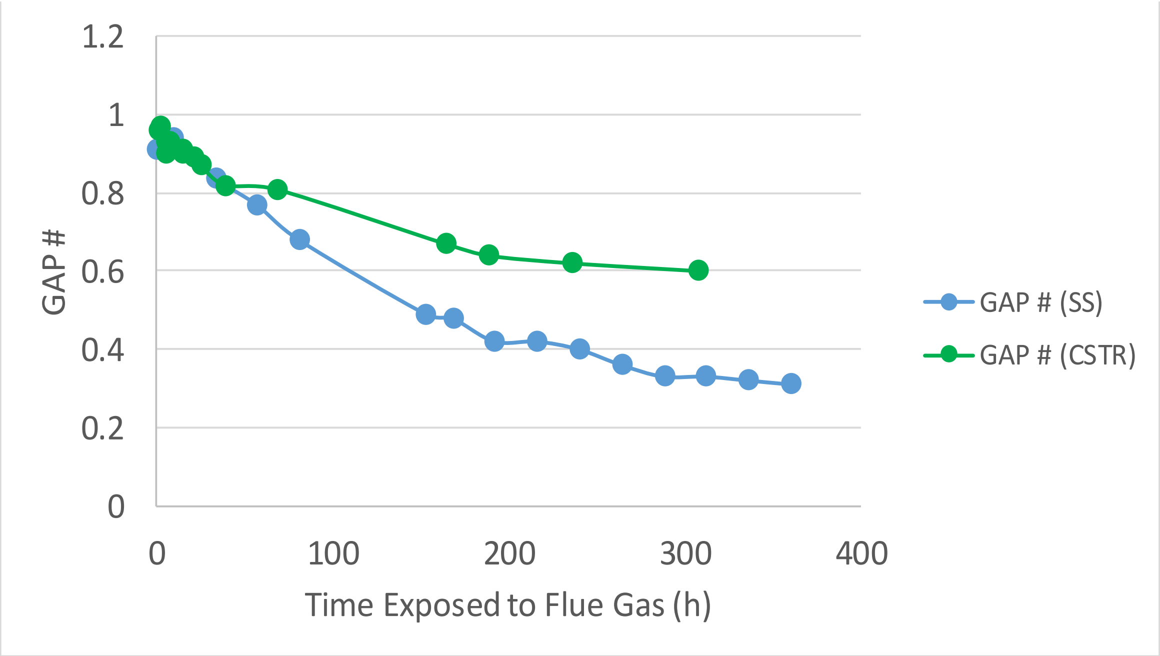
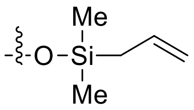
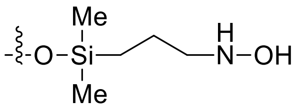
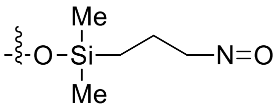
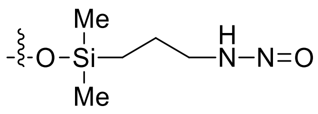
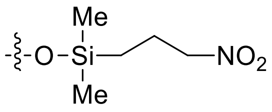
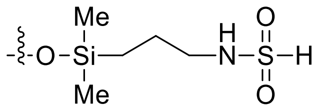


Figure 97. **Solvent Degradation (SSC / CSTR Campaigns):** Hydrothermal equilibration
Process conditions listed in **Table 18**, **Table 22**, and **Table 27**. GAP# calculated based on ^1H NMR.

While not as large a contributor to the loss of activity as urea formation, undoubtedly, some oxidation of GAP-1_m was likely occurring. The myriad of anticipated decomposition products formed at low levels precluded any identification by NMR and the silicon-containing materials did not provide useful data via GC/MS analysis. An alternate method employed to look for low levels of decomposition products was HPLC Electro Spray Q-ToF MS (high performance liquid chromatography electro spray quadripolar-time of flight mass spectrometry). An absorber sample that had seen significant thermal history was examined by this method and many of the expected compounds like carbamates, amines, ureas and silanols were seen. In addition to those, identification of oxidation products were also sought. These included olefins from ammonia loss, hydroxylamines, nitroso and N-nitroso compounds, nitrates and sulfonic amides shown below.

Surprisingly, none of these species were detected, indicating that, if any of these products were produced, they were at very low levels. Both positive and negative ionization techniques were employed. The positive mode showed substantial levels of GAP and silanols homologs as noted above (**Figure 98** / **Figure 99**).

Finally, metals analyses were performed on the sample of solvent from the CSTR campaign. It was thought that, given the harsher conditions in the CSTR than the SSC, that any metal contamination would be greater in these samples than those from the SSC campaign. **Table 30** shows that, except for low levels of iron, little metal contamination was present.

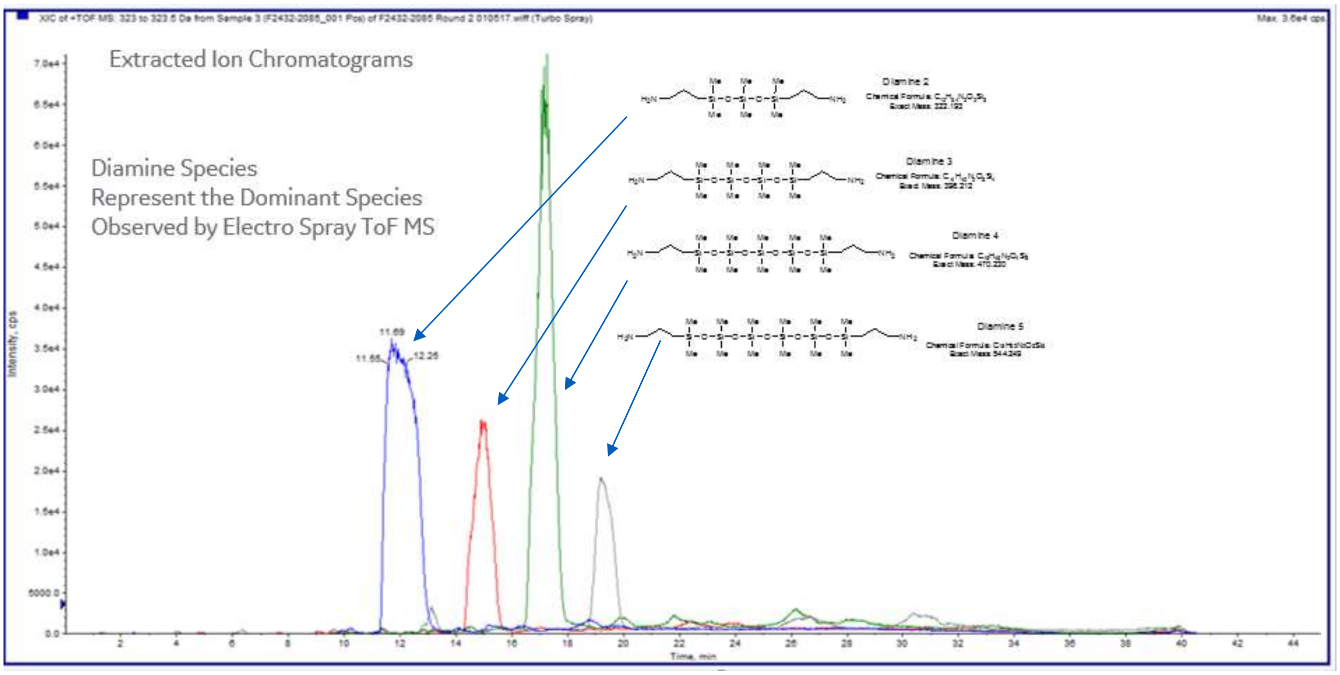


Figure 98. **Solvent Degradation (SSC Campaign):** GAP-X species
Species detected by HPLC Electro Spray Q-ToF MS

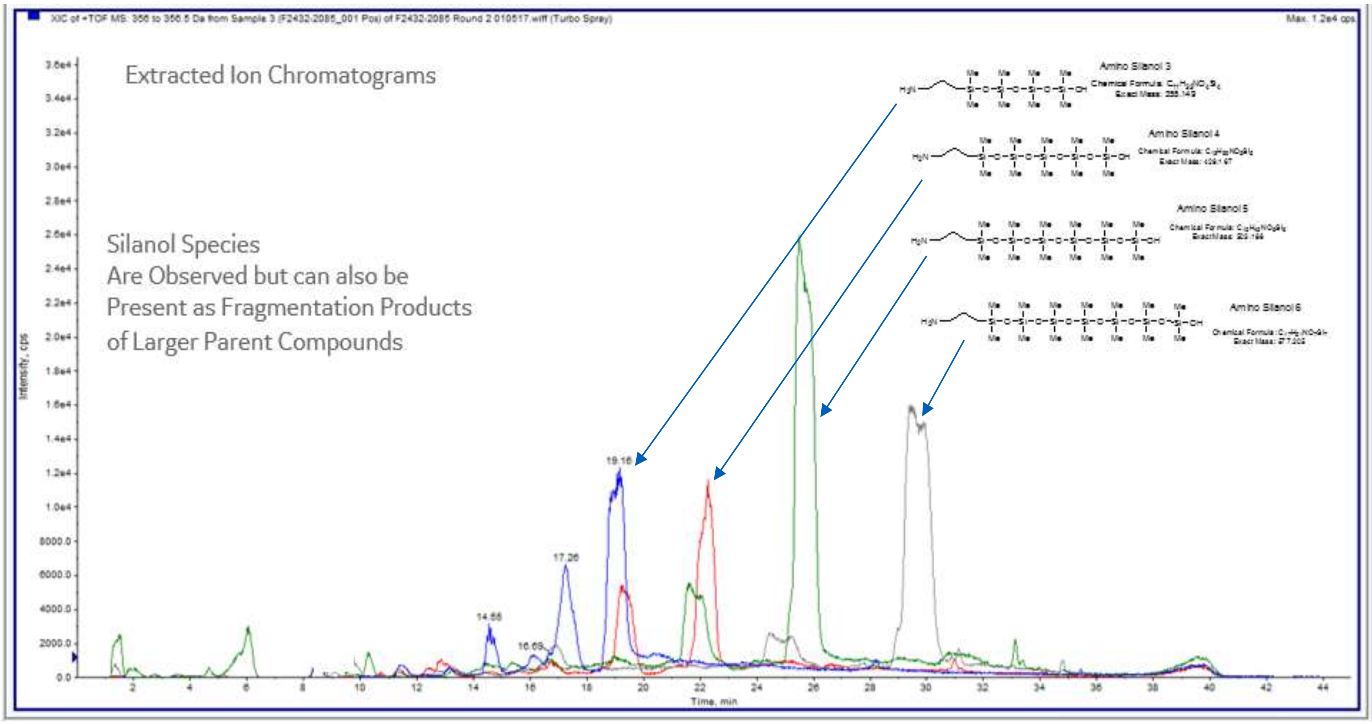


Figure 99. **Solvent Degradation (SSC Campaign):** GAP-silanol species
Species detected by HPLC Electro Spray Q-ToF MS

Table 30. **Solvent Degradation (SCR Campaign):** Metal Analysis

nple ID	LIMS ID	Rep	Al µg/g	Ba µg/g	Be µg/g	Ca µg/g	±95% CI [†]	Cd µg/g	Co µg/g	Cr µg/g	±95% CI [†]	Cu µg/g	Fe µg/g	±95% CI [†]
32-94-1628	S17-00850	A	1<x<3	<0.5	<0.9	3	±1	<0.5	<0.5	0.6	±0.2	<1	4.9	±0.3
		B	1<x<3	<0.5	<0.9	3	±1	<0.5	<0.5	0.6	±0.2	<1	4.9	±0.3
		C	1<x<3	<0.5	<0.9	3	±1	<0.5	<0.5	0.6	±0.2	<1	5.2	±0.3
		Mean[a]	**1<x<3**	**<0.5**	**<0.9**	**3**		**<0.5**	**<0.5**	**0.6**		**<1**	**5.0**	
		SD				0.4				0.02			0.2	
32-94-1925	S17-00851	A	1<x<3	<0.5	<0.9	4	±1	<0.5	<0.5	0.9	±0.2	<1	12.5	±0.3
		B	1<x<3	<0.5	<0.9	3	±1	<0.5	<0.5	0.9	±0.2	<1	12.6	±0.3
		C	1<x<3	<0.5	<0.9	3	±1	<0.5	<0.5	0.9	±0.2	<1	12.5	±0.3
		Mean[a]	**1<x<3**	**<0.5**	**<0.9**	**4**		**<0.5**	**<0.5**	**0.9**		**<1**	**12.5**	
		SD				0.8				0.01			0.1	
32-94-2103	S17-00852	A	1<x<3	<0.5	<0.9	4	±1	<0.5	<0.5	<0.2		<1	0.3<x<0.9	
		B	1<x<3	<0.5	<0.9	<1		<0.5	<0.5	<0.2		<1	0.3<x<0.9	
		C	1<x<3	<0.5	<0.9	<1		<0.5	<0.5	<0.2		<1	0.3<x<0.9	
		Mean[a]	**1<x<3**	**<0.5**	**<0.9**	**1<x<3**		**<0.5**	**<0.5**	**<0.2**		**<1**	**0.3<x<0.9**	
		SD												

nple ID	LIMS ID	Rep	K µg/g	Li µg/g	Mg µg/g	±95% CI [†]	Mn µg/g	Na µg/g	±95% CI [†]	Ni µg/g	Sr µg/g	V µg/g	Zn µg/g
32-94-1628	S17-00850	A	<3	<0.5	2.4	±0.5	<0.5	0.5<x<1.5		<0.9	<0.5	<0.5	<0.9
		B	<3	<0.5	2.4	±0.5	<0.5	0.5<x<1.5		<0.9	<0.5	<0.5	<0.9
		C	<3	<0.5	2.4	±0.5	<0.5	0.5<x<1.5		<0.9	<0.5	<0.5	<0.9
		Mean[a]	**<3**	**<0.5**	**2.4**		**<0.5**	**0.5<x<1.5**		**<0.9**	**<0.5**	**<0.5**	**<0.9**
		SD			0.02								
32-94-1925	S17-00851	A	<3	<0.5	3.0	±0.5	<0.5	2.2	±0.5	<0.9	<0.5	<0.5	<0.9
		B	<3	<0.5	3.3	±0.5	<0.5	2.2	±0.5	<0.9	<0.5	<0.5	<0.9
		C	<3	<0.5	3.2	±0.5	<0.5	2.0	±0.5	<0.9	<0.5	<0.5	<0.9
		Mean[a]	**<3**	**<0.5**	**3.2**		**<0.5**	**2.1**		**<0.9**	**<0.5**	**<0.5**	**<0.9**
		SD			0.1			0.1					
32-94-2103	S17-00852	A	<3	<0.5	<1		<0.5	4.8	±0.5	<0.9	<0.5	<0.5	<0.9
		B	<3	<0.5	<1		<0.5	4.9	±0.5	<0.9	<0.5	<0.5	<0.9
		C	<3	<0.5	<1		<0.5	4.9	±0.5	<0.9	<0.5	<0.5	<0.9
		Mean[a]	**<3**	**<0.5**	**<1**		**<0.5**	**4.9**		**<0.9**	**<0.5**	**<0.5**	**<0.9**
		SD						0.04					

4.4.3.3. 0.5 MW_e SSC Campaign (Phase 3): Gas Analysis

Gas adsorption samples were collected downstream from the water wash tower (Condition 14, **Table 27**) by passing the vapor effluent through a condensing system. The condensate was collected, and the vapor slip from the condenser was captured on gas adsorption tubes. Details of the gas adsorption tubes are shown in **Table 31**. At each sampling interval, two tubes of each type were sampled, and all tubes were shipped to GE for analysis.

Table 31. Gas Analysis (SSC Campaign): Adsorbent tubes for water wash vapor sampling

Adsorbent type	Tube size (mm)	Vendor	Analysis Company	Analytes of interest
226-10-06	6x70	SKC, Inc.	Analytics Corp.	Ammonia
226-30-18	6x70	SKC, Inc.	Analytics Corp.	Methyl amine, Ethyl amine
226-119	6x100	SKC, Inc.	Analytics Corp.	Formaldehyde, Acetaldehyde
226-01	6x70	SKC, Inc.	Analytics Corp.	Ketones (Acetone)
32010001	N/A	Ellutia, Inc.	RJ Lee	Nitrosodimethylamine, Nitrosodiethylamine, Nitromethylethylamine, Nitrosodi-n-propylamine
Carbotrap 300 (GE-supplied)	6x178	Gerstel	GE	Aminosilicone, Carbamate, TEG, D4, D5, D6, Ethylene oxide, Ethylene glycol, Dimethyl aminopropyl silanol

The results of gas adsorption analysis are shown in **Table 32**. Nitrosamines not listed were not detected above the limit of quantification of 0.011ug/tube in any samples. The analysis for ethylene glycol, D4, D5, and D6 was not quantitative. These species were detected in all samples for CSTR and SSC samples. Ammonia formation was reduced by 75% in the SSC due to a lower absorber temperature. This is also reflected in the lower amine degradation during the SSC campaign.

Table 33 lists the composition of the CO_2 stream measured for two of the conditions ran during the CSTR and SSC campaign, respectively. In both cases the CO_2 purity was above 99%. The CO_2 stream obtained during the SSC run had lower oxidation / contamination by-products. These results can be attributed to the lower desorption temperature of the SSC.

Table 32. Gas Analysis (SSC and CSTR): Clean flue gas composition

Analyte	units	10/21/2016	2/21/2017
		CSTR	SSC
Formaldehyde	ppm	0.00383	< 0.003
Ammonia	ppm	42.1	10
Acetaldehyde	ppm	Not Analyzed	0.682
Acetone	ppm	8.51	< 0.351
Ethylamine	ppm	< 0.181	< .181
Methylamine	ppm	< 0.262	< . 262
N-nitrosodi-n-propylamine	ug /tube	< 0.0011	< 0.0011
N-nitrosomethylamine	ug/tube	0.018	0.0193
EG	Presence	Present	Present
D4	Presence	Present	Present
D5	Presence	Present	Present
D6	Presence	Present	Present

SSC: $T_{desorber}$ = 235 °F; P = 2 Psig; 0.5 MWe, 18 wt.% H_2O, GAP-1 : CO_2 ~ 1.1
CSTR: $T_{desorber}$ = 262 °F; P = 7 Psig; 0.5 MWe, 3-7 wt. % H_2O, GAP-1 : CO_2 ~ 1.5

Table 33. **Gas Analysis (SSC and CSTR):** CO_2 steam

Desorber			**CSTR**	**Steam Stripper**
Test Date			**10/11/2016***	**Conditon 14**
		LOQ		
CO2 purity	vol%	5	99.4+	99+
H2	ppmv	10	ND	
O2 + Ar	ppmv	10	98	180
N2	ppmv	10	3200	1600
CO	ppmv	2	2.4	ND
Ammonia	ppmv	0.5	1	ND
NOx	ppmv	0.5	1.5	ND
NO	ppmv	0.5	na	ND
NO2	ppmv	0.5	na	ND
Total HCs	ppmv as CH4	0.1	1700	700
Total non-methane HCs	ppmv as CH4	0.1	1700	700
Methane	ppmv	0.1	0.9	0.2
Acetaldehyde	ppmv	0.05	27	6.6
Aromatic HCs	ppb as C6H6	2	ND	ND
Total Sulfur content	ppmv	0.05	trace	ND
SO2	ppmv	0.05	ND	ND
HCN	ppmv	0.2	ND	ND
Ethane	ppmv	0.1	0.1	ND
Propylene	ppmv	0.1	78	3.3
Hexanes +	ppmv	0.1	240	110
H2S	ppmv	0.01	trace	ND
Propionaldehyde	ppmv	0.1	54	15
Acetone	ppmv	0.1	27	2.1
Methanol	ppmv	0.1	17	ND
t-butanol	ppmv	0.1	ND	ND
Ethanol	ppmv	0.1	0.1	0.2
Methyl Ethyl Ketone	ppmv	0.1	0.7	ND
2-Butanol	ppmv	0.1	150	84
Isoamyl Acetate	ppmv	0.1	trace	1.4
Unknown VOX	ppmv	0.1	210	ND
Decamethylcyclopentasiloxane (D5)	ppmv	0.02	not analyzed	1.6
Hexamethylcyclotrisiloxane (D3)	ppmv	0.02	not analyzed	ND
Octamethylcyclotetrasiloxand (D4)	ppmv	0.02	not analyzed	ND
Trimethyl silanol	ppmv	0.02	not analyzed	ND

SSC: $T_{desorber}$ = 235 °F; P = 2 Psig; 0.5 MWe, 18 wt.% H_2O, GAP-1 : CO_2 ~ 1.1

CSTR: $T_{desorber}$ = 262 °F; P = 7 Psig; 0.5 MWe, 3-7 wt. % H_2O, GAP-1 : CO_2 ~ 1.5

4.4.3.4. 0.5 MW_e SSC Campaign (Phase 3): Corrosion studies

Prior results established that under the most aggressive process conditions examined (CSTR desorber conditions: 140 °C, 1 bar air/CO_2, 3 wt.% H_2O) CS1018 carbon steel coupons exhibited a high corrosion rate of approximately 2.2 mm/year. Under similar conditions, 304L stainless steel coupons exhibited corrosion rates that were indistinguishable from the control condition.

A series of 304L stainless steel (1.25” ID) and C1018 carbon steel coupons was placed in multiple locations of the PSTU (absorber tower, wash tower, rich lean heat exchanger, CSTR desorber and SSC desorber) at the beginning of the CSTR campaign. All coupons were collected at the end of the SSC campaign. The time accumulated for the absorber and rich/lean HX coupons was 900 hrs., including both the CSTR and SSC campaigns. CSTR coupons accumulated 500 hrs. while SSC coupons accumulated 400 hrs. The coupons were then cleaned according to the procedure listed in ASTM G1-03. Specifically, the coupons were exposed to the cleaning solution for 10 minutes, rinsed with deionized water, dried in a vacuum oven at 100 °C for 30 minutes, and weighed. The cleaning procedure was repeated until the slope of the weight loss vs. cleaning cycle curve matched that of control samples. (**Figure 100 and Figure *101*).**

Figure 102 shows the corrosion rates for 304L SS and CS1018 coupons placed in various locations of the PSTU. 304L stainless steel was corrosion resistant under all the conditions tested, while CS1018 coupons showed a differentiation in corrosion rates as a function of location. Corrosion rates under CSTR and SSC conditions were similar. It is conceivable that higher CSTR temperatures and CO_2 loading of the lean solvent are being balanced out by the higher water content in the working solution for the SSC. The highest rate of corrosion was recorded under the absorber conditions, due to higher oxygen content. Minimal corrosion rates were measured under the rich lean HX conditions (lean side). For both absorber and rich/lean HX, the corrosion rates were averaged over both CSTR and SSC campaigns. However, corrosion rates for CS1018 are 50 – 75 % lower than the values reported for a typical MEA plant. (HYDROCARBON PROCESSING, April 1993, pages 75-80 and May 1993 issue, pages 89-94.)

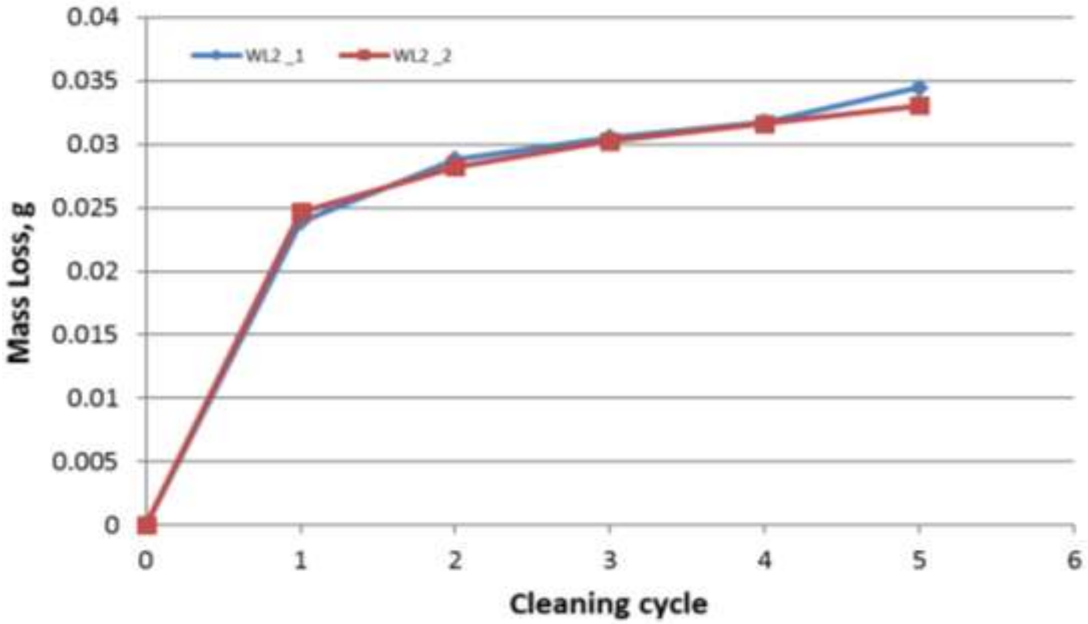


Figure 100. **Corrosion studies (SSC and CSTR):** Mass loss vs. cleaning cycle for CS1018 Absorber coupons / ASTM G1-03 Cleaning Procedure

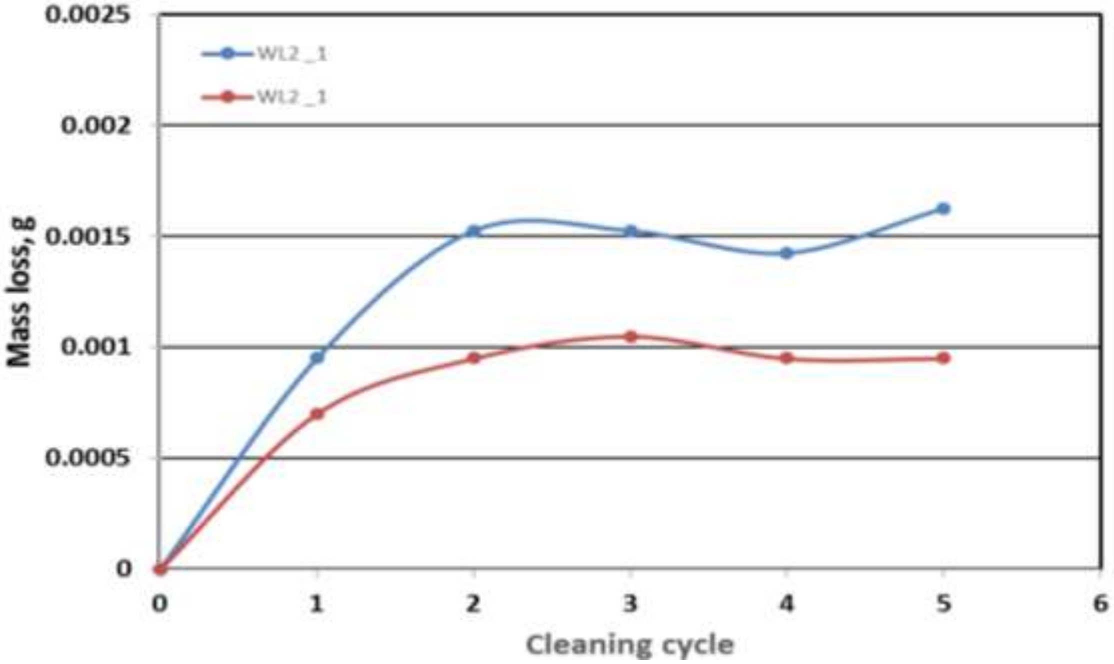


Figure 101. **Corrosion studies (SSC and CSTR): Mass loss vs. cleaning cycle for 304L SS** Absorber coupons / ASTM G1-03 Cleaning Procedure

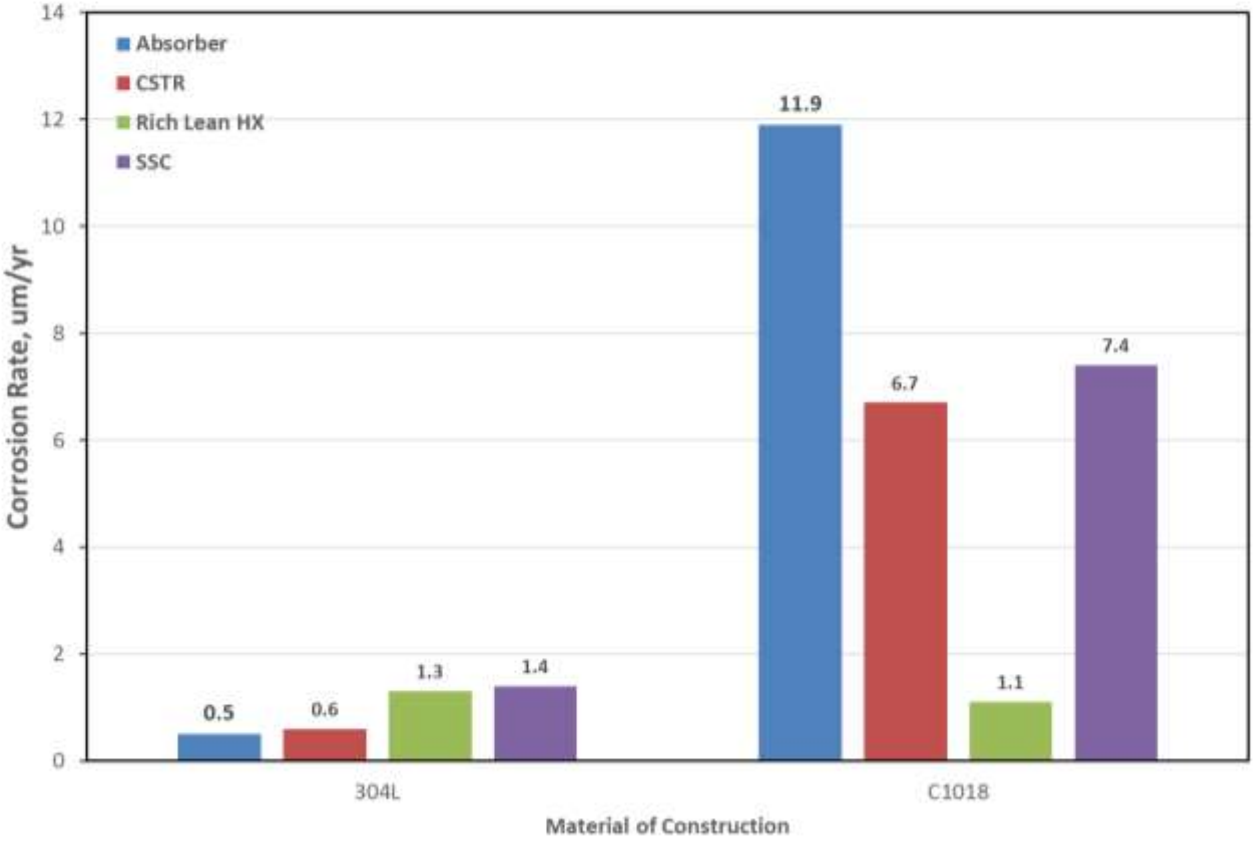


Figure 102. Corrosion rates (SSC and CSTR): 304L SS vs. C1018 at different positions in PSTU

4.4.3.5. MEA vs. Aminosilicone (CSTR and SSC) at 0.5 MW_e

GAP-1_m/TEG solvent was compared to the benchmark MEA based on the performance measured at 0.5 MW_e at NCCC. Both CSTR and SSC desorber systems were considered for the comparison, and the performance is listed in **Table 34.**

CSTR vs. SSC for GAP-1_m/TEG

Water content was 4 times lower in the CSTR (4 wt.%) vs. SSC (17 wt.%) to avoid solvent entrainment. We were able to achieve 90% capture at almost stoichiometric ratio with the SSC. CO_2 capture efficiency reached only 65% for CSTR even though solvent circulation was 25% higher. Amine degradation rate was 0.45% / day for temperatures lower than 248 ^oF for the CSTR. Less than 0.05 wt.% amine degradation was measured during the SSC campaign. Specific steam utilization was 50% higher with CSTR than SSC due to low water content.

GAP-1_m/TEG vs. MEA with SSC

Comparison of the GAP-1_m/TEG vs. MEA was conducted at 0.5 MW_e scale with the SSC. There are several process conditions that differentiate the two technologies. Water content in the working solution was almost five times lower in the case GAP-1_m/TEG (18 wt.% vs. 69 wt.%). This led to a 25% decrease in solvent recirculation to treat 5000 pph flue gas and achieve 90 % CO_2 capture efficiency. Desorption temperature was 9 ^oF lower for GAP-1_m/TEG at 2 Psig desorption pressure. Specific steam utilization (lb. CO_2 / lb. steam) increased by 10% for the GAP-1_m/TEG. As highlighted before, little amine degradation (< 0.05 wt. %/ day) was recorded for the GAP-1_m/TEG solvent.

Table 34. **GAP-1_m/TEG vs. MEA:** Performance comparison at 0.5 MW_e (NCCC)

	Amino Silicone		MEA
	CSTR	Steam Stripper Column	Steam Stripper Column
Power (MWe)	0.5	0.5	0.5
T desorber (F)	248	232-233	242
Amine : CO_2 (molar)	1.5	1.1	1.1
Lean Solvent/FG (w/w)	4	3	4
P (Psig)	7	2	10
H_2O (wt. %)	4	18	68.5
CO_2 Capture Eff. (%)	65	90	91.9
CO_2 / steam (lb : lb)	0.9	0.6	0.55
Amine Lost (wt.%/day)	~ 0.5	< 0.05	

4.5. SSC Campaign: Summary

- Controlled water addition to GAP-1_m/TEG and steam stripping desorption were first tested in a glass stripping column (GE GRC), optimized in a continuous bench scale system (2 kW_e, GE GRC), and demonstrated in a 0.5 MW_e pilot (NCCC).

- Bench Scale (2 kW_e): Small amounts of water in the working solution were found to be an effective way to enable steam stripping, lower desorption temperature, and hence reduce thermal degradation. Steam stripping also increased working capacity by 30% due to a more efficient desorption.

- Pilot Scale (0.5 MW_e):
  No special system modifications were required to the PSTU to accommodate the testing of the non-aqueous GAP-1_m solvent with the regenerator column.

90 – 95% CO_2 capture efficiency was achieved under stoichiometric conditions at 0.5 MW_e (235 °F desorption, 2 psig and 19 wt. % H_2O). Both CO_2 capture efficiency and specific duty reached optimum conditions at 18 wt.% H_2O.

Low amine degradation (< 0.05 wt.%/day) was recorded over 350 hrs. of operation.

GAP-1_m/TEG solvent exhibited a 25% increased working capacity, and 10% reduction in specific steam duty vs. MEA, at 10 °F lower desorption temperature.

5. Techno-Economic Analysis

A supercritical pulverized coal (PC) plant and CO_2-separation unit based on mono-ethanol amine (MEA) is described in Case 12 of the DOE Bituminous Baseline Study.[1]

A simplified block diagram of the power plant and CO_2-separation system is shown in **Figure 103**. The pulverized coal boiler generates steam, which is sent to the steam turbines. The flue gas is sent through a selective catalytic reduction (SCR) unit to reduce nitrogen oxides (NO_X), a bag house to remove fly ash, and a flue gas desulfurizer (FGD) to remove sulfur dioxide. The flue gas is then sent through the carbon dioxide separation unit before being vented to the stack.

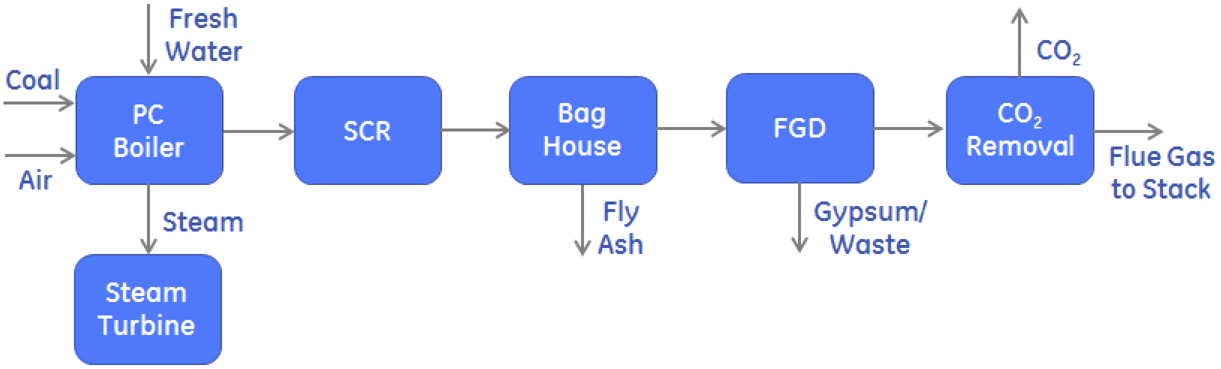


Figure 103. Coal-fired power plant block diagram with CO_2 removal.

The MEA and GAP-1_m/TEG CO_2 separation units utilize four key processes, CO_2 absorption, CO_2 desorption, sorbent handling, and CO_2 compression.

The flue gas from the power plant is processed in a direct contact cooler to reduce the temperature to 40 °C (104 °F) and then enters the absorber. **Figure 104** shows the process for the aminosilicone case. The lean sorbent enters the absorber at 40 °C (104 °F) and captures most

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[1] "Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural Gas to Electricity (Rev 2, November 2010)", DOE/2010/1397.

of the CO_2 from the flue gas. The rich sorbent leaves the absorber. The CO_2 absorption increases the temperature of the sorbent. The absorber is operated at 40-82 °C (104-180 °F) and at atmospheric pressure. The rich sorbent from the absorber is fed to the rich-lean heat exchanger and heated before being fed to the desorber (stripper) for separation of the absorbed CO_2. A 11.1 °C (20 °F) approach is assumed for this rich-lean heat exchanger. This is defined as the hot fluid outlet temperature minus the cold fluid inlet temperature. The lean sorbent from the desorber is passed through the other side of the rich-lean heat exchanger.

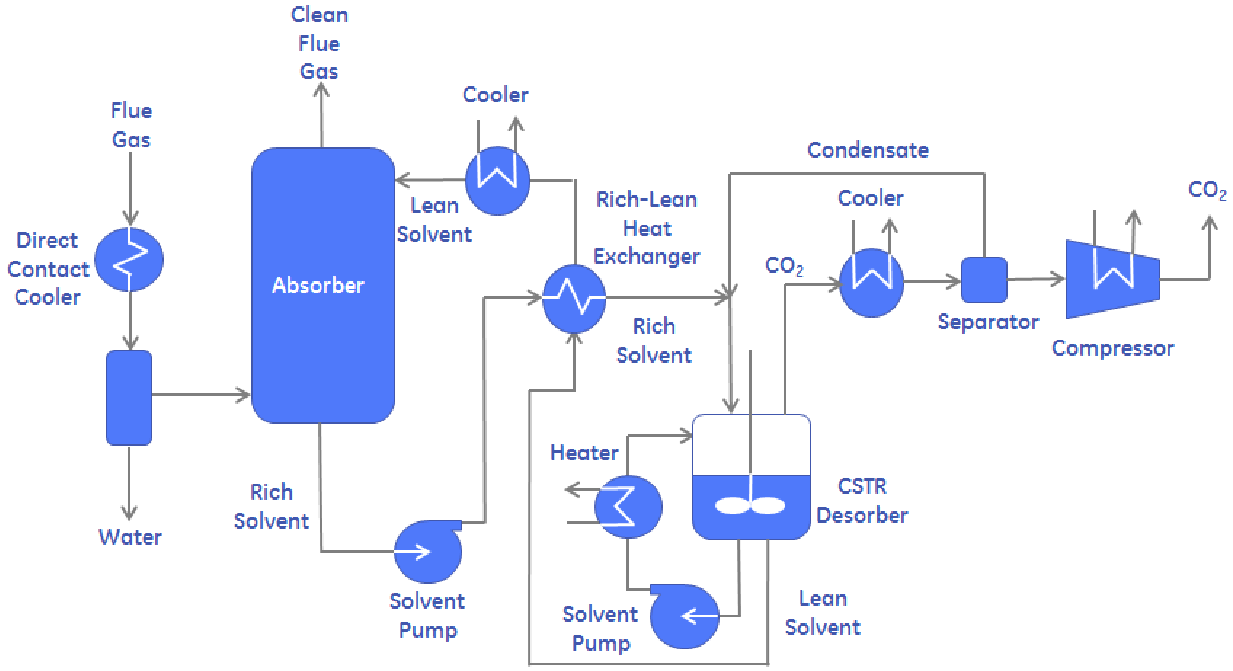

Figure 104. Aminosilicone-based CO_2 separation sub-system.

For the aminosilicone solvent baseline case (Case A, described below), the desorber operates at 140 °C (284 °F) and 4.3 atm (63 psia). For the sensitivity studies, the desorber conditions were varied from 130 to 140 °C (266 to 284 °F) and from 1.4 to 4.3 atm (20 to 63 psia). These results are presented in subsequent sections. For the MEA baseline case, the desorber reboiler conditions are about 116 °C (241 °F) and 1.6 atm (24 psia). For both systems, steam is supplied to the desorber to provide heat, which releases CO_2 from the rich sorbent. Steam is supplied from the medium- to low-pressure steam turbine crossover pipe of the steam turbine in the power plant sub-system. Steam conditions were selected based on best efficiency of the power plant and the removal cost of CO_2 from the overall system. The hot vapor from the top of the desorber consisting primarily of CO_2 is cooled in a heat exchanger utilizing water. The stream then flows to a separator where the vapor and entrained liquid are separated. The CO_2 gas is removed from the separator and then delivered to the CO_2 product compressor. The liquid from the bottom of the separator is returned back to the desorber. The lean sorbent from the desorber is pumped through the rich-lean heat exchanger to the absorber. The lean sorbent is cooled further before being fed to the absorber in order to increase the loading of CO_2 in the absorber.

5.1. Power Plant Modeling

A model of a supercritical PC plant was built in Thermoflow, a thermodynamic design tool which includes cost estimation methods for conventional coal power plants. The Thermoflow model interacted with the carbon-capture model by exchanging flue gas, process steam, and water at the boundaries between the two systems. Capital costs, operating costs, and net power output were rolled up at a plant level.

The modeling process began by calibrating to Case 11 from the Bituminous Baseline Study.[1] Gas and steam flows, pressures and temperatures throughout the plant, along with exhaust composition, auxiliary loads, and net plant output were closely matched to Case 11 to create a calibration point for the model in Thermoflow. By matching to Case 11 it was possible to replicate efficiency levels on all of the major equipment in the power block, including pumps, fans, steam turbine sections, the boiler, and environmental equipment. These efficiencies were then held fixed as the model was updated to include CO_2-capture, thus ensuring consistency between the DOE report and the analysis with carbon capture. It was also possible to tune the cost model in Thermoflow to achieve a good match for overall capital costs with Case 11 from the Bituminous Baseline Study. The cost breakdown in Thermoflow's cost estimation tool is not at the same level of detail as in the Bituminous Baseline Study, so when calibrating the plant capital costs it was necessary to calibrate only on the full plant level rather than on a component level.

Figure 3 shows a simplified block diagram of the power block, which is applicable to both the model with CO_2 capture and without. Detailed process flow information for each stream is shown in **Figure 103** and in **Table 35** for the model without CO_2 capture. This model is intended to be a close match with Case 11 from the Bituminous Baseline Study.

Power plant modeling was conducted in Thermoflow for a number of cases. As described above, the first case was similar to Case 11 in the DOE Bituminous Baseline Study which is for a supercritical PC plant without CO_2 capture. Secondly, a Thermoflow model was built for a scaled-up system for 550 MW net power with a CO_2-capture system added. For this case, the power plant model was built in Thermoflow and the carbon-capture island was modeled in Aspen Plus and Aspen Capital Cost Estimator. The scaled-up model is Case H which will be discussed in the next sections.

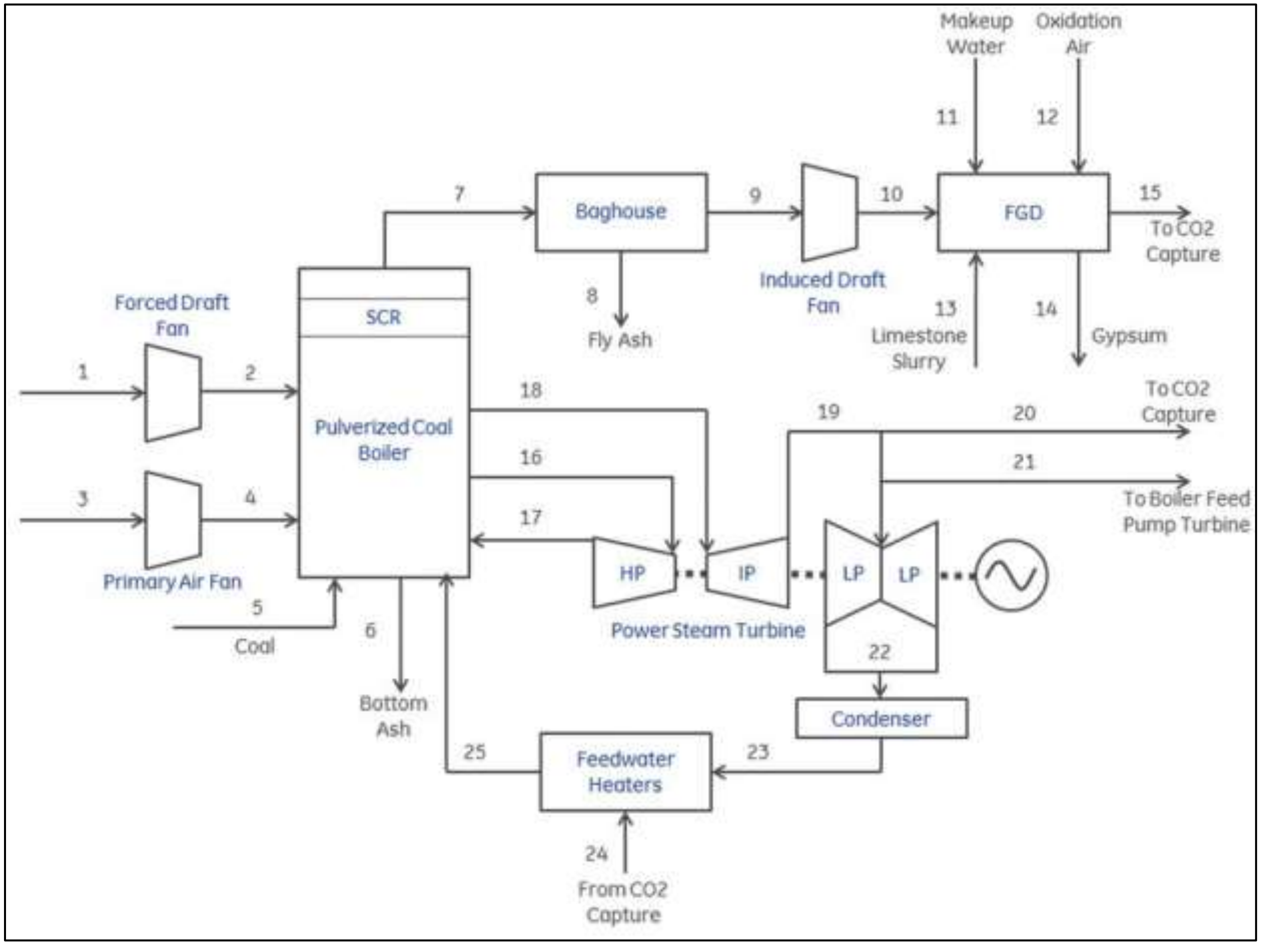

Figure 105. Block flow diagram for power plant.

Table 35. Stream table for power plant case without CO_2 capture (comparable to Case 11).[1]

	1	2	3	4	5	6	7
V-L Mole Fraction							
Ar	0.0093	0.0093	0.0093	0.0093	0.0000	0.0000	0.0088
CO_2	0.0003	0.0003	0.0003	0.0003	0.0000	0.0000	0.1485
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0101	0.0101	0.0101	0.0101	0.0000	0.0000	0.0893
N_2	0.7729	0.7729	0.7729	0.7729	0.0000	0.0000	0.7310
O_2	0.2074	0.2074	0.2074	0.2074	0.0000	0.0000	0.0202
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0022
Total	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	1.0000
V-L Flowrate (lbmol/hr.)	106,097	106,097	32,592	32,592	-	-	146,883
V-L Flowrate (lb./hr.)	3,061,401	3,061,401	940,431	940,431	-	-	4,371,358
Solids Flowrate (lb./hr.)	-	-	-	-	410,264	8,142	32,568.79
Temperature (°F)	59	65	59	77	59	-	342
Pressure (psia)	14.7	15.1	14.7	16.2	14.7	-	14.3
Enthalpy (Btu/lb.)	-4.3	-3.0	-4.3	0.1	-	-	69.2
Density (lb./ft^3)	0.076	0.078	0.076	0.081	-	-	0.047
V-L Molecular Weight	28.85	28.85	28.85	28.85	-	-	29.76

	8	9	10	11	12	13	14
V-L Mole Fraction							
Ar	0.0000	0.0088	0.0088	0.0000	0.0093	0.0000	0.0000
CO_2	0.0000	0.1485	0.1485	0.0000	0.0003	0.0000	0.0004
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0000	0.0893	0.0893	1.0000	0.0101	1.0000	0.9996
N_2	0.0000	0.7310	0.7310	0.0000	0.7729	0.0000	0.0000
O_2	0.0000	0.0202	0.0202	0.0000	0.2074	0.0000	0.0000
SO_2	0.0000	0.0022	0.0022	0.0000	0.0000	0.0000	0.0000
Total	0.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (lbmol/hr.)	-	146,883	146,883	15,884	2,284	8,483	348
V-L Flowrate (lb./hr.)	-	4,371,358	4,371,358	286,236	65,916	152,864	6,264
Solids Flowrate (lb./hr.)	32,569	-	-	-	-	33,832	56,664
Temperature (°F)	-	342	362.9	59	59	59	0
Pressure (psia)	-	13.84	15.06	14.7	14.7	14.7	0.0
Enthalpy (Btu/lb.)	-	69.2	74.7	27.1	-4.3	-	-
Density (lb./ft^3)	-	0.046	0.048	62.379	0.076	-	-
V-L Molecular Weight	-	29.76	29.76	18.02	28.85	-	18.03

	15	16	17	18	19	20	21
V-L Mole Fraction							
Ar	0.0081	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO_2	0.1372	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.1575	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
N_2	0.6767	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O_2	0.0203	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (lbmol/hr.)	161,275	203,480	168,736	168,736	152,819	-	12,899
V-L Flowrate (lb./hr.)	4,646,871	3,666,712	3,040,619	3,040,619	2,753,799	-	232,437
Solids Flowrate (lb./hr.)	-	-	-	-	-	-	-
Temperature (°F)	132	1100	664	1100	688	-	688
Pressure (psia)	14.7	3514.7	693.7	655.8	134.9	-	134.9
Enthalpy (Btu/lb.)	14.8	1495.0	1323.7	1570.5	1371.4	-	1371.4
Density (lb./ft^3)	0.063	4.319	1.141	0.722	0.200	-	0.200
V-L Molecular Weight	28.81	18.02	18.02	18.02	18.02	-	18.02

	22	23	24	25
V-L Mole Fraction				
Ar	0.0000	0.0000	0.0000	0.0000
CO_2	0.0000	0.0000	0.0000	0.0000
H_2	0.0000	0.0000	0.0000	0.0000
H_2O	1.0000	1.0000	1.0000	1.0000
N_2	0.0000	0.0000	0.0000	0.0000
O_2	0.0000	0.0000	0.0000	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000
Total	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (lbmol/hr.)	114,800	154,153	-	203,480
V-L Flowrate (lb./hr.)	2,068,688	2,777,829	-	3,666,712
Solids Flowrate (lb./hr.)	-	-	-	-
Temperature (°F)	101	104	-	557
Pressure (psia)	1.0	264.2	-	4185.2
Enthalpy (Btu/lbm)	1016.3	72.3	-	552.9
Density (lb./ft^3)	0.003	61.999	-	47.687
V-L Molecular Weight	18.02	18.02	-	18.02

Table 36 summarizes the power output from the power plant, without CO_2 capture, along with materials consumed during normal operation. It includes a detailed summary of auxiliary loads and how they combine with the steam turbine power to impact the total plant net-power output and efficiency. Auxiliary loads required only minor tuning in order to conform to the results from DOE Case 11.[1]

The Thermoflow model includes a cost estimation tool. The results from this are summarized in Table 3. The cost estimates for the model without carbon capture were tuned in order to line up with the results from Case 11 in the economic updates (June 2011 Basis) for the Bituminous Baseline Study.[2] The factors that were applied in order to achieve this match were held constant for further analysis of cases with CO_2 capture.

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[2] "Updated Costs (June 2011 Basis) for Selected Bituminous Baseline Cases", DOE/NETL – 341/082312.

Table 36. Power summary for case without CO_2 capture (comparable to DOE Case 11).[1]

POWER SUMMARY (Gross Power at Generator Terminals, kWe)	
Steam Turbine Power	580,418
Total (Steam Turbine) Power, kWe	**580,418**
Auxiliary Load Summary, kWe	
Boiler Fuel Delivery	3,216
Ash Handling	529
Primary Air Fans	1,358
Forced Draft Fans	1,524
Induced Draft Fans	7,444
Baghouse (ESP)	70
Wet FGD	5,536
Carbon-Capture Process	-
CO_2 Compression	-
Miscellaneous BOP	289
Condensate Pumps	953
Circulating Water Pumps	3,889
Cooling Tower Fans	3,284
Transformer Losses	1,820
BFP Booster Pump	498
Total Auxiliaries, kWe	**30,411**
Net Power, kWe	**550,008**
Net Plant Efficiency (HHV)	39.2%
Net Plant Heat Rate, (Btu/kWh)	8,702
Condenser Cooling duty, (10^6 Btu/hr.)	2,212
Consumables	
As-Received Coal Feed, (lb./hr.)	410,264
Limestone Sorbent Feed, (lb./hr.)	33,833
Thermal Input (kWt)	1,402,678
Raw Water Consumption (gpm)	6,740

Table 37. Equipment cost summary for case without CO_2 capture (comparable to DOE Case 11)[2]

	$	$/kW
Specialized Equipment	**$ 503,571,680**	**$ 912**
Boiler	**$ 190,948,513**	**$ 346**
Furnace	$ 81,914,520	$ 148
Convective Elements	$ 55,081,043	$ 100
Additional Waterwall	$ 5,734,579	$ 10
Soot Blowers	$ 4,858,259	$ 9
Desuperheaters and Controls	$ 8,363,538	$ 15
Air and Flue Gas Ducts	$ 5,955,797	$ 11
Coal Pulverizers and Feeders	$ 19,589,477	$ 35
FD Fan, PA Fan, ID Fan	$ 3,079,953	$ 5.6
Structural Steel, Ladders, Walkways	$ 2,481,073	$ 4.5
Rotary Air Heaters	$ 3,887,829	$ 7.0
Steam Turbine	**$ 112,162,148**	**$ 203**
Feedwater Heaters	**$ 9,790,217**	**$ 18**
Feedwater Heater 1	$ 706,216	$ 1.3
Feedwater Heater 2	$ 677,982	$ 1.2
Feedwater Heater 3	$ 631,536	$ 1.1
Feedwater Heater 4	$ 813,651	$ 1.5
Feedwater Heater 5-DA	$ 954,821	$ 1.7
Feedwater Heater 6 (6A,6B)	$ 1,665,926	$ 3.0
Feedwater Heater 7 (7A,7B)	$ 2,205,182	$ 4.0
Feedwater Heater 8 (8A,8B)	$ 2,135,025	$ 3.9
Water Cooled Condensers	**$ 4,703,533**	**$ 8.5**
Main Condenser	$ 4,138,816	$ 7.5

Table 37. Equipment cost summary for case w/o CCS (comparable to DOE Case 11)[2]

Feed Pump Turbine Condenser	$	565,023	$	1.0
Particulate and Mercury Control	**$**	**22,139,295**	**$**	**40**
Flue Gas Desulfurization	**$**	**87,523,161**	**$**	**159**
Nitrogen Oxide Control (SCR)	**$**	**39,389,787**	**$**	**71**
Stack	**$**	**9,447,807**	**$**	**17**
Continuous Emissions Monitoring System	**$**	**627,299**	**$**	**1.1**
Distributed Control System	**$**	**1,675,191**	**$**	**3.0**
Transmission Voltage Equipment	**$**	**15,090,301**	**$**	**27**
Transformers	$	13,353,578	$	24
Circuit Breakers	$	1,018,812	$	1.8
Miscellaneous Equipment	$	718,644	$	1.3
Generating Voltage Equipment	**$**	**10,074,427**	**$**	**18**
Generator Buswork	$	5,234,596	$	9
Circuit Breakers	$	4,359,515	$	7.9
Miscellaneous Equipment	$	479,706	$	0.9

Other Equipment	**$**	**126,556,231**	**$**	**229**
Pumps	**$**	**12,782,669**	**$**	**23**
Boiler Feed Pump (+ Turbine)	$	8,445,190	$	15
Boiler Feed Booster Pump	$	130,955	$	0.2
Condenser C.W. Pump	$	2,290,345	$	4.1
Condensate Forwarding Pump	$	599,474	$	1.1
Condenser Vacuum Pump	$	373,495	$	0.7
Aux Cooling Water Pump (Closed Loop)	$	40,050	$	0.1
Treated Water Pump	$	6,783	$	0.01
Diesel Fire Pump	$	172,876	$	0.3

Jockey Fire Pump	$ 5,182	$ 0.01
Demin Water Pump	$ 13,419	$ 0.02
Raw Water Pumps	$ 28,232	$ 0.1
Aux Cooling Water Pump (Open Loop)	$ 40,050	$ 0.1
Startup Boiler Feed Pump	$ 637,239	$ 1.2
Tanks	**$ 960,883**	**$ 1.7**
Hydrous Ammonia	$ 160,595	$ 0.3
Demin Water	$ 104,252	$ 0.2
Raw Water	$ 340,440	$ 0.6
Neutralized Water	$ 78,037	$ 0.1
Acid Storage	$ 32,620	$ 0.1
Caustic Storage	$ 32,620	$ 0.1
Dedicated Fire Protection Water Storage	$ 212,355	$ 0.4

	$ -	$ -
Cooling Tower	**$ 10,215,077**	**$ 19**
Auxiliary Cooling Water Heat Exchanger	**$ 138,904**	**$ 0.3**
Steam Turbine Crane	**$ 1,984,621**	**$ 3.6**
Station Instrument Air Compressors	**$ 816,256**	**$ 1.5**
General Plant Instrumentation	**$ 430,632**	**$ 0.8**
Medium Voltage Equipment	**$ 6,408,794**	**$ 12**
Transformers	$ 908,452	$ 1.6
Circuit Breakers	$ 344,459	$ 0.6
Switchgear	$ 1,805,415	$ 3.3
Motor Control Centers	$ 3,044,880	$ 5.5
Miscellaneous	$ 305,221	$ 0.6
Low Voltage Equipment	**$ 1,577,221**	**$ 2.9**
Transformers	$ 550,622	$ 1.0
Circuit Breakers	$ 460,216	$ 0.8
Motor Control Centers	$ 491,003	$ 0.9
Miscellaneous	$ 751,898	$ 1.4
Coal Handling Equipment	**$ 62,983,114**	**$ 114**
Ash Handling Equipment	**$ 22,231,445**	**$ 40**
Miscellaneous Equipment	**$ 6,026,614**	**$ 11**

Civil	**$ 82,771,128**	**$ 150**
Site Work	$ 17,302,872	$ 31
Excavation and Backfill	$ 4,839,333	$ 9
Concrete	$ 59,554,161	$ 108
Roads Parking and Walkways	$ 1,074,761	$ 1.9

Mechanical	**$ 249,878,964**	**$ 453**
On Site Transportation and Rigging	$ 8,948,256	$ 16
Equipment Erection and Assembly	$ 179,486,985	$ 325
Piping	$ 59,145,791	$ 107
Steel	$ 2,297,932	$ 4.2

Electrical Assembly and Wiring	**$ 22,045,205**	**$ 40**
Controls	$ 13,696,410	$ 25
Assembly and Wiring	$ 8,348,796	$ 15

Buildings and Structures	**$ 20,288,854**	**$ 37**
Boiler House and Turbine Hall	$ 18,282,573	$ 33
Administration Control Room, Machine Shop, Warehouse	$ 1,979,771	$ 3.6
Guard House	$ 26,510	$ 0.05

Engineering and Plant Startup	**$ 52,908,687**	**$ 96**
Engineering	$ 43,097,130	$ 78
Start Up	$ 9,811,557	$ 18

Totals		
Subtotal Contractor's Internal Cost	**$ 1,058,020,749**	**$ 1,917**
Contractors Soft & Misc. Costs	$ 200,206,199	$ 363
Subtotal Contractor's Price	**$ 1,258,226,948**	**$ 2,279**
Owner's Soft and Misc. Costs	$ 267,642,586	$ 485
Total Owner's Cost	**$ 1,525,869,535**	**$ 2,764**

Details about consumable materials are also available from the Thermoflow model. These were used with unit cost values from the economic updates (June 2011 Basis) for the Bituminous Baseline Study in order to calculate annual costs of consumables and fuel.[2] The fixed operating costs and maintenance material costs were not independently calculated by the power block model and were therefore assumed equal to the values in DOE Case 11 to avoid inconsistency. The annual cost figures are summarized in **Table 38**.

Table 38. Annual cost summary for case without CO_2 capture (comparable to DOE Case 11)[1]

			Annual Cost	Annual Unit Cost
			$	$/kWh-net
Fixed Operating Costs			**$ 38,828,811**	**$ 0.00806**
Maintenance Material Costs			$ 10,945,892	$ 0.00227
	Consumption / day	Unit Cost		
Water (/1000 gallons)	3,293	1.67	$ 1,706,242	$ 0.00035
Chemicals				
MU & WT Chem.(lbs.)	15,939	0.27	$ 1,335,191	$ 0.00028
Limestone (ton)	478	33.48	$ 4,961,323	$ 0.00103
Ammonia (19% NH_3) ton	74	330	$ 7,589,915	$ 0.00158
Subtotal Chemicals			$ 13,886,429	$ 0.00288
Other				
SCR Catalyst (m^3)	0.31	5775.94	$ 556,513	$ 0.00012
Subtotal Other			$ 556,513	$ 0.00012
Waste Disposal				
Total Ash (ton)	478	25.11	$ 3,720,271	$ 0.00077
Subtotal Waste Disposal			$ 3,720,271	$ 0.00077
Total Variable Operating Costs			**$ 19,869,457**	**$ 0.00412**
Fuel (ton)	4923	68.60	**$ 104,780,439**	**$ 0.02175**

Table 39 details the energy flows in and out of the control volume in the power block model, and confirms that the model achieves a proper energy balance.

Table 39. Energy balance for case without CO_2 capture (comparable to DOE Case 11)[1]

	HHV	Sensible + Latent Heat	Power	Total
Heat In (MMBtu/hr.)				
Coal	4797			4797
Ambient Air		53.3		53.3
FGD Water		22.0		22.0
FGD Oxidation Air		3.8		3.8
Totals	4797	79		4876
Heat Out (MMBtu/hr.)				
Bottom Ash		4.4		4.4
Fly Ash + FGD Ash		1.7		1.7
Flue Gas		611		611
Unburned Carbon		13.3		13.3
Boiler Losses		42.1		42.1
Fuel Delivery Losses		2.2		2.2
Main Condenser		1970		1970
BFPT Condenser		230		230
Steam Piping Losses		11.1		11.1
ST/Generator Mech/Elec/Gear Losses		22.7		22.7
BFPT Mech Losses		0.7		0.7
Pumps Mech/Elec Losses		2.4		2.4
Fans Mech/Elec Losses		3.8		3.8
FGD Energy Losses		31.7		31.7
Misc. Losses and Auxiliaries		52.6		52.6
Net Power			1877	1877
Totals	0	2999	1877	4876

Table 40 summarizes the pieces of equipment which contribute to the total water consumption in the power block model.

Table 40. Water consumption for case without CO_2 capture (comparable to DOE Case 11)[1]

Water Use	Water Consumption (gpm)
Carbon-Capture Process	
FGD Makeup	573
Cooling Tower	3,558
Total	**4,130**

5.2. CO_2-Capture System ASPEN Plus Model Development

An ASPEN Plus model was developed for a supercritical commercial-scale process with aminosilicone-based solvent. The base case chosen was similar to Case 11 in the DOE-NETL study.[1] Models were developed for a number of different CO_2-capture cases with varying absorber and desorber operating conditions. In order to compare the different cases of the carbon-capture island, the flue gas flow rate was fixed to match the Case 11 from the DOE NETL study which produces 550 MW net power without CO_2 capture. Comparing these cases facilitated final selection of the best case that had the lowest overall removal cost of CO_2. The best case was then scaled up to 550 MW net power with CO_2 capture. Further, two more cases were modeled starting from the scaled-up best case to further optimize the power plant and the carbon-capture island integration. The details of the selected cases are explained in the subsequent sections. The overview of the model is presented in Figure 4.

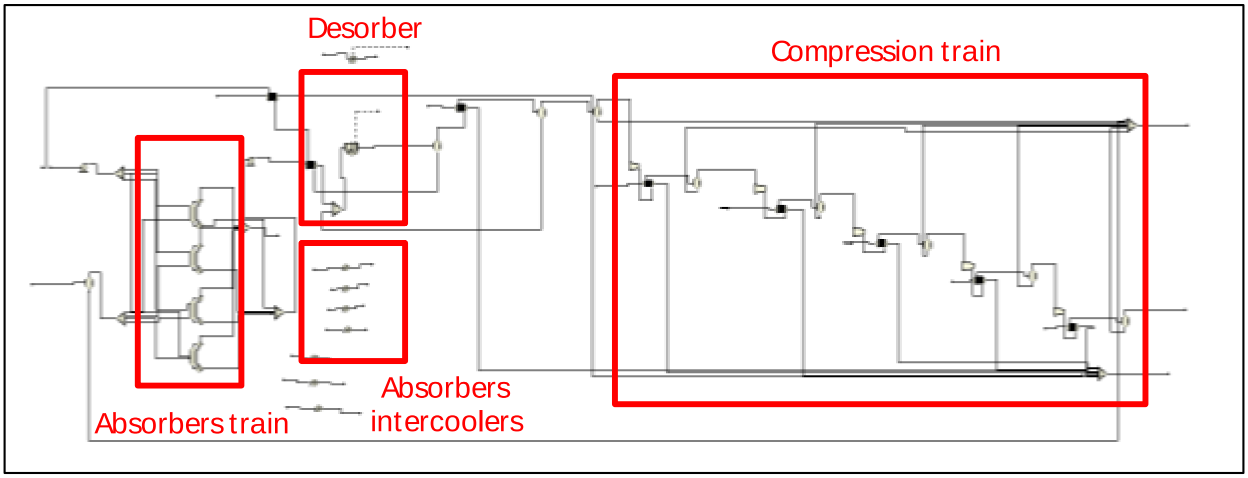

Figure 106. Aspen Plus model for CO_2 separation sub-system

Each part of the process will be discussed below.

5.2.1. Absorber Design

The CO_2-capture process was designed for a supercritical PC power plant, and the best case was scaled up to achieve 550 MW of net power with CO_2 capture. Flue gas enters the post-combustion CO_2-capture island from the coal power plant. The flue gas flow rate and composition were determined from the results of the power plant model using Thermoflow. The flue gas is cooled to 40 °C in a direct contact cooler, where condensed water is removed and sent to a waste water treatment plant. The absorber train consists of 4 units, and flue gas is evenly split among each of the columns. The flow sheet from the ASPEN Plus model of the absorber train is shown in **Figure 107**.

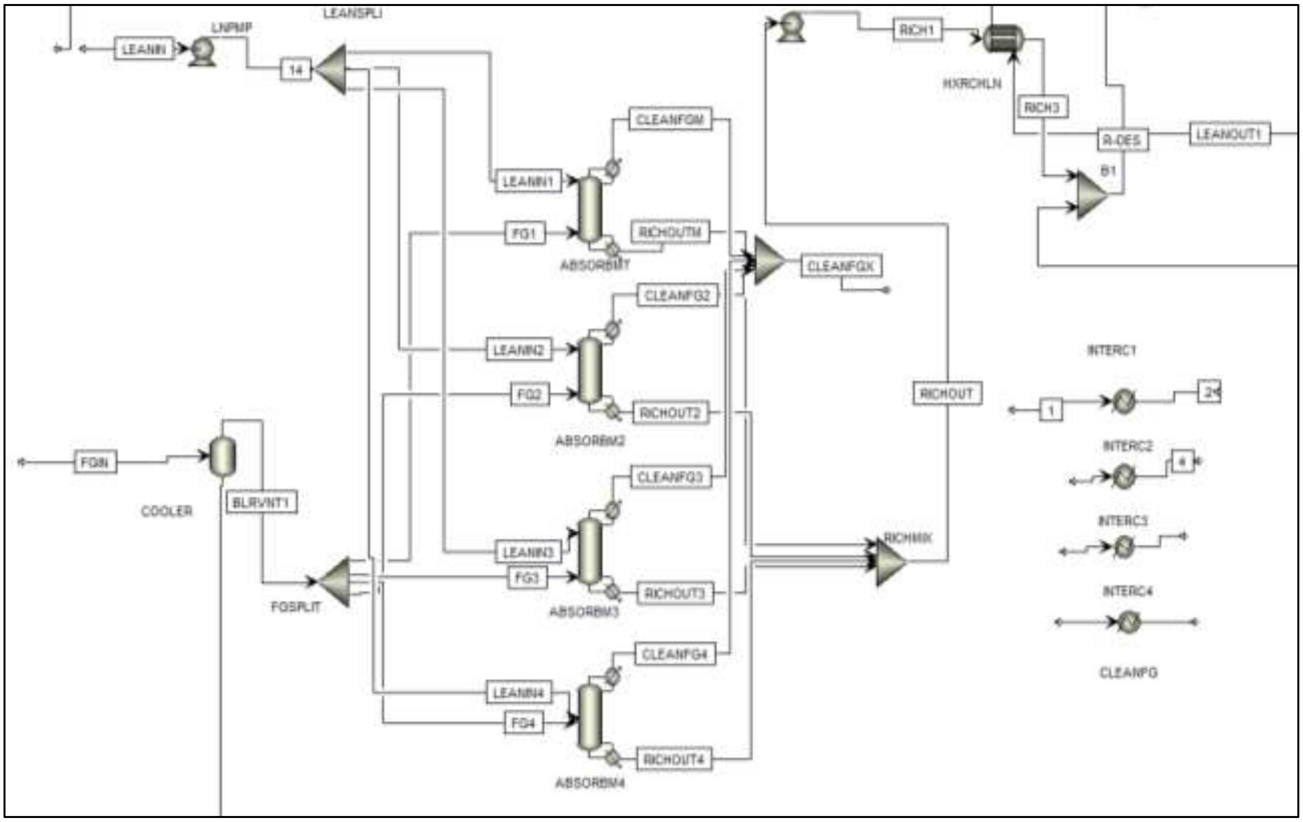

Figure 107. Aspen Plus flow sheet for the absorber train portion of the carbon-capture process

The absorbers are designed as RadFrac unit operations in Aspen Plus, where mass transfer is modeled based on rate-based calculations and chemical reactions are assumed to be in equilibrium. These assumptions were made based on bench-scale experiments conducted in the prior award (DE-FE0007502).

During the last cooperative agreement, an ASPEN Plus model for the bench-scale process was developed, and the packing type used in the model for the absorber corresponded to the actual packing used in the bench-scale process. Because there is a range of choices for packing type for commercial-scale processes, sensitivity analysis was conducted with respect to packing type in order to understand its effect on system performance. This analysis was conducted at a fixed lean solvent flow rate to the absorber train, and the change in CO_2 capture was determined. Results of this sensitivity analysis are shown on **Figure 108**.

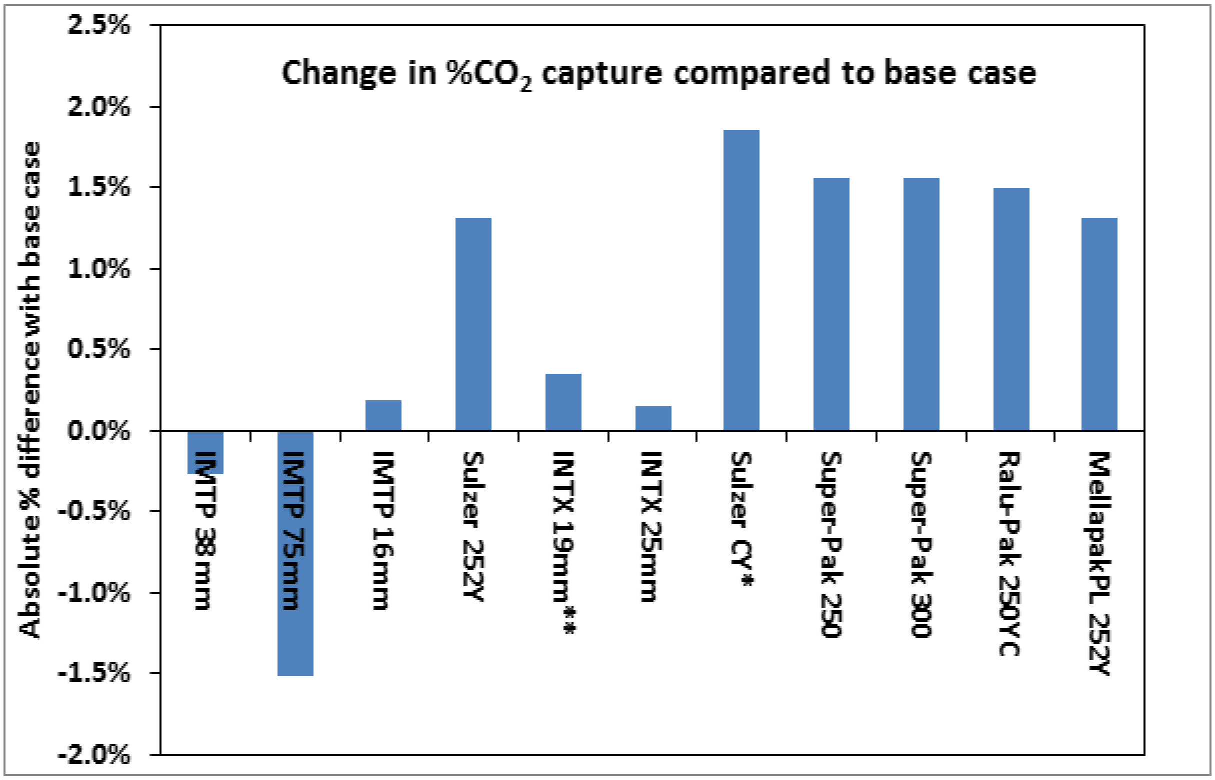

Figure 108. Effect of packing type on percent of CO_2 captured

It can be seen that, overall, structured packing offers higher performance compared to random packing for this system. The best case shown provides ~2% improvement in capture efficiency compared to the base case. The packing type which is available at the NCCC is Mellapak Plus 252Y, and therefore this packing was selected for further analysis. Also, this packing is commercially available in carbon steel (CS), which is significantly less expensive than stainless steel (SS). Because of the aminosilicone's lower corrosivity relative to other solvents, carbon steel packing may be used.

Packing Height Sensitivity Analysis

The sensitivity analysis with respect to packing height was conducted for Mellapak Plus 252Y structured packing, and the results are presented in **Figure 109**. It can be seen the reduction of packing height from 95 ft. to 50 ft. reduces the absolute value of CO_2 capture by ~0.6%, and therefore the lean solvent flow rate would need to be increased slightly to obtain 90% capture. The height of the packing was selected to be 50 ft., because the capital cost of the absorber train offsets the cost of a small lean-solvent flow rate increase. Diameter of each absorber was optimized to avoid flooding, and it was determined to be 33 ft. for the final cases.

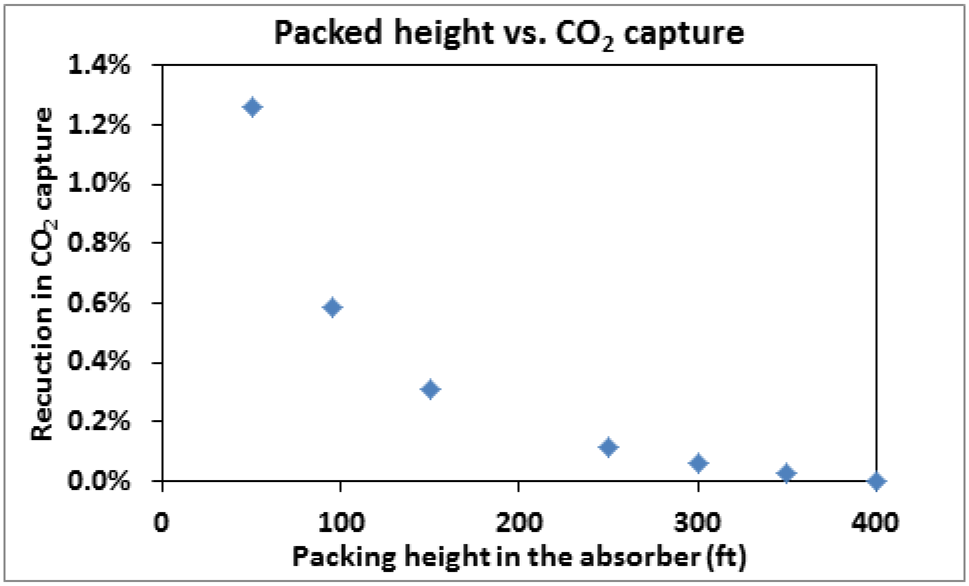

Figure 109. The effect of packing height on CO_2 capture

5.2.2. Desorber Design

It was previously shown that the aminosilicone-based solvent has significantly lower vapor pressure compared to MEA, and this property facilitates operating the desorption process at higher temperatures and pressures without significant solvent losses. This advantageous property also enables the desorption of CO_2 to be accomplished in a continuous stirred-tank reactor (CSTR) versus a distillation column, which reduces the CAPEX of the desorber system by ~50%. Among other advantages are easier operation and maintenance and smaller footprint.

The desorber system includes a recirculation loop with a high-pressure pump and heat exchanger to provide sufficient heat transfer surface area and increase liquid/gas interfacial area. The ASPEN Plus model flow diagram for the desorber is presented below in **Figure 110**.

For each of the cases considered below, recirculation loop pump and heat exchanger sizes were calculated and used for capital cost estimation.

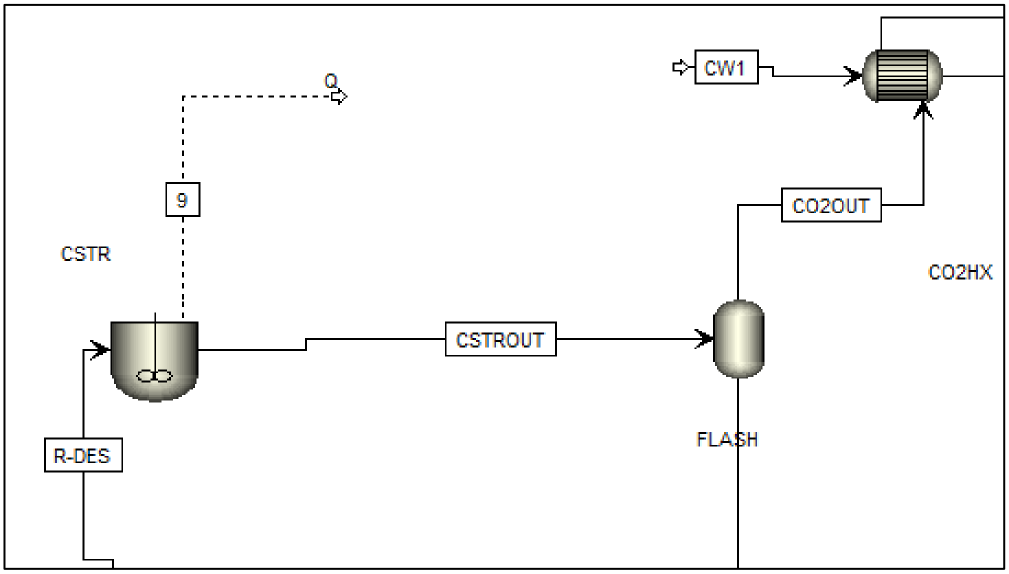

Figure 110. The desorber section of the ASPEN Plus flow sheet

The main design parameters for the desorber are temperature, pressure, and residence time. The current optimized desorber operates at a temperature of 130 °C, pressure of 63 psia, and residence time of 11 minutes. The residence time was selected based on a sensitivity analysis which showed that CO_2 desorption approached equilibrium at 11 minutes. The volume of the desorber is calculated based on this residence time.

The values used for the overall heat transfer coefficients for the desorber jacket and recirculation loop heat exchanger were selected based on a literature search and prior calculations, and are presented in **Table 41**.

Table 41. The heat transfer coefficients used in the desorber model

Type of heat transfer unit	*Overall heat transfer coefficient U (Btu/hr·ft^2·F)*
Jacketed vessels: steam to organics, SS wall, average	100
Shell and Tube heat exchanger: steam to light organics, average	185

The volume of the desorber is calculated based on a residence time of 11 minutes. The amount of heat which can be transferred through the desorber jacket can be calculated based on the following equation:

$$Q_{reactor} = U * A * LMTD$$

The total heat required for the desorber system is calculated by the ASPEN Plus model, and the heat duty for the recirculation loop heat exchanger is also determined. Based on these values, the appropriate size for heat exchanger and number of cycles/minute are calculated. The results for each of the aminosilicone-based cases studied for the carbon capture system are presented below in Table 8.

Table 42. Size of desorber and recirculation loop for different carbon capture cases

	Desorber CSTR		Recirculation loop	
	Total height, ft.	Diameter, ft.	HEX area, ft^2	Number of cycles/min
Case A	70	33.0	10,128	0.25
Case B	53	33.0	10,214	0.34
Case C	38	33.0	10,452	0.50
Case D	37	33.0	10,432	0.51
Case E	44	33.0	9,649	0.20
Case H	54	33.0	12,511	0.20

5.2.3. Rich-Lean Heat Exchanger

In order to recover as much heat as possible from the hot lean solvent stream leaving the desorber, a rich-lean heat exchanger will be utilized to preheat the rich cold solvent leaving the absorber train. In current simulations, the rich-lean heat exchanger is modeled as a shell and tube unit with a constant value of the overall heat transfer coefficient of 75 Btu/hr·ft^2·F. This value was previously estimated from heat transfer film coefficients based on known physical properties and design assumptions. In the current system, this unit represents ~25% of the total equipment cost for the CO_2-capture process. Therefore, additional work will be done in the future to find the optimal design for this heat exchanger, to increase the value of the overall heat transfer coefficient, which will reduce the CAPEX of the CO_2-capture system.

Heat Transfer Coefficient

The overall heat transfer coefficient for shell and tube heat exchangers can be calculated from Equation 1.[3]

$$U_o = \frac{1}{\frac{1}{h_o} + R_{do} + \frac{xA_o}{k_w A_{wm}} + \left(\frac{1}{h_i} + R_{di}\right) A_o/A_i} \qquad \text{Equation 1}$$

where h_0 and h_i are individual film heat-transfer coefficients, R_{do} and R_{di} are fouling resistances; and (xA_0/k_wA_{wm}) is wall resistance.

Two separate methods were used to calculate individual film heat-transfer coefficients for tube and shell sides.

Shell-Side Individual Film Heat-Transfer Coefficient

Shell-side heat-transfer coefficient for an ideal tube bank h_k can be determined from Equation 2.[3]

$$h_k = j_k c \frac{W}{S_m} \left(\frac{k}{c\mu}\right)^{2/3} \left(\frac{\mu_b}{\mu_w}\right)^{0.14} \qquad \text{Equation 2}$$

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[3] Green, D.; Perry, R.“Perry’s Chemical Engineering Handbook, 8th edition”.

where j_k is the factor determined from the correlation for j-factor for and ideal tube bank (Figure 9), c is specific heat, k is the thermal conductivity, μ_b is bulk viscosity of the solvent, μ_w is viscosity evaluated at the mean surface temperature, W is mass flow rate, and S_m is one cross-flow section.

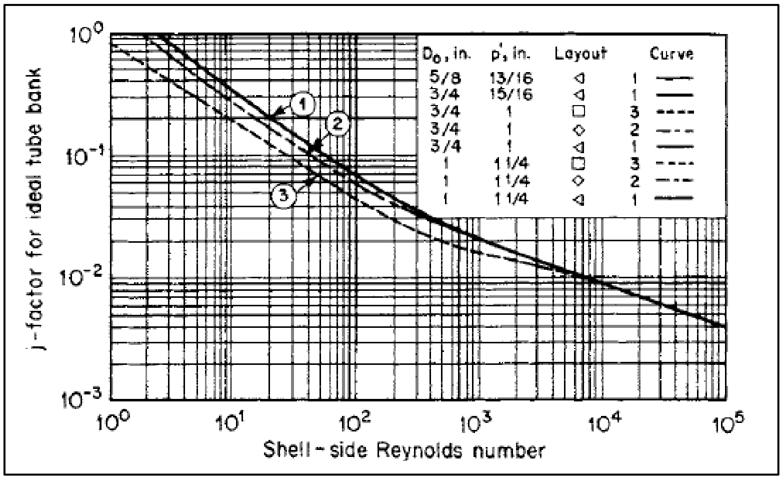

Figure 111. Correlation of j factor for ideal tube bank.[3]

The shell side Reynolds number can be determined from Equation 3.[3]

$$(N_{Re})_s = D_o W / \mu_b S_m \qquad \text{Equation 3}$$

Steps for calculation of shell-side heat transfer coefficient are described below.

1) Identify assumptions for these calculations:
    a. Reynolds number on the shell side for MEA and GAP-1m/TEG system is the same, and equals 1,000.
    b. Ratio of bulk-to-wall viscosity is assumed to be 10. Due to the higher temperature of the wall surface versus bulk, the viscosity will be lower at the surface. The estimated value has little impact on the heat transfer coefficient due to the small exponent in Equation 2. Ten was chosen as a conservative estimate.
    c. Tube diameter is 1.5 inch.

2) Calculate ratio of W/S_m from Equation 3.

3) Find j_k value from the plot in **Figure 111**.

4) Substitute physical properties of the solvent, value of j_k, and the value of W/S_m into the equation 2 to find h_o.

Tube-Side Individual Film Heat-Transfer Coefficient

The tube side heat transfer coefficient for circular tubes can be determined from the following Nusselt number correlation for laminar flow.[4]

$$Nu = 1.86(Re\mathrm{Pr})^{0.33}(\frac{d}{L})^{0.33}(\frac{\mu_{wall}}{\mu_{bulk}})^{0.14} \qquad \text{Equation 4}$$

Also, Nusselt number can be correlated to the heat transfer coefficient h through the following expression.[5]

$$Nu = \frac{hd}{12k} \qquad \text{Equation 5}$$

Below are the steps for the calculation of the tube-side heat transfer coefficient.

1) Identify assumption for these calculations:
    a. Reynolds number on the tube side for MEA and GAP-1m/TEG system is the same, and it equals 1,000 (laminar flow). This number was selected as a moderate value corresponding to a flow of ~ 10 ft./sec.
    b. Tube diameter is 1.5 in.
2) Calculate Prandtl number for each solvent system.
3) Calculate Nusselt number from Equation 4.

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[4] Towler, G.; Sinnott, R. "Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design".

[5] "Simplified Approach to Estimating Tube Side Heat Transfer Coefficients", http://vganapathy.tripod.com/tubeht.html.

4) Calculate h_i from Equation 5.

Overall Heat-Transfer Coefficient

The overall heat transfer coefficient can be calculated from Equation 1, and below are the steps for calculations.

1) Identify assumptions for these calculations:
    a. Thickness of the pipe wall is 0.25 in.
    b. Pipe material is carbon steel.
    c. Fouling coefficient is 5,000 $W/m^2 \cdot K$

2) Use Equation 1 to determine overall heat transfer coefficient, U.

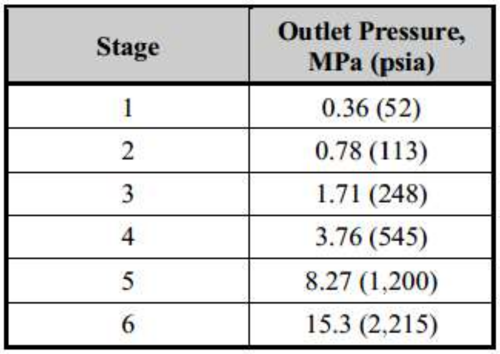
These calculations were used to determine the overall heat transfer coefficients for a 30/70 MEA/water system and to compare it to the 60/40 GAP-1m/TEG system. The values of overall heat transfer coefficient for 60/40 GAP-1m/TEG and 30/70 MEA/water are 75 and 93 $Btu/(hr \cdot ft^2 \cdot F)$, respectively.

It has to be noted that this value of U is specific to the assumptions made and considered conditions. Due to the high viscosity of the rich GAP-1m/TEG solvent, turbulent flow might be a challenge for the tube side of the heat exchanger, and pressure drop would also need to be considered for the final design. So, a velocity in the laminar regime was chosen. To increase the overall heat transfer, shell-side Reynolds number can be potentially increased.

Compression Train

The purpose of the compression train it to deliver a high-purity CO_2 stream at 2215 psia for transportation and storage. The discharge pressures at each stage are presented in **Table 43**.

Table 43. The outlet pressures at each stage in the compression train



Stage	Outlet Pressure, MPa (psia)
1	0.36 (52)
2	0.78 (113)
3	1.71 (248)
4	3.76 (545)
5	8.27 (1,200)
6	15.3 (2,215)

Since the desorber operates at 63 psia in the aminosilicone-based process, the first stage of the compression train can be removed, significantly reducing the cost of the compression train. The pressurized gas stream is cooled to 40 °C after each compressor with cooling water and all liquid condensate is removed in a vapor/liquid flash separator. Cooling water is supplied from the power plant cooling tower system. The compressors at each stage have a polytropic efficiency of 86% and mechanical efficiency of 98%.

The final CO_2 stream has to satisfy the conceptual design limits for enhanced oil recovery as listed in Exhibit 2-1 of the NETL QGESS titled “CO_2 Impurity Design Parameters”.[6] aminosilicone base-case model.

Table 44 shows the required specifications for the product CO_2 stream. Table 10 also shows the composition of the CO_2 stream for the aminosilicone base-case model.

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[6] Quality Guidelines for Energy System Studies, “Cost Estimation Methodology for NETL Assessments of Power Plant Performance”, DOE/NETL-2011/1455.

Table 44. Case H CO_2 stream outlet composition as compared to EOR specifications

Component	Unit	Enhanced Oil Recovery specification		CASE H
		Conceptual design	Range in Literature	
CO_2	Vol % (min)	95	90-99.8	99.39
H_2O	ppm_v	500	20-650	812
N_2	Vol%	1	0.01-2	<0.01
O_2	Vol%	0.001	0.001-1.3	<0.001
Ar	Vol%	1	0.01-1	0

It can be seen that final high pressure CO_2 stream generated by the aminosilicone-based process has slightly higher water amount than the EOR specifications. In future work the amount of cooling will be increased in order to match specification limits.

Multiple cases were considered for technical and economic analysis, and below is the summary table of all cases with specific conditions.

Table 45. Summary of major cases considered for the aminosilicone-based CO_2 separation system

	Absorber intercoolers (Y/N)	*Number of absorbers*	*Intercooler load (each)*	*Desorber T,°F*	*Desorber P (psia)*	*Number of desorbers*	*Absorber packing type*	*Packing material*	*Sulfur in FG (ppm)*
Case A	N	4	NA	284 °F	63	2	Rachig rings	CS	5
Case B	Y	4	30 MW	284 °F	63	2	Rachig rings	CS	5
Case C	Y	4	60 MW	284 °F	63	2	Rachig rings	CS	5
Case D	Y	4	60 MW	284 °F	63	2	MellapakPL 252Y	CS	5
Case E	Y	4	60 MW	266 °F	63	2	MellapakPL 252Y	CS	5
Case F	Y	3	80 MW	266 °F	63	2	MellapakPL 252Y	CS	5
Case G	Y	3	80 MW	266 °F	63	2	MellapakPL 252Y	CS	5

Case G was scaled up to 552 MW net power including the CO_2-capture island to generate Case H.

The CO_2-capture system block flow diagram scaled–up to 552 MW net power for Case H is presented on **Figure 112** and the corresponding stream table is presented in **Table 45**.

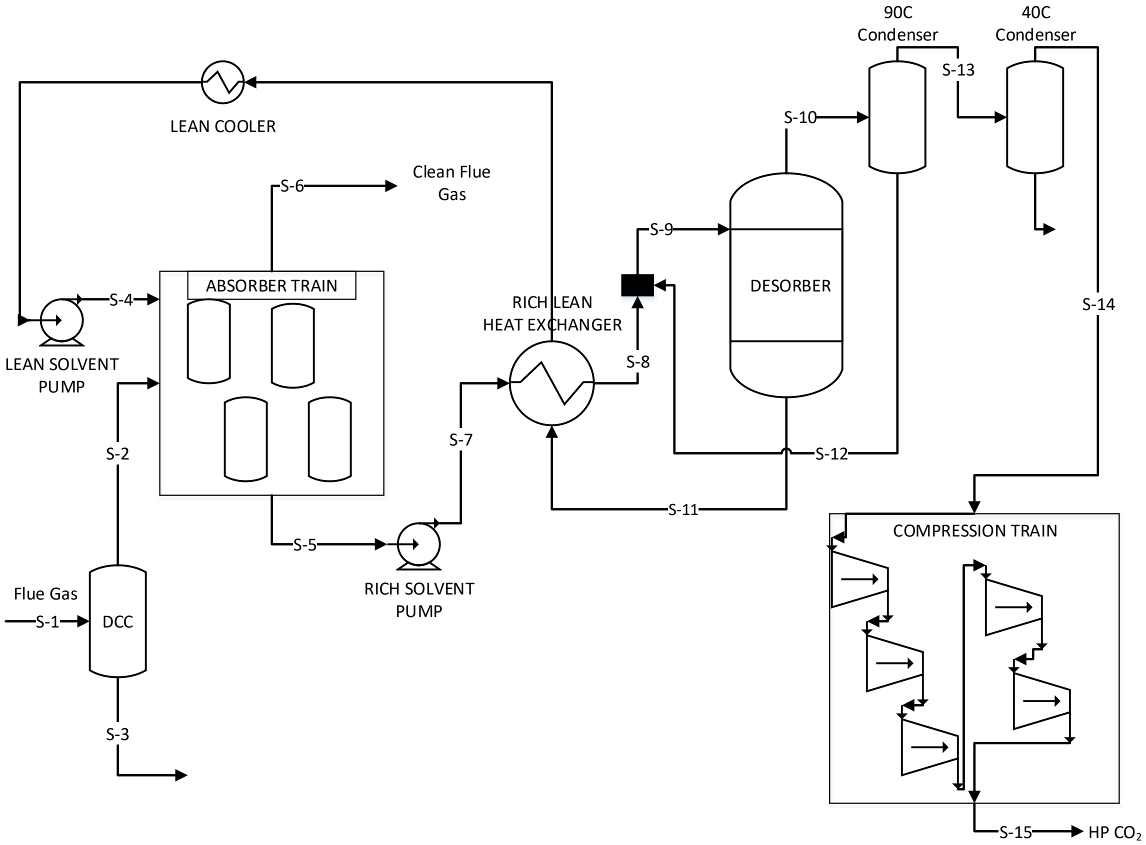

Figure 112. Block flow diagram of CO_2-capture system for Case H

Table 46. Stream table for CO_2-capture system for Case H.

Stream Number	**S-1**	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**
Mole Fraction								
H_2O	0.1517	0.0731	0.9999	0.2420	0.2820	0.0436	0.2820	0.2820
CO_2	0.1353	0.1478	0.0001	0.0090	0.0007	0.0192	0.0007	0.0007
N_2	0.6890	0.7528	0.0000	0.0001	0.0010	0.9057	0.0010	0.0010
O_2	0.0240	0.0262	0.0000	0.0000	0.0000	0.0316	0.0000	0.0000
GAP1	0.0000	0.0000	0.0000	0.2190	0.0215	0.0000	0.0215	0.0215
GAP1CARB	0.0000	0.0000	0.0000	0.0789	0.2631	0.0000	0.2631	0.2631
TEG	0.0000	0.0000	0.0000	0.4510	0.4317	0.0000	0.4317	0.4317
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Total Flow lbmol/hr.	212,156	194,164	17,992	136,228	142,321	161,256	142,321	142,321
Total Flow lb./hr.	6,100,920	5,776,755	324,165	23,414,975	24,648,212	4,516,809	24,648,212	24,648,212
Temperature F	135	104	104	104	122	128	123	240
Pressure psia	14.7	14.7	14.7	15	14.7	14.7	93	93
Vapor Frac	1	1	0	0	0	1	0	0
Enthalpy Btu/lb.	-1329.5	-1089.4	-6791.9	-2272.7	-2407.9	-264.7	-2407.7	-2350.2
Density lb./cuft	0.066	0.072	61.142	56.338	58.046	0.065	58.025	53.743
Average MW	28.757	29.752	18.017	171.881	173.187	28.010	173.187	173.187

Stream Number	S-9	S-10	S-11	S-12	S-13	S-14	S-15
Mole Fraction							
H_2O	0.2853	0.1629	0.2574	0.8924	0.1444	0.0170	0.0008
CO_2	0.0007	0.8299	0.0085	0.0020	0.8509	0.9778	0.9939
N_2	0.0010	0.0044	0.0000	0.0000	0.0045	0.0052	0.0053
O_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GAP1	0.0218	0.0018	0.2159	0.0689	0.0001	0.0000	0.0000
GAP1CARB	0.2618	0.0006	0.0757	0.0244	0.0000	0.0000	0.0000
TEG	0.4294	0.0003	0.4424	0.0122	0.0000	0.0000	0.0000
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Total Flow lbmol/hr.	143,095	31,144	138,883	774	30,370	26,423	25,991
Total Flow lb./hr.	24,686,221	1,259,768	23,426,717	38,009	1,221,759	1,148,988	1,141,107
Temperature F	240	266	266	194	194	104	124
Pressure psia	63	63	63	63	63	63	2215
Vapor Frac	0	1	0	0	1	1	1
Enthalpy Btu/lb.	-2352.1	-3887.1	-2202.7	-3549.3	-3927.6	-3839.2	-3822.1
Density lb./cuft	53.705	0.327	50.617	43.516	0.361	0.453	15.526
Average MW	172.517	40.450	168.680	49.124	40.229	43.484	43.904

5.2.4. System Utilities for CO_2 Capture Process

The CO_2 capture process adds additional auxiliary load on coal power plants, and the main contributors are solvent pumps, CO_2 compressors, flue gas blowers, cooling water fans and pumps. **Table 47** shows the power summary for Case H of the CO_2-capture system. It should be noted that the main feed-gas blower is part of the power plant, and only the additional power to increase the flue gas pressure to the required inlet pressure of the CO_2-capture process is shown in Table 13. The cooling tower is also part of the power plant, and its operation and capital costs are included in the power plant island costs. Therefore, the table shows only the power for the cooling water pumps, which deliver water from the cooling tower to the CO_2-capture process. CO_2 separation auxiliaries include lean and rich solvent pumps.

Table 47. Power summary for Case H

POWER SUMMARY	
AUXILIARY LOAD SUMMARY, kWe	
Feed Gas Blower	911
CO_2 Separation Auxiliaries	2,098
CO_2 Compression	43,088
Cooling Water Pumps	6,866
TOTAL AUXILIARIES, kWe	52,963
COOLING WATER, ton/hr.	45,600
STEAM, ton/hr.	750

5.3. CO_2 Separation Unit Key Assumptions

The CO_2-seperation process model used the following design assumptions given in Case 11 of DOE NETL Bituminous Baseline Study.[1]

1) Composition of flue gas leaving the FGD (wet basis) is shown in Table 14.

2) The flow rate of flue gas leaving the FGD (based on DOE Case 11 550 MW net supercritical PC plant): 4,713,221 lb./hr. The flow rate for the scaled-up cases varied due to differences in overall plant efficiency with the various CO_2-capture system configurations.

3) Pressure and temperature of flue gas leaving FGD: 14.8 psia and 135 °F

4) Conditions for LP steam available from power plant: 556 °F (base case, sensitivity was conducted with respect to steam conditions)

5) Conditions for cooling water: feed = 60 °F, return = 80 °F with a minimum approach of 30 °F (sensitivity was conducted with respect to cooling water conditions)

6) CO_2 removal from flue gas: greater than 90%

7) CO_2 purity: greater than 95 vol%

8) CO_2 delivery pressure and temperature: 2,215 psia and 124 °F

The MEA and aminosilicone-based solvent baseline models are based on a typical temperature-swing sorbent separation process. The systems have four process variables that dominate the performance with a given sorbent and they are absorber temperature, desorber temperature, desorber pressure, and rich-lean heat exchanger approach temperature. The system models account for the major energy penalties for CO_2 separation, and they include the energy required:

(1) for vaporization of water

(2) to desorb the carbon dioxide (i.e., reaction energy)

(3) for sensible heating of the sorbent

The energy is supplied by feeding steam to the desorber unit. The models also account for CO_2-compression energy and auxiliary loads.

The sorbent-rich loading is defined as the weight % of CO_2 in the rich sorbent leaving the absorber column. The sorbent lean loading is defined as the weight % of CO_2 in the lean sorbent leaving the desorber column. The sorbent net loading is defined as the difference between the rich loading and the lean loading and was obtained from bench-scale experiments for the GAP-1m/TEG system.

A detailed MEA Aspen Plus^{TM} model that was built under this project was used to compare the results for this study.

The main features of the MEA model include an absorber, rich-lean heat exchanger, and a desorber. The same unit operations are important for the GAP-1m/TEG system. The baseline MEA case is built from the description given in the Bituminous Baseline Study.[1] **Figure 113** shows a comparison of the plant efficiency reported for Case 12 in the Bituminous Baseline Study with the plant efficiency calculated using GE Global Research's models for MEA and the power plant.

Table 48. Flue gas composition leaving FGD

	Volume %
CO_2	13.53
H_2O	15.17
N_2	68.9
O_2	2.40
	ppmv
SOx	5-42
NOx	74

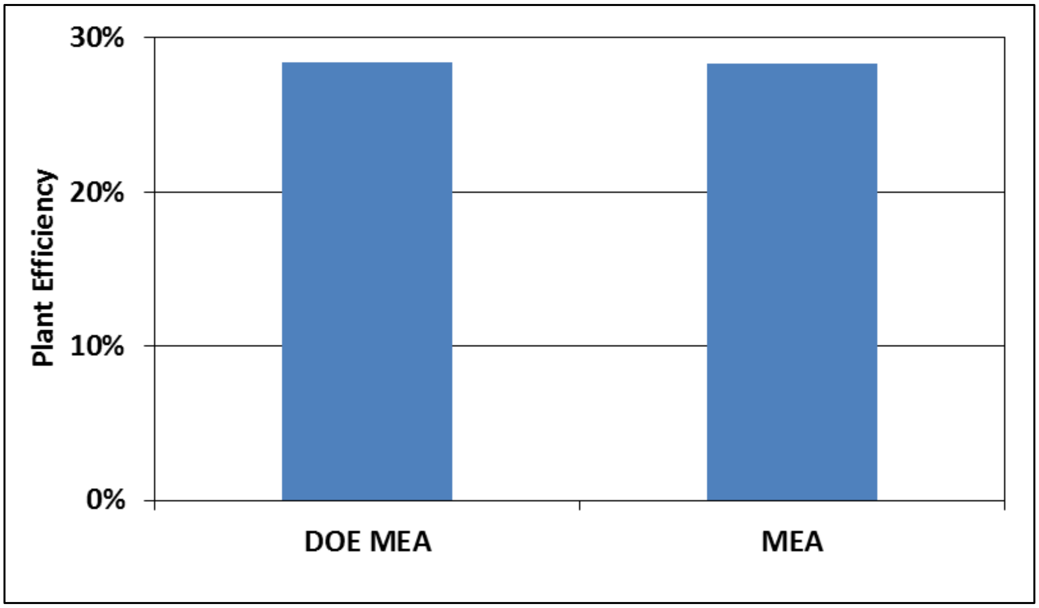

Figure 113. Comparison of estimated plant efficiency of CO_2 capture system using MEA vs. DOE estimated efficiency.

5.3.1. Studies of Integrated Power Plant with CO2-Capture Plant

A number of different process options were studied for the aminosilicone-based CO_2 capture system. **Table 49** lists the modifications that were made from Case A to Case L.

Table 49. List of major cases for CO_2 capture system using aminosilicones

MEA	Base MEA (DOE Case 11 w CC and, Case 12)
Aminosilicone Cases	
Case A	284 °F, 63 psia
Case B	Added Absorber Intercoolers
Case C	Increased Intercooling
Case D	Structured Packing
Case E	Reduced Desorber Temperature
Case F	Reduced Number of Absorbers
Case G	Reduced Absorber Diameter
Scaled Up Aminosilicone Cases	
Case H	Scaled to 550 MW Net / CSTR
Case I	Cooling Water Integration / CSTR
Case J	Waste Heat Recovery / CSTR
Case K	Low Pressure Desorption / CSTR
Case L	Low Pressure Desorption / Steam Stripper Column

Figure 114 shows the plant efficiency for the different cases as compared to Case 12 in the DOE NETL Bituminous Baseline Study.[1] The plant efficiency for Case G is 30.1% as compared to 28.4% for the case using MEA. After scaling up the power island and the carbon-capture island to 550 MW net power, two more cases were evaluated that utilized heat integration between the two islands. The efficiency of the best case was improved to 30.4% by utilizing the heat integration strategies. The plant efficiency for Case L is 30.4 %, assuming a decrease in CAPEX by 25% vs. Case K due to an increase in working capacity with the steam stripper column and reduced desorption temperature. **Figure 115** shows the energy penalty for each case.

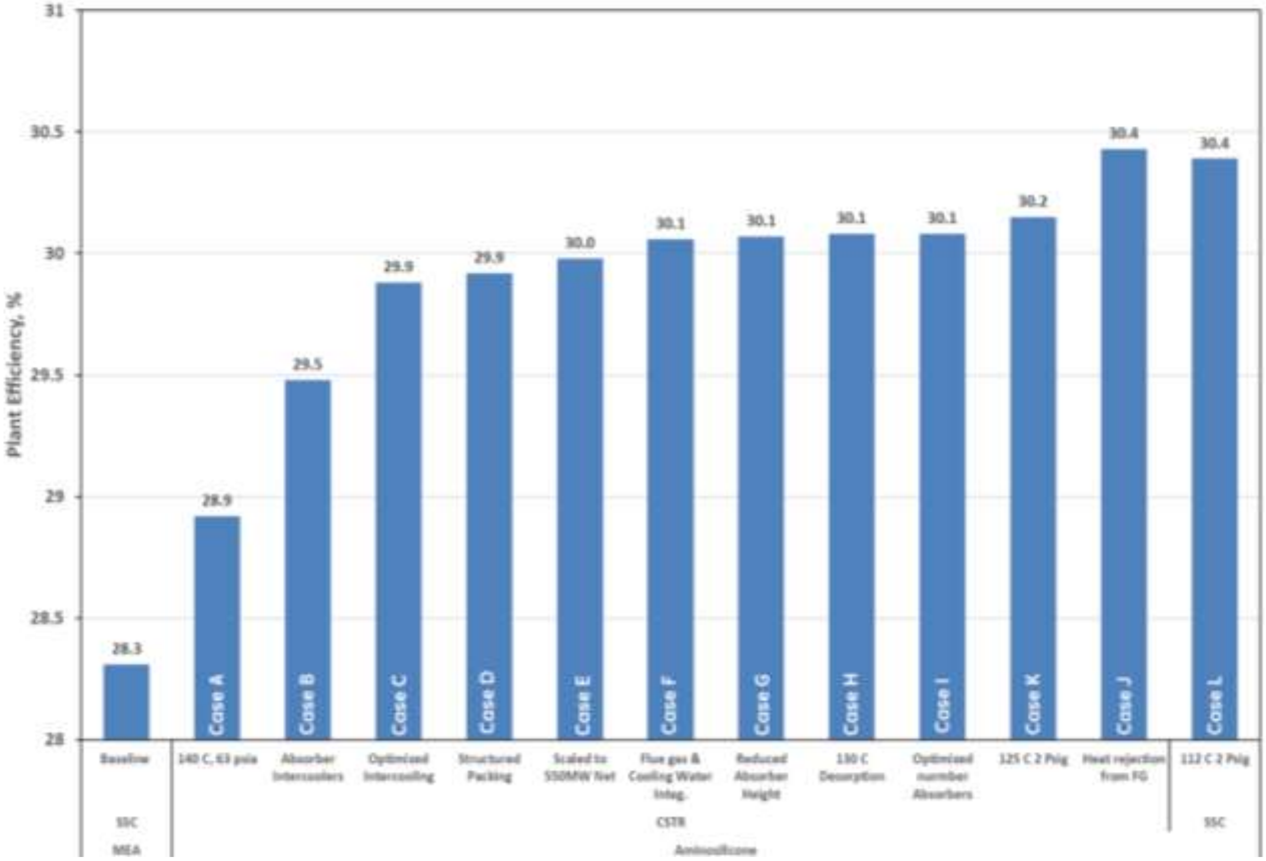

Figure 114. Plant efficiency of for each case

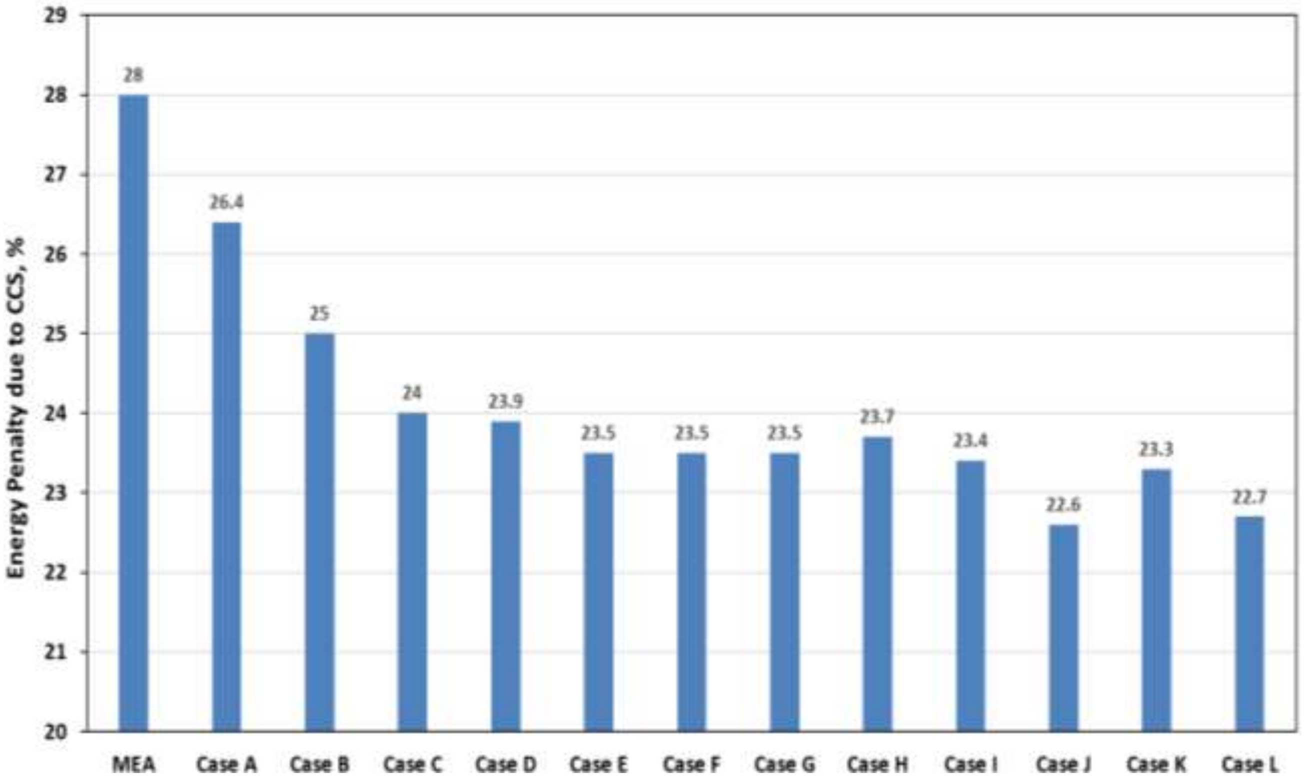

Figure 115. Energy penalty due to CO_2-capture system for each case

5.3.2. Steam Reboiler Factor

One of the most important factors that determines the energy penalty using carbon capture is the steam penalty. A steam penalty factor in kWh/lb. can be calculated based on the steam condition that is used in the carbon capture island. The energy penalty of carbon capture on a power plant is highly dependent on this factor and hence the steam extraction conditions. This factor was calculated by power plant modeling in Thermoflow and was estimated at 0.076 kWh/lb. and 0.074 kWh/lb. if steam is extracted at 571.4 °F/75 psia and 530.9 °F/60 psia for desorber operating temperatures of 284 °F and 266 °F, respectively. The effect of this factor can be seen in the plant efficiency in Figure 12 between Case D and Case E.

After the power plant model was calibrated to Case 11, it was altered to allow for integration with the carbon capture process. One of the larger interactions between the power block and the carbon capture models is the export of process steam for use in the capture plant's desorber. Extracting such a large amount of steam has a significant impact on the design of the power cycle. In the model calibrated to Case 11, the low-pressure (LP) steam flow was sufficient to require a 4-flow low-pressure steam turbine. In the case with carbon capture almost half of the LP steam flow is diverted to the carbon-capture plant and thus only a 2-flow LP steam turbine is required. The selection of a 2-flow LP steam turbine over a 4-flow makes a large difference to steam turbine cost (~$60MM). Additionally, the selection of the crossover pressure is heavily influenced by the CO_2-capture process steam extraction. The desorber in the carbon-capture plant is designed to extract the maximum amount of heat from the process steam by condensing it to a saturated liquid. This sets a minimum steam pressure that can be utilized. If steam were extracted at too low of a pressure, it would not condense at the operating temperatures of the desorber, and a significantly larger extraction of steam would be required. Extracting steam above the minimum pressure doesn't yield significant cost savings, and is worse from a performance perspective, so the operating temperature of the desorber directly sets the optimum crossover pressure in the power block. Because of this, the desorber operating temperature was reduced from 284 °F to 266 °F (Case D to Case E) in order to allow an extraction of steam at a lower pressure, for an improvement in cycle efficiency. In this design, the steam side of the desorber operates at 54 psia, so the crossover pressure was selected to be 60 psia.

The condensate water returning from the desorber is still warm, but is only available at a low pressure. Returning the condensate to the condenser would be a waste of valuable heat, and would drive up the cooling tower duty. Alternatively, the condensate could be used for feedwater heating, either by passing it through the hot side of one or more feedwater heaters before returning it to the condenser, or by pumping the condensate to a high enough pressure to be admitted to the de-aerating feedwater heater. In this model it was selected to return the condensate to the de-aerating feedwater heater, but further optimization of this aspect of the design may be possible.

It is also important to consider an optimization of equipment affecting the flow of flue gases to the CO_2-capture equipment. Sulfur content in the exhaust gases has a detrimental effect on CO_2-capture hardware and solvents, so additional flue gas desulfurization equipment in the power block can be justified based on a reduction in maintenance and material costs for the CO_2-capture plant. Increasing the effectiveness of the flue gas desulfurization system comes at a cost of both increased capital costs and increased auxiliary loads. In the design of this plant the flue gas sulfur content was optimized in order to minimize the cost of CO_2-capture. Initially the flue gas desulfurization system was designed to leave 42 ppm of SO_2 in the flue gas. In order to decrease the amount of SO_2, the cost of flue gas desulfurization equipment increases significantly. The optimal point for minimized CO_2capture cost was found at 5 ppm of sulfur. **Figure 116** shows the cost and auxiliary load deltas that were found during the optimization of the flue gas desulfurization system.

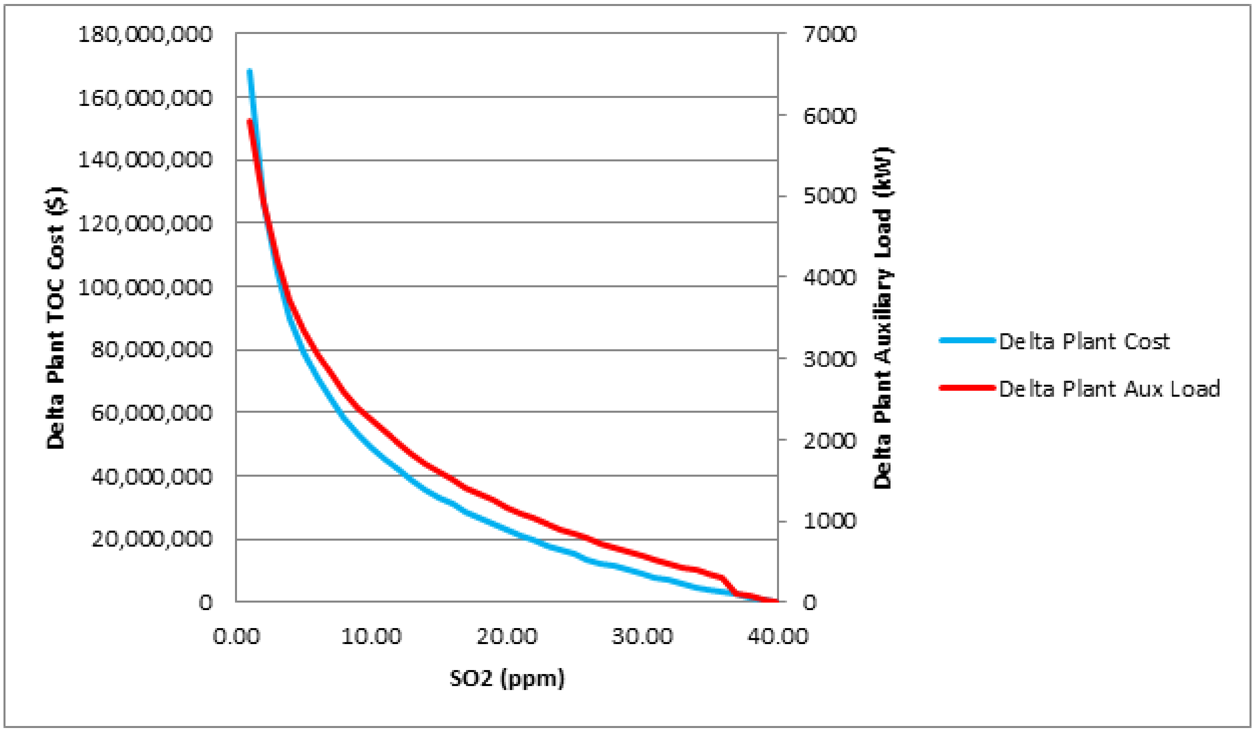

Figure 116. Flue gas desulfurization optimization

Detailed process flow information for each stream in Case H (Case G scaled to 550 MW net) is provided in **Table 50**. The stream numbers in **Table 50** are in reference to the simplified block diagram in **Figure 104**, and are consistent with the numbering scheme shown for the case without CO_2 capture.

Table 50. Stream properties from power plant modeling of Case H. The stream numbers correspond to the block flow diagram shown in **Figure 104**

	1	2	3	4	5	6	7
V-L Mole Fraction							
Ar	0.0093	0.0093	0.0093	0.0093	0.0000	0.0000	0.0088
CO_2	0.0003	0.0003	0.0003	0.0003	0.0000	0.0000	0.1485
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0101	0.0101	0.0101	0.0101	0.0000	0.0000	0.0893
N_2	0.7729	0.7729	0.7729	0.7729	0.0000	0.0000	0.7310
O_2	0.2074	0.2074	0.2074	0.2074	0.0000	0.0000	0.0202
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0022
Total	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	1.0000
V-L Flowrate (lbmol/hr)	139,244	139,244	42,774	42,774	-	-	192,772
V-L Flowrate (lb./hr.)	4,017,852	4,017,852	1,234,242	1,234,242	-	-	5,737,068
Solids Flowrate (lb./hr.)	-	-	-	-	538,439	10,686	42,744
Temperature (°F)	59	65	59	77	59	-	342
Pressure (psia)	14.7	15.1	14.7	16.2	14.7	-	14.3
Enthalpy (Btu/lbm)	-4.3	-3.0	-4.3	0.1	-	-	69.2
Density (lb/ft^3)	0.076	0.078	0.076	0.081	-	-	0.047
V-L Molecular Weight	28.85	28.85	28.85	28.85	-	-	29.76

	8	9	10	11	12	13	14
V-L Mole Fraction							
Ar	0.0000	0.0088	0.0088	0.0000	0.0093	0.0000	0.0000
CO_2	0.0000	0.1485	0.1485	0.0000	0.0003	0.0000	0.0004
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0000	0.0893	0.0893	1.0000	0.0101	1.0000	0.9996
N_2	0.0000	0.7310	0.7310	0.0000	0.7729	0.0000	0.0000
O_2	0.0000	0.0202	0.0202	0.0000	0.2074	0.0000	0.0000
SO_2	0.0000	0.0022	0.0022	0.0000	0.0000	0.0000	0.0000
Total	0.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (lbmol/hr.)	-	192,772	192,772	20,917	3,052	11,339	467
V-L Flowrate (lb/hr.)	-	5,737,068	5,737,068	376,920	88,056	204,322	8,424
Solids Flowrate (lb/hr.)	42,744	-	-	-	-	45,194	75,672
Temperature (°F)	-	342	362.9	59	59	59	0
Pressure (psia)	-	13.84	15.06	14.7	14.7	14.7	0.0
Enthalpy (Btu/lbm)	-	69.2	74.7	27.1	-4.3	-	-
Density (lb/ft^3)	-	0.046	0.048	62.379	0.076	-	-
V-L Molecular Weight	-	29.76	29.76	18.02	28.85	-	18.03

	15	16	17	18	19	20	21
V-L Mole Fraction							
Ar	0.0081	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO_2	0.1372	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.1577	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
N_2	0.6766	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O_2	0.0204	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (lbmol/hr.)	211,766	266,843	221,783	221,783	197,442	83,241	197,442
V-L Flowrate (lb/hr.)	6,100,922	4,808,520	3,996,538	3,996,538	3,557,905	1,500,000	413,566
Solids Flowrate (lb/hr.)	-	-	-	-		-	-
Temperature (°F)	132	1100	663	1100	531	528	531
Pressure (psia)	14.7	3514.7	693.7	655.8	60.0	54.1	60.0
Enthalpy (Btu/lbm)	14.9	1495.0	1323.2	1570.5	1298.3	1297.3	1298.3
Density (lb/ft^3)	0.063	4.319	1.143	0.722	0.103	0.093	0.103
V-L Molecular Weight	28.81	18.02	18.02	18.02	18.02	18.02	18.02

	22	23	24	25
V-L Mole Fraction				
Ar	0.0000	0.0000	0.0000	0.0000
CO_2	0.0000	0.0000	0.0000	0.0000
H_2	0.0000	0.0000	0.0000	0.0000
H_2O	1.0000	1.0000	1.0000	1.0000
N_2	0.0000	0.0000	0.0000	0.0000
O_2	0.0000	0.0000	0.0000	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000
Total	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (lbmol/hr.)	75,343	115,437	83,241	197,442
V-L Flowrate (lb/hr.)	1,357,682	2,080,170	1,500,000	4,808,520
Solids Flowrate (lb/hr.)	-	-	-	-
Temperature (°F)	101	107	286	557
Pressure (psia)	1.0	258.5	133.6	4185.2
Enthalpy (Btu/lbm)	1023.5	75.2	255.5	552.9
Density (lb/ft^3)	0.003	61.959	57.758	47.687
V-L Molecular Weight	18.02	18.02	18.02	18.02

Table 51 summarizes power output from the power plant along with materials consumed during normal operation for Case H. It includes a detailed summary of auxiliary loads and how they contribute with the steam turbine power and CO_2 capture and compression loads to impact the total plant net power output and efficiency.

Table 51. Power summary from power plant modeling of Case H

POWER SUMMARY (Gross Power at Generator Terminals, kWe)	
Steam Turbine Power	647,695
Total (Steam Turbine) Power, kWe	**647,695**
Auxiliary Load Summary, kWe	
Boiler Fuel Delivery	4,221
Ash handling	694
Primary Air Fans	1,783
Forced Draft Fans	2,000
Induced Draft Fans	9,746
Baghouse (ESP)	91
Wet FGD	11,857
CO_2 Island Auxiliaries	9,875
CO_2 Compression	43,088
Miscellaneous BOP	118
ST Auxiliaries	446
Condensate Pumps	699
Circulating Water Pumps	3,142
Cooling Tower Fans	5,262
Transformer Losses	2,031
BFP Booster Pump	652
Total Auxiliaries, kWe	**42,743**
Net Power, kWe	**551,989**
Net Plant Efficiency (HHV)	30.0%
Net Plant Heat Rate, (Btu/kWh)	10,383
Condenser Cooling duty, (10^6 Btu/hr.)	3,544
Consumables	
As-Received Coal Feed, (lb/hr.)	538,439
Limestone Sorbent Feed, (lb/hr.)	45,180
Thermal Input (kWt)	1,840,906
Raw Water Consumption (gpm)	6,740

The net power for Case H is calculated to be ~552MW.

The cost summary for the power plant model with CO_2 capture (Case H) is shown in **Table 52**. The total cost of the power block increased by ~$333MM over the case without CO_2 capture.

Table 52. Equipment cost summary from power plant modeling of Case H

	$	$/kW
Specialized Equipment	**$ 609,811,487**	**$ 1,105**
Boiler	**$ 234,107,909**	**$ 424**
Furnace	$ 101,283,882	$ 183
Convective Elements	$ 65,610,249	$ 119
Additional Waterwall	$ 7,507,987	$ 14
Soot Blowers	$ 6,098,788	$ 11
Desuperheaters and Controls	$ 10,253,053	$ 19
Air and Flue Gas Ducts	$ 7,467,654	$ 14
Coal Pulverizers and Feeders	$ 24,580,927	$ 45
FD Fan, PA Fan, ID Fan	$ 3,878,047	$ 7.0
Structural Steel, Ladders, Walkways	$ 3,064,060	$ 5.6
Rotary Air Heaters	$ 4,363,261	$ 7.9
Steam Turbine	**$ 89,908,464**	**$ 163**
Feedwater Heaters	**$ 11,359,687**	**$ 21**
Feedwater Heater 1	$ 542,457	$ 1.0
Feedwater Heater 2	$ 527,972	$ 1.0
Feedwater Heater 3	$ 527,728	$ 1.0
Feedwater Heater 4	$ 537,078	$ 1.0
Feedwater Heater 5-DA	$ 895,946	$ 1.6
Feedwater Heater 6 (6A,6B)	$ 2,390,574	$ 4.3
Feedwater Heater 7 (7A,7B)	$ 2,764,842	$ 5.0
Feedwater Heater 8 (8A,8B)	$ 3,173,090	$ 5.7
Water Cooled Condensers	**$ 3,201,005**	**$ 5.8**
Main Condenser	$ 2,467,013	$ 4.5
Feed Pump Turbine Condenser	$ 733,991	$ 1.3
Particulate and Mercury Control	**$ 26,720,630**	**$ 48**

Flue Gas Desulfurization	**$ 151,257,175**	**$ 274**
Nitrogen Oxide Control (SCR)	**$ 52,211,298**	**$ 95**
Stack	**$ 10,733,066**	**$ 19**
Continuous Emissions Monitoring System	**$ 627,300**	**$ 1.1**
Distributed Control System	**$ 1,737,273**	**$ 3.1**
Transmission Voltage Equipment	**$ 16,574,415**	**$ 30**
Transformers	$ 14,739,549	$ 27
Circuit Breakers	$ 1,045,579	$ 1.9
Miscellaneous Equipment	$ 789,287	$ 1.4
Generating Voltage Equipment	**$ 11,373,267**	**$ 21**
Generator Buswork	$ 5,935,887	$ 11
Circuit Breakers	$ 4,895,854	$ 8.9
Miscellaneous Equipment	$ 541,526	$ 1.0
Other Equipment	**$ 154,572,349**	**$ 280**
Pumps	**$ 15,195,073**	**$ 28**
Boiler Feed Pump (+ Turbine)	$ 11,234,334	$ 20
Boiler Feed Booster Pump	$ 173,367	$ 0.3
Condenser C.W. Pump	$ 1,858,945	$ 3.4
Condensate Forwarding Pump	$ 377,533	$ 0.7
Condenser Vacuum Pump	$ 398,799	$ 0.7
Aux Cooling Water Pump (Closed Loop)	$ 43,656	$ 0.1
Treated Water Pump	$ 7,199	$ 0.01
Diesel Fire Pump	$ 172,817	$ 0.3
Jockey Fire Pump	$ 5,182	$ 0.01
Demin Water Pump	$ 14,251	$ 0.03
Raw Water Pumps	$ 34,857	$ 0.1
Aux Cooling Water Pump (Open Loop)	$ 43,656	$ 0.1
Startup Boiler Feed Pump	$ 830,475	$ 1.5
Tanks	**$ 1,052,452**	**$ 1.9**
Hydrous Ammonia	$ 168,509	$ 0.3
Demin Water	$ 116,820	$ 0.2
Raw Water	$ 395,305	$ 0.7

Neutralized Water	$ 86,820	$ 0.2
Acid Storage	$ 36,341	$ 0.1
Caustic Storage	$ 36,341	$ 0.1
Dedicated Fire Protection Water Storage	$ 212,316	$ 0.4
Cooling Tower	**$ 15,094,192**	**$ 27**
Auxiliary Cooling Water Heat Exchanger	**$ 152,969**	**$ 0.3**
Steam Turbine Crane	**$ 1,403,592**	**$ 2.5**
Station Instrument Air Compressors	**$ 955,936**	**$ 1.7**
General Plant Instrumentation	**$ 446,686**	**$ 0.8**
Medium Voltage Equipment	**$ 8,499,153**	**$ 15**
Transformers	$ 1,225,828	$ 2.2
Circuit Breakers	$ 501,147	$ 0.9
Switchgear	$ 2,149,781	$ 3.9
Motor Control Centers	$ 4,217,678	$ 7.6
Miscellaneous	$ 404,719	$ 0.7
Low Voltage Equipment	**$ 2,328,973**	**$ 4.2**
Transformers	$ 822,781	$ 1.5
Circuit Breakers	$ 670,152	$ 1.2
Motor Control Centers	$ 725,143	$ 1.3
Miscellaneous	$ 110,898	$ 0.2
Coal Handling Equipment	**$ 77,179,135**	**$ 140**
Ash Handling Equipment	**$ 24,903,817**	**$ 45**
Miscellaneous Equipment	**$ 7,360,371**	**$ 13**

Civil	**$ 105,551,677**	**$ 191**
Site Work	$ 19,774,449	$ 36
Excavation and Backfill	$ 6,839,480	$ 12
Concrete	$ 77,768,896	$ 141
Roads Parking and Walkways	$ 1,168,852	$ 2.1

Mechanical	**$ 332,077,085**	**$ 602**
On Site Transportation and Rigging	$ 11,121,067	$ 20
Equipment Erection and Assembly	$ 239,556,407	$ 434
Piping	$ 78,972,668	$ 143
Steel	$ 2,426,944	$ 4.4

Electrical Assembly and Wiring	**$ 30,318,365**	**$ 55**
Controls	$ 18,598,808	$ 34
Assembly and Wiring	$ 11,719,557	$ 21

Buildings and Structures	**$ 22,448,094**	**$ 41**
Boiler House and Turbine Hall	$ 20,400,100	$ 37
Administration Control Room, Machine Shop, Warehouse	$ 2,021,483	$ 3.7
Guard House	$ 26,510	$ 0.05

Engineering and Plant Startup	**$ 56,170,844**	**$ 102**
Engineering	$ 45,503,738	$ 82
Start Up	$ 10,667,106	$ 19

Totals		
Subtotal Contractor's Internal Cost	**$ 1,310,949,901**	**$ 2,375**
Contractors Soft & Misc. Costs	$ 253,644,708	$ 460
Subtotal Contractor's Price	**$ 1,564,594,609**	**$ 2,834**
Owner's Soft and Misc. Costs	$ 293,990,948	$ 533
Total Owner's Cost	**$ 1,858,585,556**	**$ 3,367**

Table 53 shows the calculated annual costs for the power block configured for CO_2 capture. The fixed operating costs and the maintenance and material costs in this case were assumed to be equal to the values in DOE case 12 of the cost updates to the Bituminous Baseline Study.[2]

Table 53. Annual costs from power plant modeling of Case H

			Annual Cost	Annual Unit Cost
			$	$/kWh-net
Fixed Operating Costs			**$ 61,032475**	**$ 0.01262**
Maintenance Material Costs			$ 18,136,161	$ 0.00375
	Consumption / day	Unit Cost		
Water (/1000 gallons)	4,647	1.67	$ 2,407,817	$ 0.00050
Chemicals				
MU & WT Chem.(lbs.)	22,493	0.27	$ 1,884,197	$ 0.00039
Limestone (ton)	638	33.48	$ 6,625,304	$ 0.00137
Ammonia (19% NH_3) ton	97	330	$ 9,961,176	$ 0.00206
Subtotal Chemicals			$ 18,470,677	$ 0.00382
Other				
SCR Catalyst (m^3)	0.41	5775.94	$ 730,381	$ 0.00015
Subtotal Other			$ 730,381	$ 0.00015
Waste Disposal				
Total Ash (ton)	627	25.11	$ 4,882,568	$ 0.00101
Subtotal Waste Disposal			$ 4,882,568	$ 0.00101
Total Variable Operating Costs			**$ 26,491,442**	**$ 0.00548**
Fuel (ton)	6461	68.60	**$ 137,516,215**	**$ 0.02844**

Table 54 details the energy flows in and out of the control volume of the full power plant model with CO_2 capture.

Table 54. Energy balance from power plant modeling of Case H

	HHV	Sensible + Latent Heat	Power	Total
Heat In (MMBtu/hr.)				
Coal	6296			6296
Ambient Air		69.9		69.9
FGD Water		29.0		29.0
FGD Oxidation Air		6.6		6.6
Totals	6296	105		6401
Heat Out (MMBtu/hr.)				
Bottom Ash		5.8		5.8
Fly Ash + FGD Ash		2.3		2.3
Flue Gas		590		590
HP CO2		139		139
Unburned Carbon		17.4		17.4
Boiler Losses		55.3		55.3
Fuel Delivery Losses		2.9		2.9
Main Condenser		3124		3124
BFPT Condenser		410		410
Steam Piping Losses		14.3		14.3
ST/Generator Mech/Elec/Gear		25.0		25.0
BFPT Mech Losses		0.9		0.9
Pumps Mech/Elec Losses		3.0		3.0
Fans Mech/Elec Losses		5.0		5.0
FGD Energy Losses		42.0		42.0
Misc. Losses and Auxiliaries		80.7		80.7
Net Power			1884	1884
Totals	0	4517	1884	6401

Table 55 shows the air emissions for Case H.

Table 55. Air emissions for Case H (based on net power)

	lb/MMBtu
SO_2	~0
NO_x	0.3
Particulates	~0
Hg	~0
CO_2	72.3

The carbon balance for Case H is shown in **Table 56**.

Table 56. Carbon balance for Case H

Carbon In, (lb/hr.)		Carbon Out (lb/hr.)	
Coal	343,255	Stack Gas	37,153
Air (CO_2)	667	FGD Product	2,216
FGD Reagent	5,436	CO_2 Product	309,989
Total	**349,358**	**Total**	**349,358**

The sulfur balance for Case H is shown in **Table 57**.

Table 57. Sulfur balance for Case H

Sulfur In, (lb/hr.)		Sulfur Out (lb/hr.)	
Coal	13,515	FGD Product	13,481
		Stack Gas	0
		Waste Solvent	34
Total	**13,515**	**Total**	**13,515**

Table 58 summarizes the pieces of equipment which contribute to the total water consumption in the power plant model with CO_2 capture.

Table 58. Water consumption for power plant modeling of Case H

Water Use	Water Consumption (gpm)
FGD Makeup	754
Cooling Tower	5,702
Total	**6,456**

5.4. Economic Analysis

CAPEX estimations for the carbon-capture island were completed for MEA and the aminosilicone-based cases in order to calculate the first year COE, first year removal cost of CO_2, and first year avoided cost of CO_2. The annual costs were estimated as follows:

Annual cost includes the following items:

- Power Island – CAPEX, OPEX, and fuel - The estimated values were compared against DOE estimated values for Case 11 of the cost updates for the Bituminous Baseline Study.[2] Further estimates were conducted for a power island that would be required for 550 MW net power with carbon capture using aminosilicone-based solvent.
- Capital recovery and other fixed charges- The recovery charges are dependent on the Capital Charge Factor (CCF). The CCF used in this study was chosen based on NETL's cost estimation methodology using the case for High risk IOU for five years.[6]
- Cost of cooling water- The cost of cooling water from the Bituminous Baseline Study was used for the non-scaled cases.[2] For the scaled-up cases, the increased cooling water demand increased cooling tower CAPEX and OPEX.
- CO_2 transport, storage and monitoring- $10/tonne as provided by DOE in the cooperative agreement.

- Solvent cost- Solvent cost of \$20/lb was used in this study. This solvent cost is based off of the estimates made for solvent cost in the previous DOE award (DE-FE0007502). Further, a sensitivity analysis was conducted with respect to solvent cost, which is provided in the subsequent section.
- Fixed O&M costs- Estimated using a plant on stream factor of 310.25 days and a charge of \$875/day.
- Maintenance and material cost- Estimated using 1.6% of the material cost.

The details of the calculations are provided below

Power Island – CAPEX, OPEX, and Fuel – this cost is the same for all non-scaled cases. It can also be calculated using the expression below:

$$Power\ island\ cost = COE \cdot power\ generated$$

COE, which is used in this expression, is equal to 80.95 mils/kWh, from Case 11 COE w/o TS&M.[2]

For the scaled-up cases, the cost was estimated using Thermoflow calculations.

Capital Recovery and other Fixed Charges

The capital recovery was calculated based on the following formula:

$$Capital\ recovery = Capital\ charge\ factor * installed\ CAPEX$$

The capital charge factor (CCF) value is selected based on several factors:

- Type of power plant financial structure (IOU vs. IPP)
- High risk or low risk finance structure
- Capital expenditure period: three years vs. five years.

Table 25 reports capital charge factors for a variety of finance structures.[6]

Table 59. Capital charge factors for various finance structures

Finance Structure	High Risk IOU		Low Risk IOU	
Capital Expenditure Period	Three Years	Five Years	Three Years	Five Years
Capital Charge Factor (CCF)	0.111	0.124	0.105	0.116
Finance Structure	High Risk IPP		Low Risk IPP	
Capital Expenditure Period	Three Years	Five Years	Three Years	Five Years
Capital Charge Factor (CCF)	0.177	0.214	0.149	0.176

The value selected for the post-combustion CO_2-capture process is 12.4%, which corresponds to a high risk IOU structure with a five year capital expenditure period.

First year COE was calculated based on the following formula:

$$COE = \frac{total\ annual\ costs}{power\ generated}$$

First year removal cost for CO_2 was calculated using the expression below:

$$Removal\ cost\ \left(\frac{\$}{ton}\right) = \frac{COE_{with\ capture} - COE_{without\ capture}}{lb\ of\ CO2\ separted * power\ generated}$$

Total Cost of Cooling Water

The total cost of cooling water was determined based on the amount of cooling water required as predicted by the ASPEN Plus model for the carbon-capture process and the cost of cooling water.

CO_2 Transport, Storage, and Monitoring

This cost was calculated based on the amount of CO_2 separated and the cost of transportation, storage, and Monitoring (TS&M).

Maintenance Material Costs

The maintenance material costs were calculated from the formula below:

$$Maintenance\ material\ costs = Equipment\ and\ material\ costs * Maintenance\ and\ material\ cost\ \%$$

The first year removal cost of CO_2 was estimated for a supercritical power plant with carbon capture using MEA as a solvent. The results are shown in **Figure 117** as compared to Case 12 in the Bituminous Baseline Study Cost Update.[2] The values are in good agreement with each other.

Figure 117. Comparison of first year removal cost of CO_2 using MEA vs. DOE estimated value[2]

The removal cost was estimated for a supercritical power plant using the aminosilicone-based material as a solvent for carbon capture. As mentioned earlier for the first few cases (Case A-G) the power plant island was taken as the same size as Case 11 in the Bituminous Baseline Study.[1] This was done to determine the effect of different parameters of the carbon-capture island on process economics without changing the size and other variables of the power island. Once a best case was found for the conditions of the carbon-capture island, then the scale was adjusted to get to a 550 MW net power with carbon capture (shown as Case H-J).

Capital cost estimations for the aminosilicone cases were done using Aspen Cost Estimator with a cost basis of Q1, 2010. The costs were then adjusted using the CEPCI index to get a final cost basis of 2011. The total CAPEX for the DOE Case 12 as compared to Case H and Case J are shown in **Figure 118**. As seen in the figure, Case H is <75% and Case J is <77% of the CAPEX of a system using MEA solvent. The lower CAPEX for Case L (SSC) as compared to Case H is due to an increased working capacity with steam stripper column desorption,. Furthermore, increased water content in the working solution let to an improved heat transfer coefficient in the cross HX, hence lower CAPEX.

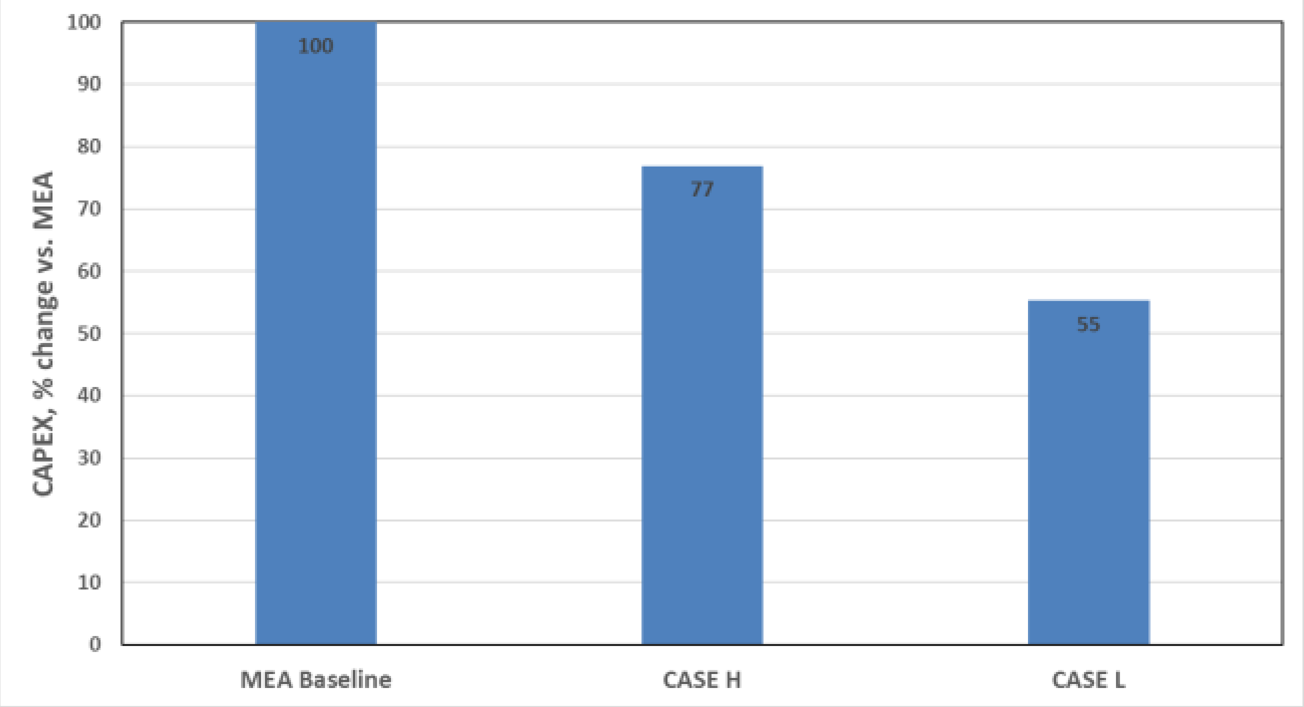

Figure 118. Total CAPEX comparison of two scaled-up cases using aminosilicone solvents vs. DOE Case 12 using MEA

First year COE was calculated (with and without TS&M) as shown in **Figure 119** and **Figure 120**. Case L COE w/o TS&M is 11.9 as compared to 13.73 cents/kWh for the MEA based system. When TS&M is included in the analysis, then Case L COE is 12.8 vs. 14.73 cents/kWh for the MEA based system.

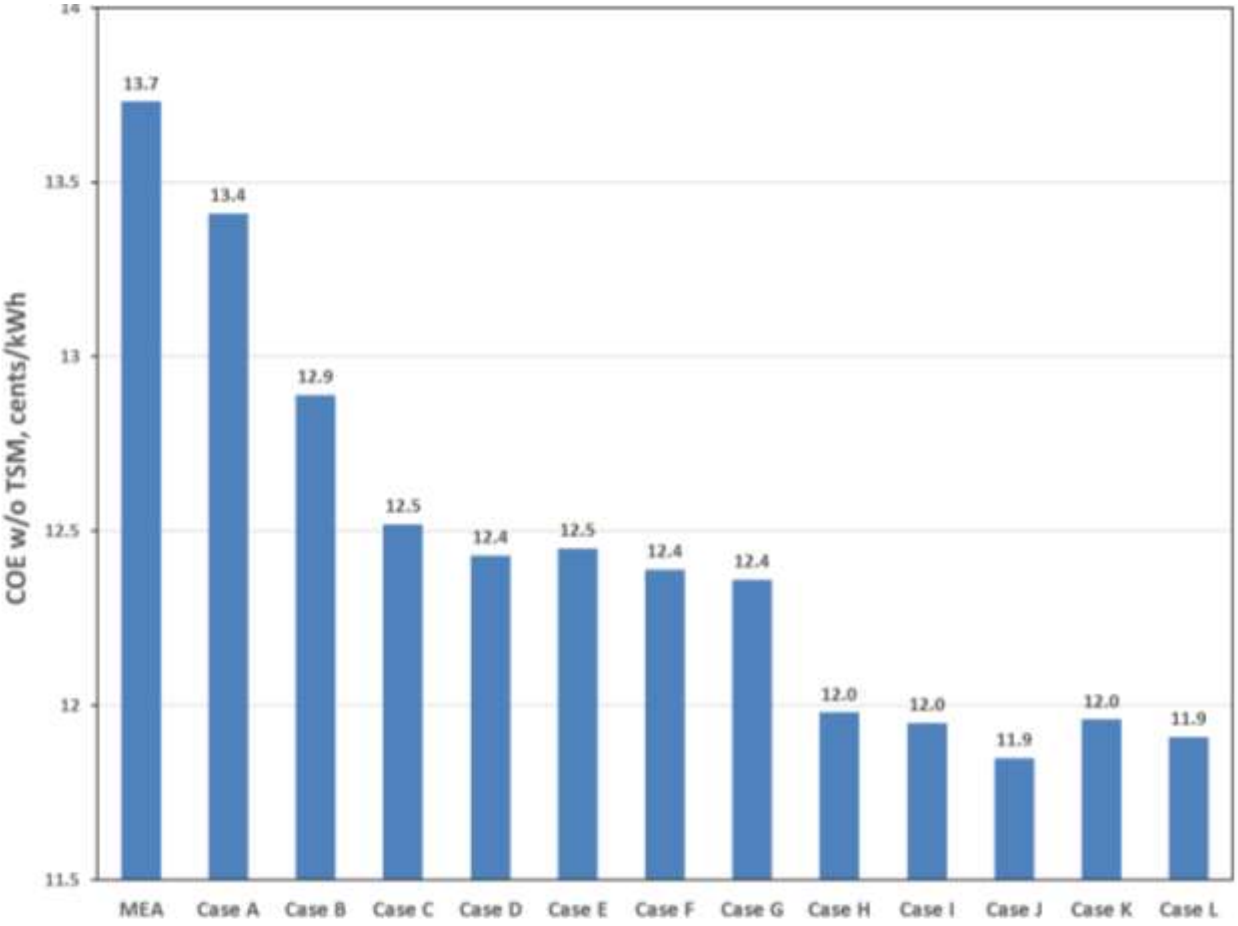

Figure 119. Cost of electricity without TS&M for various cases as compared to DOE Case 12

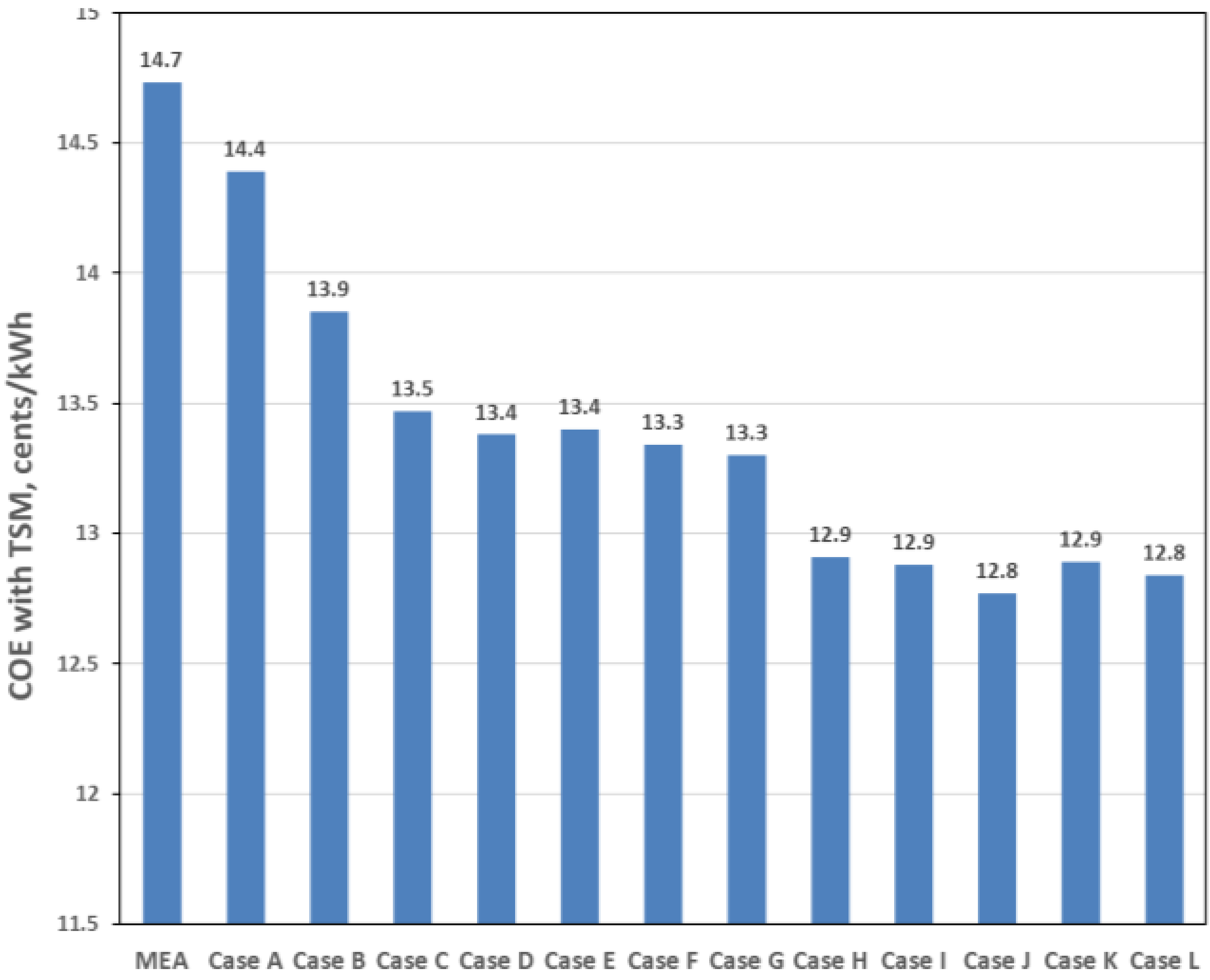

Figure 120. Cost of electricity with TS&M for various cases as compared to DOE Case 12.

The first year removal cost of CO_2 for Case K (CSTR, low P) is 47.78 $/ton of CO_2 as compared to 60.25$/ton of CO_2 when MEA is used. For steam stripper desorber, the first year removal cost of CO_2 for case L (SSC, low P) is 42.4 $/ton of CO_2. This shows a significant reduction in removal cost when aminosilicone solvent is used for carbon capture.

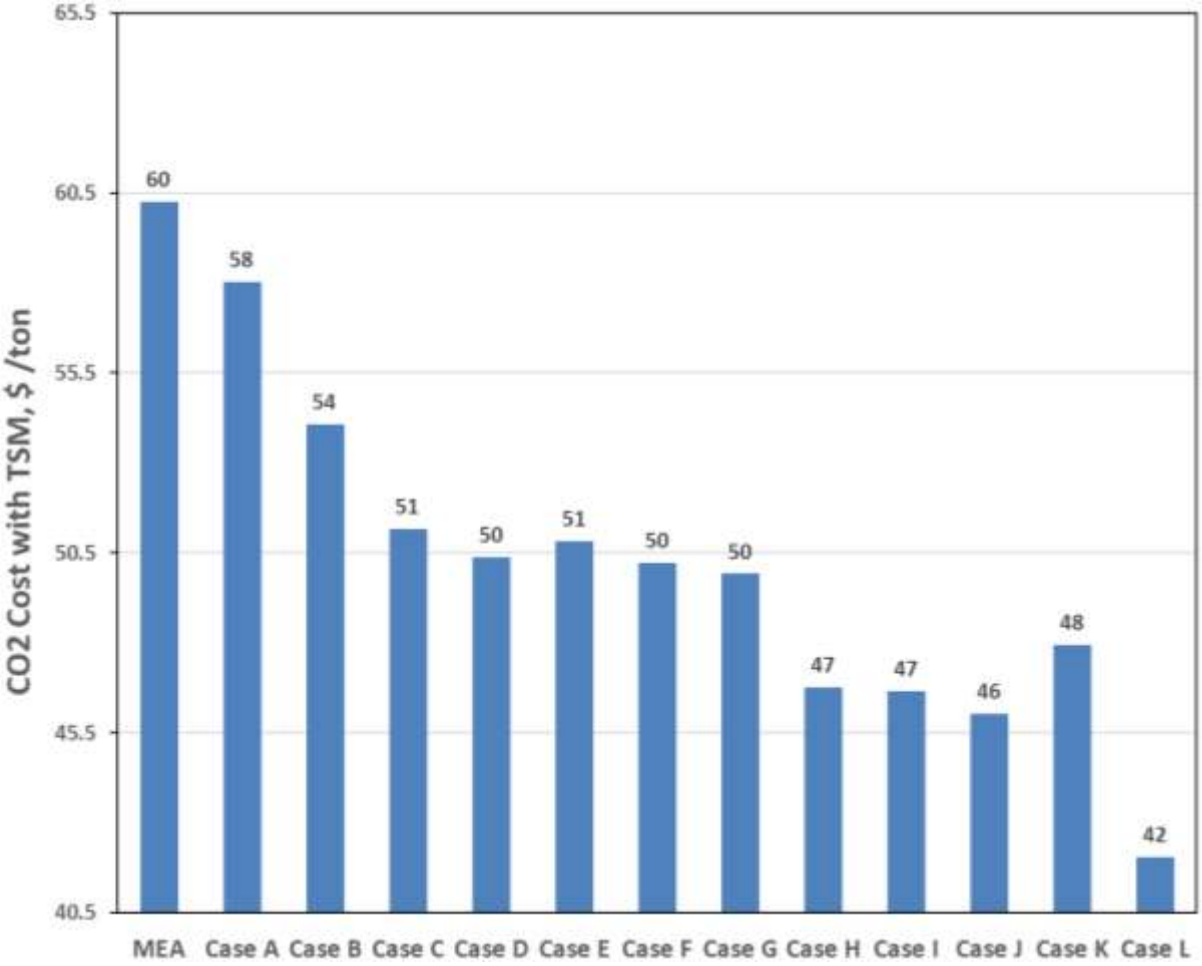

Figure 121. First year removal cost of CO_2 in $/ton for various cases as compared to DOE Case 12

5.5. Sensitivity Analysis

In order to understand the effect of the main parameters on the cost of CO_2 removal and efficiency of the power plant, the sensitivity analysis was conducted with respect to the following parameters:

- Heat rate of the desorber
- Auxiliary load of the pumps and compressors for CO_2 capture island
- Required amount of cooling water
- Installed CAPEX of CO_2-capture island
- Power island capital cost
- Solvent cost
- Sulfur amount in incoming flue gas
- Solvent make-up yearly rate

The results of the sensitivity analysis are presented below.

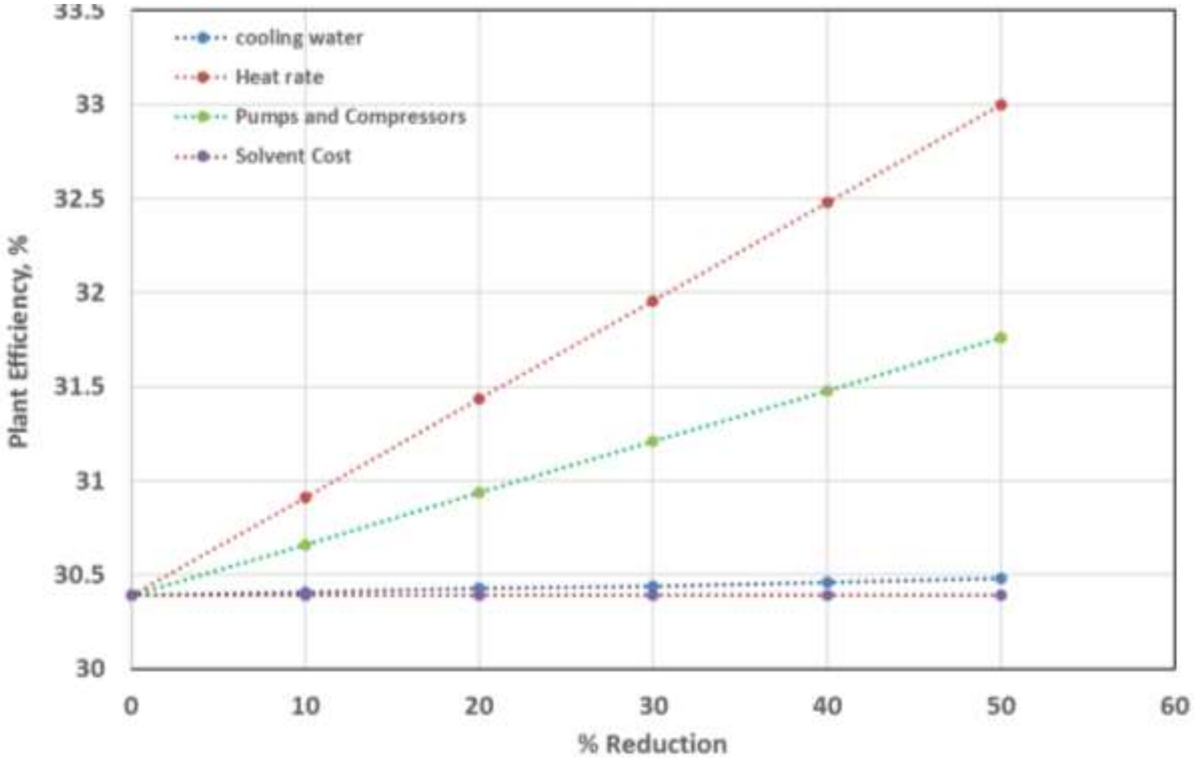

Figure 122. Sensitivity analysis of effect of different variables on plant efficiency for Case K

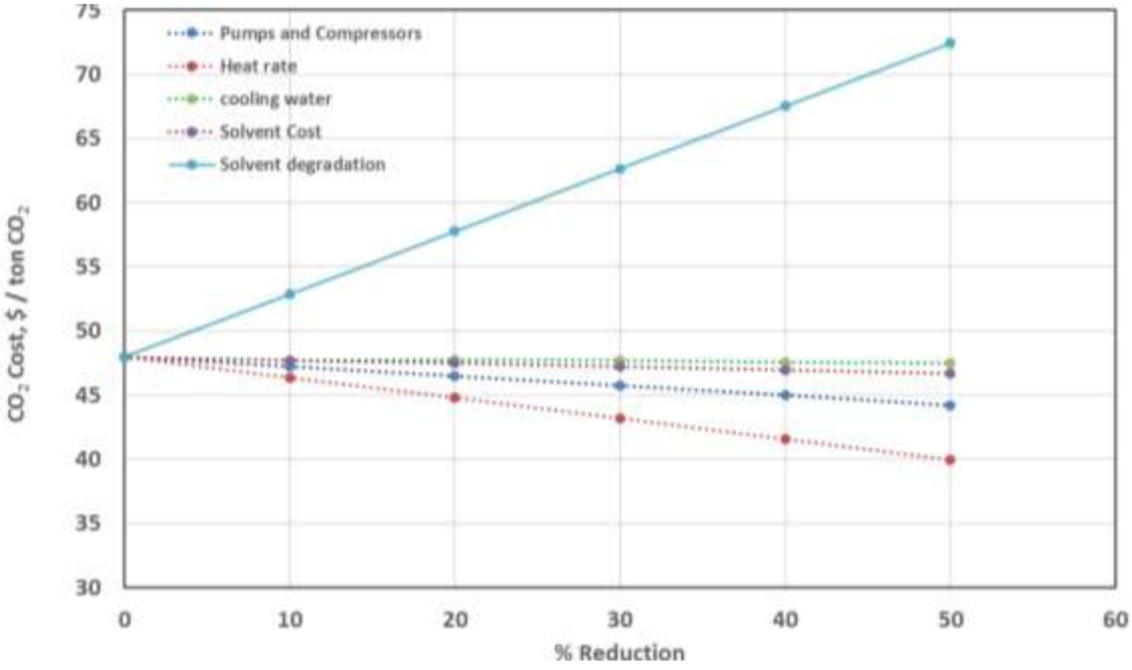

Figure 123. Sensitivity analysis of effect of different variables on removal cost of CO_2 for Case K.

It can be seen from these plots, that Installed CAPEX of the CO_2-capture island and desorber heat rate have the most positive significant impact on CO_2 removal cost. Cooling water amount, auxiliary power, and solvent cost (at this low level of degradation) have a lesser effect. However, the CO_2 cost is negatively dominated by the solvent degradation rate, as the aminosilicone is a more expansive solvent than MEA. Based on the 0.5 MW_e Demo performed at NCCC, the solvent make-up rate was 15% / yr. for SSC, and 120% / yr. for CSTR. Figure 22 and 23 shows the predicted values for CO_2 cost assuming the measured make-up solvent degradation rates. For CSTR absorber, the high solvent degradation rate renders a cost of CO_2 over \$100/ ton CO_2. On the other hand, lower solvent make-up rate and improved performance for the steam stripper column led to a cost of CO_2 of \$48 / ton of CO_2. This shows a significant reduction in removal cost vs MEA when aminosilicone solvent is used for carbon capture.

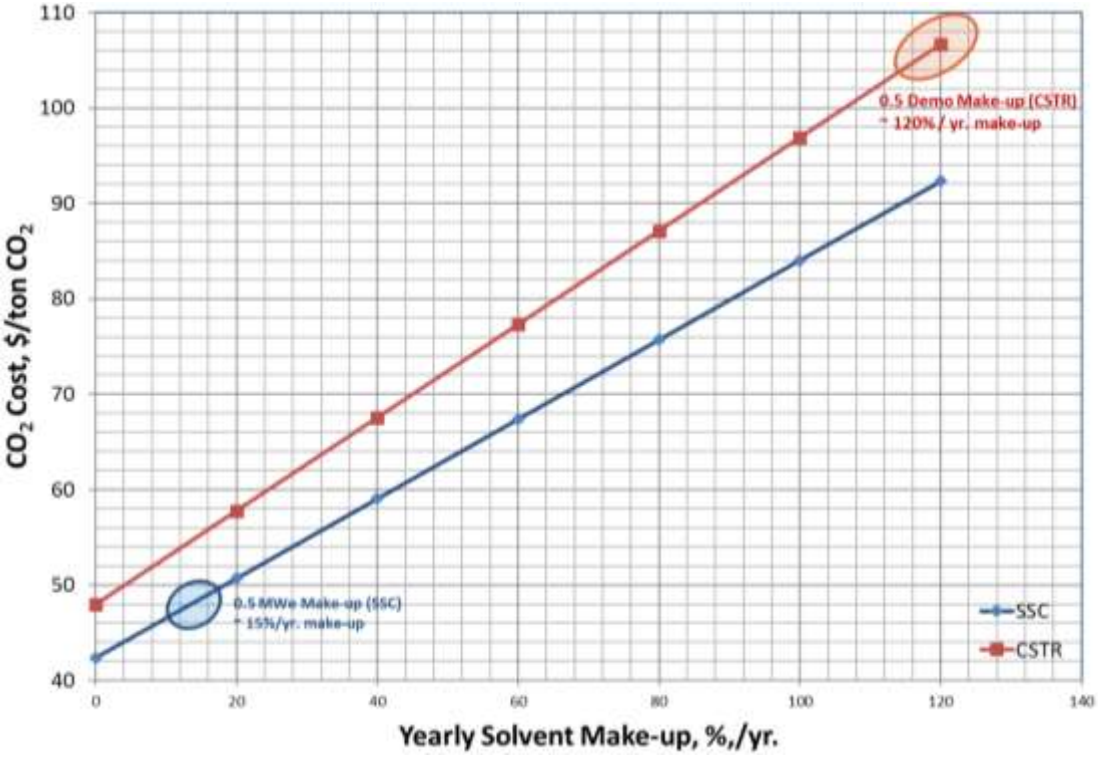

Figure 124. Sensitivity analysis of effect of yearly solvent make-up on removal cost of CO_2 for Case K (CSTR desorber, low P) and Case L (SSC, low P)

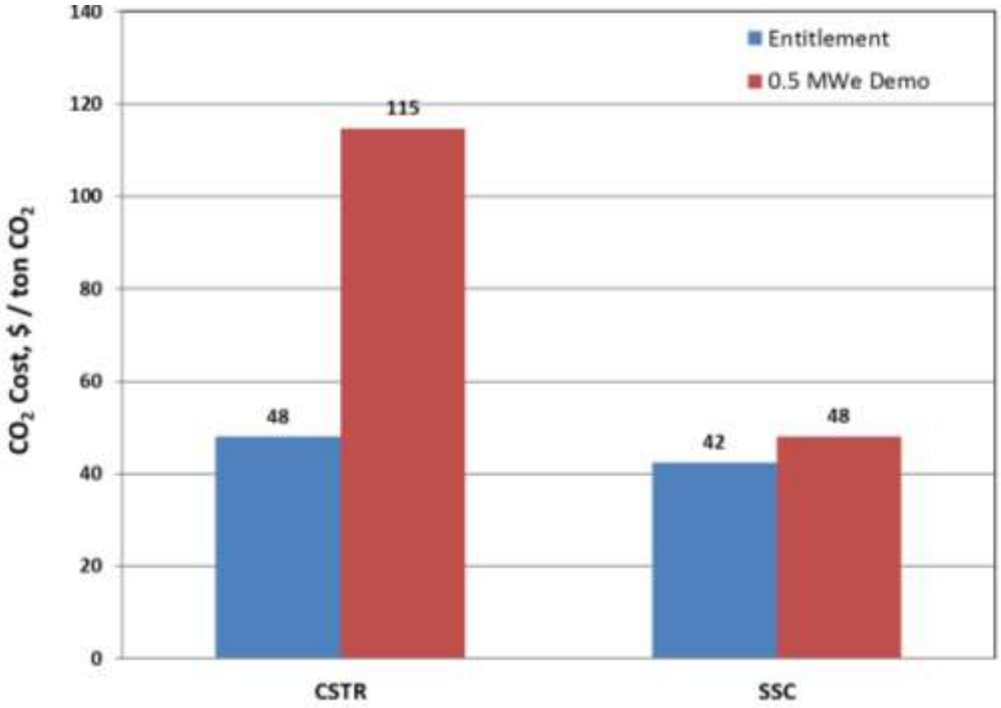

Figure 125. CO_2 cost for CSTR (continuous stirred tank reactor) and Steam Stripper Column (SSC) desorbers: Entitlement vs. Prediction based on measured yearly solvent make-up rates at 0.5 MW_e Demo (NCCC)

6. Technology EH&S Assessment

The following sections describe the Environmental, Health, and Safety (EH&S) assessment for a CO_2 capture system for a 550 MW coal-fired power plant and for the manufacturing process of GAP-1_m. Plant-wide engineering controls are described. Five components of the solvent, CAS#2469-55-8 (GAP-0), CAS#106214-84-0 (GAP-1-4), TEG, and methanol and xylene (minor contaminants from the aminosilicone) are included in this assessment. One by-product, GAP-1m/SO_X salt, and DDBSA were also identified for analysis. The chemicals associated with the manufacturing process include methanol, xylene, allyl chloride, potassium cyanate, sodium hydroxide (NaOH), tetramethyldisiloxane (TMDSO), tetramethyl ammonium hydroxide (TMAH), Karstedt catalyst, octamethylcyclotetrasiloxane (D_4), Aliquat 336, methyl carbamate, potassium chloride, trimethylamine, and (3-aminopropyl) dimethyl silanol (referred to as silanol in this report).

Finally, the toxicological effects of the chemicals associated with the CO_2 capture system and the manufacturing process are reviewed. Details of the containment, handling, disposal processes, safety data sheets, shipping, storage equipment requirements, and relevant regulatory requirements are also summarized.

6.1. Air, Water, and Solid Waste Identification for the Aminosilicone-based CO_2 Capture System for a 550 MW Coal-Fired Power Plant

This section describes the potential ancillary or incidental air, water, and solid wastes from the proposed technology and identifies and estimates their magnitude for a 550 MW coal-fired power plant. In addition to the absorption solvents, the possible by-products, waste products, and flue gas contaminants were considered. The CO_2 capture system was designed to minimize possible environmental degradation products and bioaccumulation thereof. The design also examined the full-scale conditions at the point of discharge to the environment.

The aminosilicone solvent used in the continuous CO_2 absorption/desorption process is a 60%wt GAP-1_m / 40%wt TEG mixture. Greenchem's technical bulletins, materials safety data sheets (MSDS's), and additional EH&S paperwork requested from Greenchem suggest that the triethylene glycol does not contain any contaminants.

The GAP-1_m (or DAP-0) is supplied by Milliken & Company (SiVance LLC). GAP-1_m has some methanol and xylene contaminants that come from SiVance's manufacturing process. To estimate the concentration of the contaminants, SiVance measured the composition of 5 delivered lots of GAP-1_m with an Agilent 6890 gas chromatogram (GC) and a model 5973 mass spectrometer (MS). The methanol was less than 100 ppm, and the xylene concentration was less than 50 ppm in the 5 lots. However due to statistical analysis of the capability of the current manufacturing process, SiVance specified the concentration limits to be 500 ppm for each, as shown in **Table 60**. Thus, 500 ppm will be used as the de-facto concentration in the mass balance discussed below. The molecular weight distribution of GAP-1_m was also measured, showing a mixture of X = 0, 1, 2, 3, and 4 as included in **Table 61**. The GAP-0 and GAP-(1-4) components of GAP-1m have been registered separately as CAS#2469-55-8 and CAS#106214-84-0, respectively. The final solvent composition fed into the CO_2 absorption/desorption process is summarized in Table 3.

Table 60. Composition range and specifications of GAP-1_m from SiVance

	Methanol (ppm)	**Xylene (ppm)**	**Molecular Weight (g/mol)**	**Total Amine Activity (%)**
Specification	<500	<500	<345	>96%
Range of 5 lots	<100[7]	<50[8]	301-317	96-100

Table 61. Representative distribution of GAP-1_m components

GAP-0	**GAP-1**	**GAP-2**	**GAP-3**	**GAP-4**
44%	30%	15%	8%	3%

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[7] Jose Valle, SiVance GAP-1m Method detection limit for Methanol, personal communication, Dec. 16, 2013.

[8] Jose Valle, SiVance GAP-1m Method detection limit for Xylene, personal communication, Dec. 16, 2013.

Table 62. Composition of the aminosilicone solvent

CO_2 Capture Solution	GAP-1_m (60%wt)				TEG (40%wt)
Components	GAP-0	GAP 1-4	Methanol	Xylene	Triethylene glycol
CAS #	2469-55-8	106214-84-0	67-65-1	1330-20-7	112-27-6
Composition	26 wt %	34 wt %	<300 ppm	<300 ppm	40 wt %

The process flow and mass balance diagram for a continuous CO_2 absorption/desorption system for a 550 MW coal-fired power plant is shown Figure 2. The flue gas composition for the 550 MW plant was specified in the cooperative agreement between GE Global Research and the DOE.[9] Before entering the CO_2 absorption/desorption system, flue gas is cleaned and prepared in Flue-Gas Desulfurization (FGD), pre-scrubber, cooler, and condenser units. The gas, labeled 1 in **Figure 126**, is fed into the CO_2 absorption unit (Absorber). The composition and flow rate of the gas is included in **Table *63***. It is primarily CO_2, nitrogen (N_2), water (H_2O), and oxygen (O_2), with low levels of sulfur oxides (SO_x) and nitrogen oxides (NO_x).

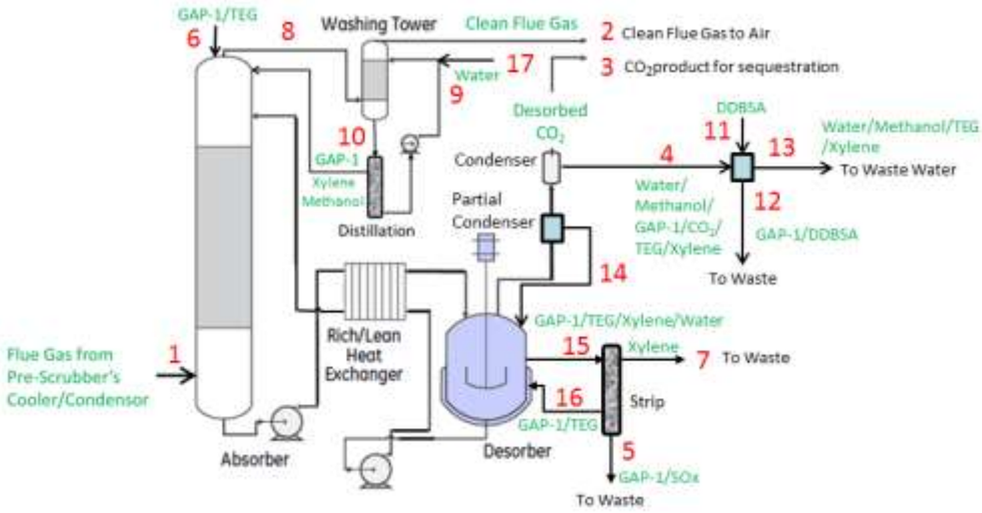

Figure 126. Continuous CO_2 absorption/desorption system for a 550 MW coal-fired power plant

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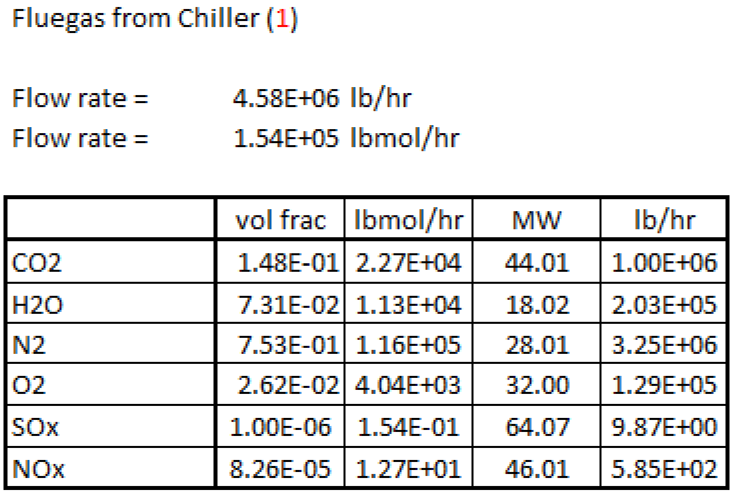
[9] DOE-GE Global Research Contract; Award Number DE-FE0013755.

Table 63. Composition and flow rate of stream 1, inlet flue gas



Fluegas from Chiller (1)

Flow rate = 4.58E+06 lb/hr
Flow rate = 1.54E+05 lbmol/hr

	vol frac	lbmol/hr	MW	lb/hr
CO2	1.48E-01	2.27E+04	44.01	1.00E+06
H2O	7.31E-02	1.13E+04	18.02	2.03E+05
N2	7.53E-01	1.16E+05	28.01	3.25E+06
O2	2.62E-02	4.04E+03	32.00	1.29E+05
SOx	1.00E-06	1.54E-01	64.07	9.87E+00
NOx	8.26E-05	1.27E+01	46.01	5.85E+02

As the gas enters the absorber, it mixes with the 60%wt GAP-1$_m$/40% wt TEG absorption solvent. The gas passes upward through the column while the liquid flows down. As it mixes, the GAP-1$_m$ reacts with CO_2 to make a carbamate salt. The column is designed to capture 90% of the inlet CO_2. The salt is soluble in the liquid and is carried down to the bottom of the column with the solvent. The GAP-1$_m$ also reacts with the SO_x gases to form heat stable salts. This reaction is very efficient, and all of the incoming SO_x is removed from the gas stream. This amino-sulfate salt is dispersed into the solvent and carried to the bottom of the column with the solvent. Since water and triethylene glycol are miscible, some water vapor dissolves into the solvent and is carried with the liquid to the bottom of the column. Meanwhile, none of the N_2, O_2, or NO_x dissolves or reacts with the solvent, as confirmed by GE Global Research's bench-scale studies.[10] As the cleaned flue gas exits the top of the column, a small amount of GAP-1m, TEG, xylene, and methanol may exit with the gases. To prevent release to the environment, these are captured with a water wash tower. The GAP-1$_m$, xylene, and methanol are separated from the water with a distillation column and returned to the top of the absorption column. The water is returned to the water wash tower. The cleaned flue gas, shown as stream 2 in **Figure 126**, is released to the atmosphere via a stack. Its composition and flow rate is shown in **Table 64**.

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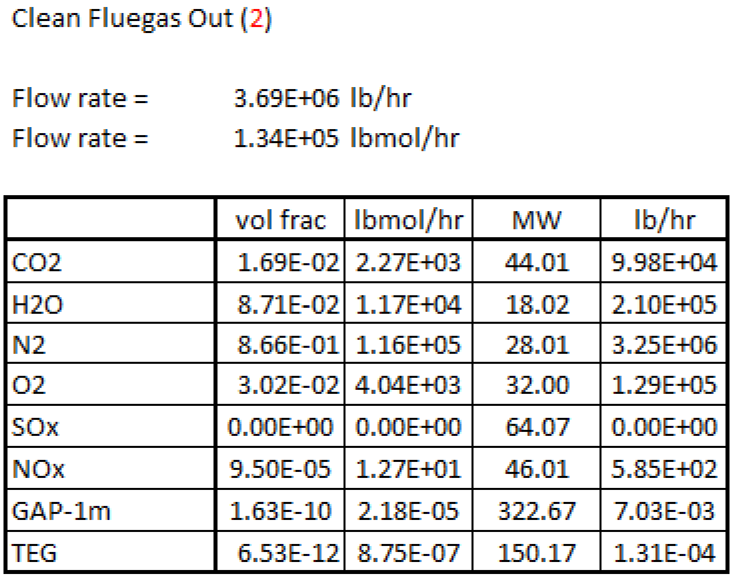
[10] Wood, B., et al. 2014. "Bench-Scale Silicone Process for Low-Cost CO_2 Capture: Final Scientific/ Technical Report"

Table 64. Composition and flow rate of stream 2, cleaned flue gas



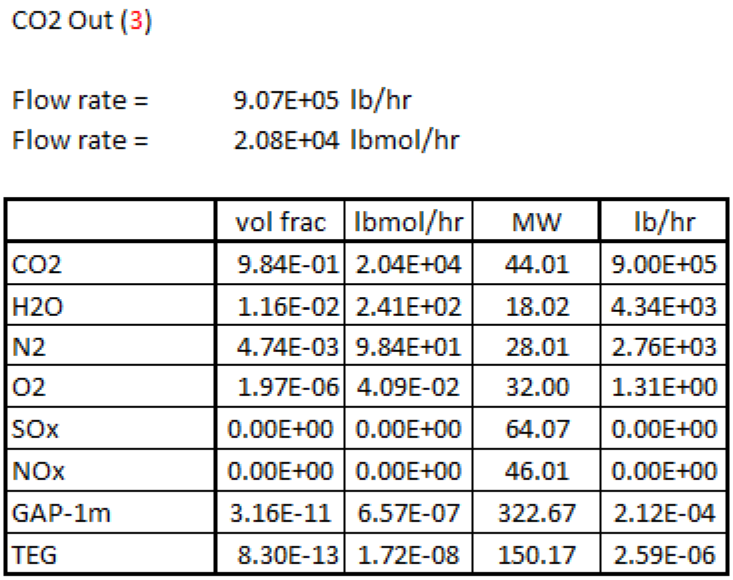
Clean Fluegas Out (2)

Flow rate = 3.69E+06 lb/hr
Flow rate = 1.34E+05 lbmol/hr

	vol frac	lbmol/hr	MW	lb/hr
CO2	1.69E-02	2.27E+03	44.01	9.98E+04
H2O	8.71E-02	1.17E+04	18.02	2.10E+05
N2	8.66E-01	1.16E+05	28.01	3.25E+06
O2	3.02E-02	4.04E+03	32.00	1.29E+05
SOx	0.00E+00	0.00E+00	64.07	0.00E+00
NOx	9.50E-05	1.27E+01	46.01	5.85E+02
GAP-1m	1.63E-10	2.18E-05	322.67	7.03E-03
TEG	6.53E-12	8.75E-07	150.17	1.31E-04

Meanwhile, the liquid at the bottom of the absorption column is pumped through a heat exchanger into a desorption vessel (Desorber). Here, the liquid is heated until the carbamate salt decomposes, releasing CO_2 gas. Some GAP-1_m, TEG, water, xylene, and methanol may also vaporize with the CO_2 product. The gas stream goes through a series of condensers and compressors to remove the contaminants from the gas stream. The clean gas stream, shown as stream 3 in **Figure 126**, is collected as the CO_2 product. See Table 6 for composition and flow rate. A second stream rich in GAP-1_m, TEG, xylene, and a fraction of water, is recycled to the Desorber. A third condensed stream, stream 4 in **Figure 126**, is mostly water and methanol with a small amount of GAP-1_m, TEG, and xylene (see **Table 66**). This stream is treated with a stream of dodecylbenzenesulfonic acid (DDBSA) (stream 11), detailed in **Table 67**, and allowed to settle. A small stream of GAP-1m/DDBSA salt (stream 12), detailed in **Table 68**, is then removed from the water and disposed of as industrial, non-hazardous solid waste. Stream 13 (see **Table 69**), which contains water, methanol, TEG, and xylene, would also be disposed of as non-hazardous solid waste, which could include sending it to a wastewater treatment facility, depending on site-specific considerations. This would not be an option if GAP-1_m were still present in this waste stream. The classifications of solid waste in regards to RCRA are discussed in detail in Section E of this report.

Table 65. Composition and flow rate of stream 3, CO_2 product



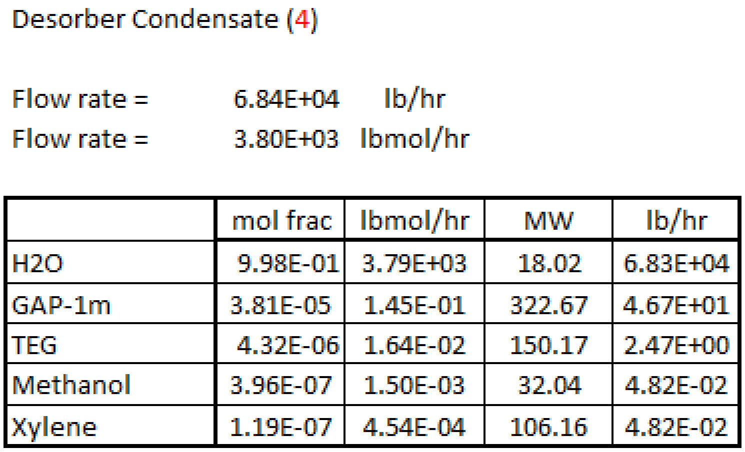
CO2 Out (3)

Flow rate = 9.07E+05 lb/hr

Flow rate = 2.08E+04 lbmol/hr

	vol frac	lbmol/hr	MW	lb/hr
CO2	9.84E-01	2.04E+04	44.01	9.00E+05
H2O	1.16E-02	2.41E+02	18.02	4.34E+03
N2	4.74E-03	9.84E+01	28.01	2.76E+03
O2	1.97E-06	4.09E-02	32.00	1.31E+00
SOx	0.00E+00	0.00E+00	64.07	0.00E+00
NOx	0.00E+00	0.00E+00	46.01	0.00E+00
GAP-1m	3.16E-11	6.57E-07	322.67	2.12E-04
TEG	8.30E-13	1.72E-08	150.17	2.59E-06

Table 66. Composition and flow rate of stream 4, Desorber condensate



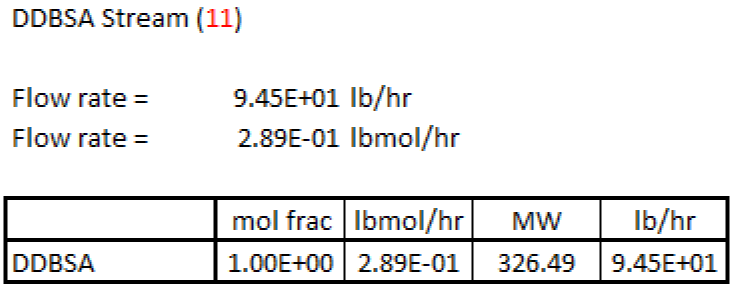
Desorber Condensate (4)

Flow rate = 6.84E+04 lb/hr

Flow rate = 3.80E+03 lbmol/hr

	mol frac	lbmol/hr	MW	lb/hr
H2O	9.98E-01	3.79E+03	18.02	6.83E+04
GAP-1m	3.81E-05	1.45E-01	322.67	4.67E+01
TEG	4.32E-06	1.64E-02	150.17	2.47E+00
Methanol	3.96E-07	1.50E-03	32.04	4.82E-02
Xylene	1.19E-07	4.54E-04	106.16	4.82E-02

Table 67. Composition and flow rate of stream 11, DDBSA stream

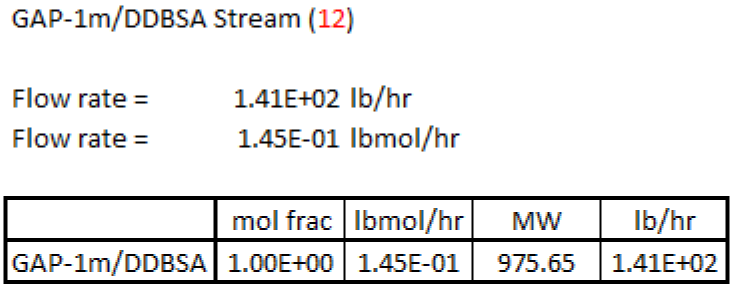


DDBSA Stream (11)

Flow rate = 9.45E+01 lb/hr
Flow rate = 2.89E-01 lbmol/hr

	mol frac	lbmol/hr	MW	lb/hr
DDBSA	1.00E+00	2.89E-01	326.49	9.45E+01

Table 68. Composition and flow rate of stream 12, GAP-1_m/DDBSA stream

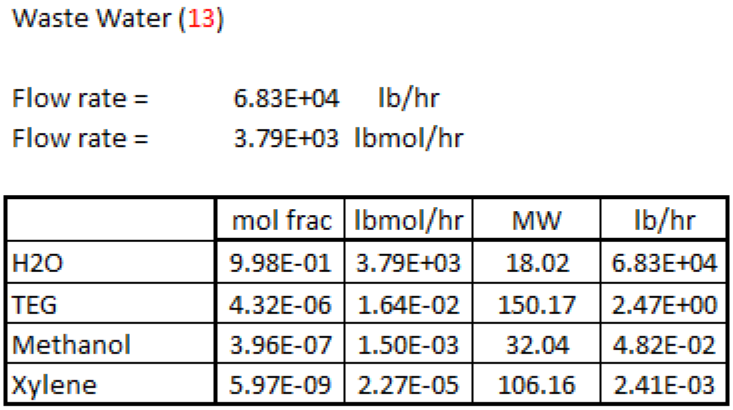


GAP-1m/DDBSA Stream (12)

Flow rate = 1.41E+02 lb/hr
Flow rate = 1.45E-01 lbmol/hr

	mol frac	lbmol/hr	MW	lb/hr
GAP-1m/DDBSA	1.00E+00	1.45E-01	975.65	1.41E+02

Table 69. Composition and flow rate of stream 13, waste water.



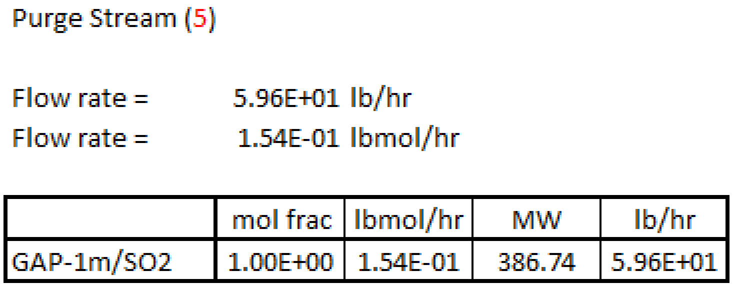
Waste Water (13)

Flow rate = 6.83E+04 lb/hr
Flow rate = 3.79E+03 lbmol/hr

	mol frac	lbmol/hr	MW	lb/hr
H2O	9.98E-01	3.79E+03	18.02	6.83E+04
TEG	4.32E-06	1.64E-02	150.17	2.47E+00
Methanol	3.96E-07	1.50E-03	32.04	4.82E-02
Xylene	5.97E-09	2.27E-05	106.16	2.41E-03

A second exit stream (stream 15) from the Desorber prevents buildup of GAP-1_m/SO_x and xylene waste products in the system. This stream has the same composition as the material in the Desorber. It is rich in GAP-1m and TEG but contaminated with GAP-1_m/SO_x compounds and xylene. To remove the contaminants, the material is vacuum-distilled. The bottoms will consist of GAP-1_m/SO_x compounds (stream 5, **Table 70**) and the lights will consist of xylene (stream 7,). Stream 5 would be disposed of as industrial, non-hazardous waste and stream 7 would be disposed of under Subpart C of RCRA as hazardous waste. The requirements for this disposal and the details of the waste classification are discussed in Section E of this report. The remaining GAP-1_m and TEG is returned to the Desorber. A third, cleaned exit stream is recycled back to the Absorber as part of the continuous CO_2 removal system. GAP-1m and TEG are added to the Absorption tower (stream 6) to replenish that lost in waste streams 5 and 12. See **Table 71** for flow rate and composition. Water is added to the wash tower (Stream 17) to replenish that lost in the flue gas. See **Table 72** for flow rate and composition.

Table 70. Composition and flow rate of stream 5, Desorber purge stream



Purge Stream (5)

Flow rate = 5.96E+01 lb/hr
Flow rate = 1.54E-01 lbmol/hr

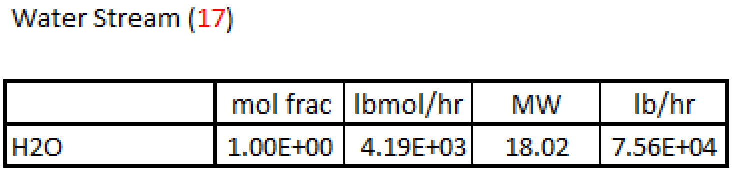
	mol frac	lbmol/hr	MW	lb/hr
GAP-1m/SO2	1.00E+00	1.54E-01	386.74	5.96E+01

Table 71. Composition and flow rate of stream 6, solvent make-up stream.

	mass fraction	lb/hr
GAP-1m	6.59E-01	1.55E+02
TEG	2.00E-01	4.69E+01
H2O	1.41E-01	3.31E+01
GAP-1m/SO2	1.00E-06	2.35E-04

Flow Rate= 2.35E+02 lb/hr.

Table 72. Composition and flow rate of stream 17, water stream



Water Stream (17)

	mol frac	lbmol/hr	MW	lb/hr
H2O	1.00E+00	4.19E+03	18.02	7.56E+04

6.2. Toxicological Effects of Components in the Continuous CO_2

6.2.1. Absorption/Desorption Process

The following section details a description of the various toxicological effects of the substances identified above in Section 6.1. A thorough literature search was conducted to examine potential human health effects and eco-toxicity. Where information was lacking for a particular material, the material was either compared to similar substances or Quantitative Structure Activity Relationships (QSARs) models[11] were used to predict toxicity levels of the particular chemical. The EPA has worked with various computer programming companies to develop numerous QSARs programs to predict the hazard and toxicological effects of many chemicals.

The substances of interest in **Figure 126** are: GAP-1_m, xylene, methanol, TEG, GAP-1_m/SO_x, and DDBSA. As shown in **Table 62**, GAP-1_m can be considered as a mixture of two compounds: CAS #2469-55-8 (GAP-0) and CAS #106214-84-0 (GAP-(1-4)). The GAP-1_m/SO_x salt is not a registered compound, and toxicity information is not readily available. Typically, acid/primary amine salts are less toxic than the free amine itself. For example, 1, 4 diaminobutane is a linear alkyl amine similar in structure to the GAP materials, except it is a carbon chain. Its National Fire Protection Association (NFPA) rating is Health hazard: 4, Fire: 2, Reactivity Hazard: 0, on a scale of 0-4 where 4 is severe. In contrast, its acid salt, 1, 3-Diaminopropane dihydrochloride, has a NFPA rating of Health hazard: 2, Fire: 0, Reactivity Hazard: 0. The acid salt is much less severe. Thus, for analysis

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[11] http://www.epa.gov/nrmrl/std/qsar/qsar.html

here the toxicity of GAP-1_m/SO_x is assumed to be less than or equal to its components, GAP-1m and SO_x. Thus, the substances considered here are: the components of GAP-1_m (CAS #2469-55-8 (GAP-0) and CAS #106214-84-0 (GAP-(1-4)), xylene, methanol, TEG, and DDBSA.

Several literature resources were searched including: MSDS, ATMI[12], REACH compliance registration[13], and SAP EHS Regulatory Content Substance Reports[14]. As discussed in footnote #8, much of the requested toxicology data has not been measured or published for CAS #2469-55-8 (GAP-0) and CAS #106214-84-0 (GAP-(1-4)). Instead, the QSAR models ECOSAR, EPIWIN, Toxtree, PBT Profiler, and T.E.S.T were used to predict potential human health effects and eco-toxicity for these materials. These models use the physical characteristics of the various parts of the chemical structure to predict the characteristics of the whole molecule. For example, molecules that contain the primary amine group, $-NH_2$, are known to have toxicity to fish. The siloxane group is known to be hydrophobic and decompose slowly in the environment. These and other "molecular descriptors" are combined through a series of mathematical equations to predict the hazard and toxicity properties of the entire molecule.

Through the years, the EPA has learned that the accuracy of the aquatic toxicity models (ECOSAR) is limited for very hydrophobic molecules. As the molecule becomes more hydrophobic, less disperses into water, preventing the chemical from contacting aquatic life. A common method of measuring hydrophobicity is the octanol/water partition coefficient (Kow). It is defined as the ratio of a chemical's concentration in n-octanol to its concentration in water at equilibrium. The log Kow is more commonly reported. When the log Kow is less than or equal to 5.0 for fish and daphnid, or 6.4 for green algae, ECOSAR provides reliable toxicity estimates for acute effects. If the log K_{ow} exceeds those general limits, the decreased water solubility of these oleophilic

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[12] http://www.supplier.milliken.com/en-us/EHS/atmivpep.pdf

[13] REACH is the Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals. It is the regulative framework on chemicals for the European Union (EU). CAS# 2469-55-8 (GAP-0) is scheduled for REACH registration in 2018. Until then, no compliance information is available to the public. CAS #106214-84-0 (GAP-(1-4)) is not scheduled for registration until sometime after 2018, suggesting that its toxicity profile is considered to be less than that for GAP-0. No compliance information is available from REACH to the public at this time.

[14] SAP NetWeaver Portal (https://erc-viewer.sap.com/irj/portal/ajax); SAP America Inc 3999 West Chester Pike Newtown Square, PA 19073 USA.

chemicals limits the acute toxicity effects during a 48-hour to 96-hour test. For chronic exposures, the applicable log Kow range is extended up to log Kow = 8.0. If the log Kow of the chemical exceeds 8.0, no chronic toxic effects are expected even with long-term exposures.[15]

The following sections summarize the results of various tests used to estimate the toxicity to humans and the environment of the chemicals used in the aminosilicone-based CO2-capture process. When available, experimental data were included. If not available, modeling data were included and are indicated as predicted in the tables below. Resource information was also provided for clarification of how the data were obtained.

GAP-1_m: CAS# 2469-55-8 (GAP-0) and CAS# 106214-84-0 (GAP-1-4)

Some of the ingestion, eye, and skin effects for GAP-1_m have been experimentally tested previously as shown in **Table 73** and **Table 74**. Generally, GAP-1_m is a severe skin and eye irritant but has low ingestion toxicity. Toxtree and TEST models were used to predict the carcinogenic and mutagenic toxicity of the GAP-1m compounds. The models suggest low probability of genotoxic, carcinogenic, and mutagenic toxicity.

Since much of the aquatic toxicity data for the GAP-1_m materials needed to be derived from modeling, the log Kow values were calculated to determine if the models are valid for this material. Specifically, the log Kow was calculated for the GAP-x series of x = 0, 1, 2, 3, and 4, the components of GAP-1m. These are plotted in **Figure 127**. It shows that the log Kow values are directly proportional to the molecular weight of the GAP species. The log Kow validity limits are also plotted for fish, daphnia, and algae. ECOSAR model predictions are valid for the CAS# 2469-55-8 (GAP-0) component of GAP-1m for acute and chronic toxicity to fish, daphnia, and algae. The CAS# 106214-84-0 (GAP-1-4) component is more complex. The molecules become less water

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[15] Tolls, J; Müller, M; Willing, A, et al. (2009) “A New Concept for the Environmental Risk Assessment of Poorly Water Soluble Compounds and Its Application to Consumer Products”, Integr Environ Assess Manag 5(3), 2009, p. 374-378.

soluble as x increases. Thus for x = 1, only acute algae and chronic toxicity predictions are valid. For x = 2, only chronic toxicity predictions are valid. For x = 3 & 4, none of the predictions are valid. Knowing this information, the toxicity predictions were calculated and the results included in **Table 73** for CAS# 2469-55-8 (GAP-0) and **Table 74** for CAS# 106214-84-0 (GAP-1-4). Since GAP-(1-4) (CAS# 106214-84-0) is a mixture of x = 1-4, the most unfavorable, valid toxicity result was used to represent the mixture. The results suggest that the GAP-1_m material can be quite toxic to aquatic ecosystems. This concurs with the results found with analogous organic amines that are known to be harmful to aquatic wildlife.

A second model, EPIWIN, predicted the effect of GAP-1_m on soil-based environments. It suggests that it does not biodegrade easily, tending to persist in the environment. Compounds with siloxane segments are known to degrade slowly.[16] The lipophilic structure of the siloxane chain also tends to adsorb well to soil. A Koc > 500 L/kg suggests that it blends and adheres well to most soils. The results show that both CAS# 2469-55-8 (GAP-0) and CAS# 106214-84-0 (GAP-1-4) adhere well to soil, making it difficult to remove.

The modeling results for Bio-Concentration Factor, are graphed in **Figure 127**. Bio-Concentration Factor (BCF) is the measure of how readily a chemical moves in and out of the lipid layer of the fish. This is important because humans eat fish, possibly consuming concentrated amounts of the chemical. In the model, the BCF values are most affected by the molecular weight, structure, and solubility partition of the compound between non-polar, fatty substances and water. BCF values greater than 5000 are considered to be a concern for potential bioaccumulation in the environment. The BCF values for GAP-1m (x = 0-4) are plotted in **Figure 128**, showing a bell shaped curve. The GAP-0 and GAP-4 have the lowest BCF values while GAP-2 has the highest. It is possible that the model suggests that the molecular weight of GAP-0 is low enough that the fish can excrete the compound without it concentrating in the fat layers. GAP-4 is likely too big to be absorbed. GAP 1, 2, and 3 (especially 2) are small and lipophilic enough to be absorbed and difficult to excrete. As a result, they concentrate in the lipid layer of the fish.

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[16] http://www.wiley-vch.de/books/biopoly/pdf_v09/vol09_15.pdf

Table 73. GAP-0 toxicity

CAS# 2469-55-8, GAP-0	**Toxicity Test Result**	**Species**	**Time (hrs)**	**Resource/Model Software**
Ingestion LD_{50} (mg/kg)	500	Rat	N/A	SiVance MSDS[17]
Eye Irritation/Damage	Severe Irritant	Rabbit	24 hours (100 µL)	SiVance MSDS17
Dermal LD_{50} (mg/kg)	>2 g/kg	N/A	N/A	SiVance MSDS17
Skin Corrosion/Irritation	Severe Irritant	Rabbit	24 hours (100 µL)	SiVance MSDS17
Predicted Octanol Water Partition Coefficient, log K_{ow}	4.27	N/A	N/A	ECOSAR
Predicted Genotoxicity	Negative	N/A	N/A	Toxtree
Predicted Non-Cancer Toxicity	Negative	N/A	N/A	Toxtree
Predicted Mutagenicity	Negative	N/A	N/A	TEST
Predicted Fish Toxicity LC_{50} (ppm)	1.54	N/A	96	ECOSAR
Predicted Fish Toxicity LC_{50} (ppm), Chronic	0.74	N/A	N/A	ECOSAR
Predicted Daphnia LC_{50} (ppm)	0.24	Daphnia	48	ECOSAR
Predicted Daphnia Toxicity LC_{50} (ppm), Chronic	0.020	Daphnia	N/A	ECOSAR
Predicted Algae EC_{50} (ppm)	0.12	N/A	N/A	ECOSAR
Predicted Algae Toxicity EC_{50} (ppm), Chronic	1.02	N/A	N/A	ECOSAR
Predicted Biodegradability	Not readily biodegradable	N/A	N/A	EPIWIN
Predicted Soil Adsorption Coefficient, K_{oc} (L/kg)	1751	N/A	N/A	EPIWIN
Predicted Bioconcentration Factor (BCF)	305	N/A	N/A	EPIWIN

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[17] SiVance, LLC MSDS for DAP-0

Table 74. GAP-1-4 Predicted toxicity based on molecular modeling

CAS# 106214-84-0, GAP-1-4	Toxicity Test Result	Species	Time (hrs)	Resource/Model Software
Predicted Ingestion LD_{50} (mg/kg)	>2444	Rat	N/A	T.E.S.T.
Intraperitoneal LD_{50} (mg/kg)	80	Mouse	N/A	SiVance MSDS17
Eye Irritation/Damage	Severe Irritant	Rabbit	24 hours (100 µL)	SiVance MSDS17
Skin Corrosion/Irritation	Severe irritant	Rabbit	24 hours (100 µL)	SiVance MSDS17
Predicted Octanol Water Partition Coefficient K_{ow}	See Figure 3	N/A	N/A	ECOSAR
Predicted Developmental Toxicity	Positive	N/A	N/A	Toxtree - GAP1-3
Predicted Genotoxicity	Negative	N/A	N/A	Toxtree - GAP1-4
Predicted Non-Cancer Toxicity	Negative	N/A	N/A	Toxtree - GAP1-4
Predicted Mutagenicity	Negative	N/A	N/A	TEST - GAP1-4
Predicted Fish Toxicity LC_{50} (ppm), Chronic	0.000279	N/A	N/A	ECOSAR - GAP-2
Predicted Daphnia LC_{50} (ppm), Chronic	0.000967	N/A	N/A	ECOSAR - GAP-2
Predicted Algae EC_{50} (ppm), Acute	0.014	N/A	96	ECOSAR – GAP-1
Predicted Algae EC_{50} (ppm), Chronic	0.000841	N/A	N/A	ECOSAR - GAP-2
Predicted Biodegradability	Not readily biodegradable	N/A	N/A	EPIWIN
Predicted Soil Adsorption Coefficient, K_{oc} (L/kg)	>11,250	N/A	N/A	EPIWIN
Predicted Bioconcentration Factor (BCF)	See Figure 4	N/A	N/A	EPIWIN

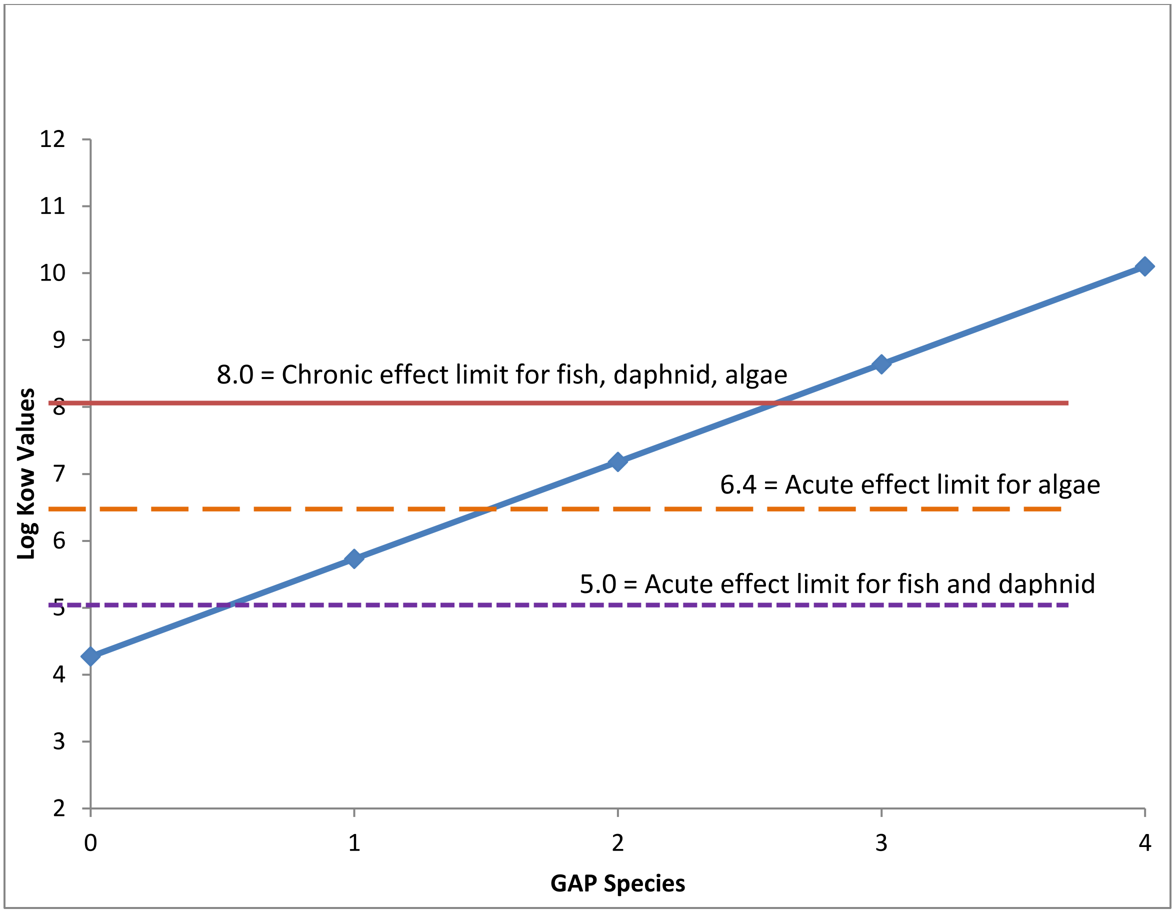

Figure 127. Log K_{ow} values of GAP-0-4 with ECOSAR validity limits

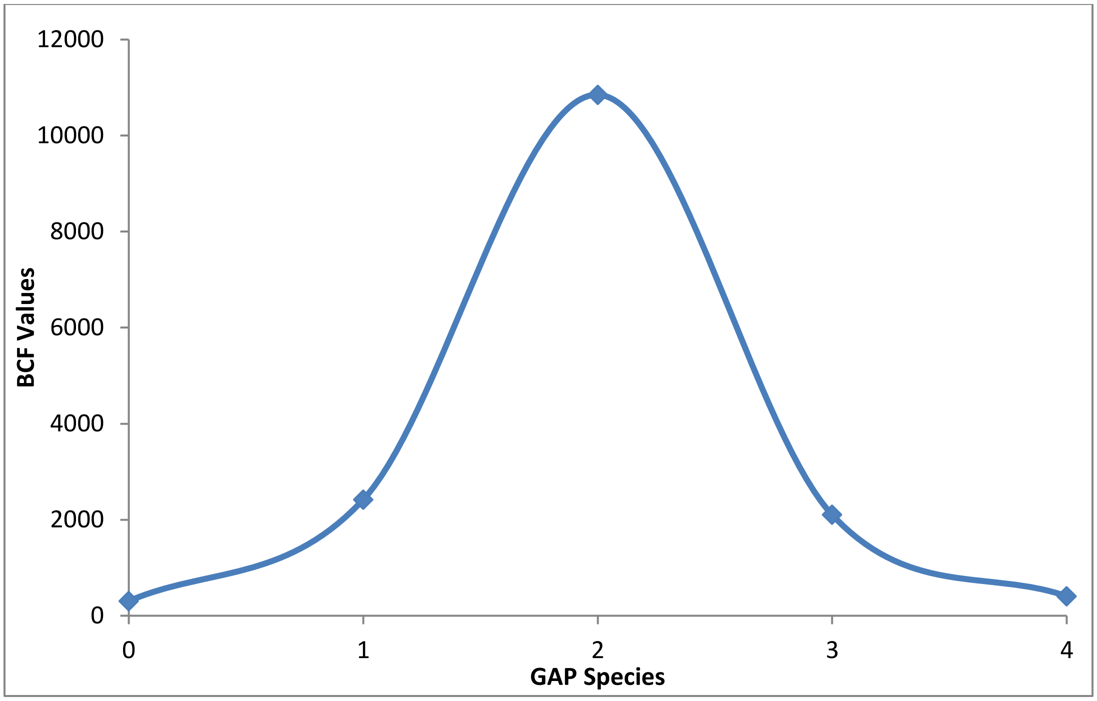

Figure 128. Predicted BCF values of GAP-0-4

Xylene (CAS # 1330-20-7) Toxicological Data

Toxicological data for xylene is more widely available and is included in **Table 75**. Based on the ingestion, dermal and inhalation data, proper ventilation and protective equipment is recommended when using large volumes of xylene. Also, xylene is a severe eye irritant. Proper splash goggles should be worn around xylene. In the Integrated Risk Information System (IRIS), the EPA has documented the oral reference doses (RfD) and the inhalation reference concentration (RfC), defining the daily oral exposure (mg/kg/day) and continuous inhalation exposure (mg/m^3), respectively, that are likely to be without appreciable risk of health effects during a lifetime. RfD and RfC values only address the risk of non-cancer effects. For xylene, IRIS has stated "data are inadequate for an assessment of human carcinogenic potential." [18]

The octanol/water partition coefficient of 3.16 suggests that xylene is not very water soluble, but approximately 25 mg/L (LC$_{50}$) is toxic to fish. The BCF value for xylene is a range from 2.14-2.20

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[18] http://www.epa.gov/iris/subst/0270.htm

to include the three isomeric forms of xylene, suggesting that it is not bio- accumulative in fish (since BCF is less than 5,000). The data also suggest that it is readily biodegradable and does not adsorb well to soil.

Table 75. Xylenes toxicological data

	Toxicity Test Result	Species	Time (hrs)	Resource
Ingestion LD_{50} (mg/kg)	4,300	Rat	N/A	Ashland MSDS[19]
Inhalation LC_{50} (ppm)	6,700	Rat	4	Ashland MSDS19
Dermal LD_{50} (mg/kg)	>2,000	Rabbit	N/A	Ashland MSDS19
Developmental Toxicity	Data Inadequate	N/A	N/A	Acros MSDS[20]
Carcinogenicity	Data Inadequate	N/A	N/A	Acros MSDS20
Mutagenicity	Data Inadequate	N/A	N/A	Acros MSDS20
Skin Irritation	Moderate	Rabbit	24	Acros MSDS20
Eye Irritation	Severe	Rabbit	24	Acros MSDS20
Reference Concentration (RfC) (mg/m^3)	0.1	N/A	24	IRIS18
Reference Dose (RfD) (mg/kg/day)	0.2	N/A	24	IRIS[18]
Biodegradability	readily biodegradable	N/A	N/A	EPA[21]
Soil Adsorption Coefficient, K_{oc} (L/kg)	196-311	N/A	N/A	EPA[22]
Bio-concentration Factor (BCF)	2.14-2.20	N/A	N/A	EPA21
Octanol Water Partition Coefficient K_{ow}	3.16	N/A	N/A	Ashland MSDS19
Fish Toxicity LC_{50} (mg/L)	23.53 – 29.97	Pimephales promelas	96	Ashland MSDS19
Daphnia LC_{50} (mg/L)	>100-<1,000	Daphnia magna	24	Ashland MSDS19

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[19] http://www.sfm.state.or.us/cr2k_subdb/MSDS/XYLENE_5_AROMATIC_SOLVENT.PDF

[20] http://cnl.colorado.edu/cnl/images/MSDS/fisher%20xylene.pdf

[21] http://www.epa.gov/safewater/pdfs/factsheets/voc/tech/xylenes.pdf

[22] http://www.epa.gov/superfund/health/conmedia/soil/pdfs/appd_k.pdf

Methanol (CAS # 67-65-1) Toxicological Data

Like xylene, toxicological data for methanol are more readily available and are shown in **Table 76**. The inhalation value of 83.2 mg/L suggests that proper ventilation or respiration protection equipment is needed when working with large volumes of methanol.

The octanol/water partition coefficient is very low because methanol is miscible with water. It readily interacts with aquatic life when mixed with water. The low aquatic toxicity as shown by the >10000 mg/L LC_{50} for fish and Daphnia suggest that use of proper wastewater treatment techniques can be an effective method to eliminate this waste.

Table 76. Methanol toxicological data

	Toxicity Test Result	Species	Time (hrs)	Resource
Ingestion LD_{50} (mg/kg)	5,628	Rat	N/A	Thermo Fisher Scientific MSDS[23]
Inhalation LC_{50} (mg/L)	>83.2	Rat	4	Thermo Fisher Scientific MSDS23
Dermal LD_{50} (mg/kg)	15,800	Rabbit	N/A	Thermo Fisher Scientific MSDS23
Oral LD_{50} (mg/kg)	5,600	Rat	N/A	Airgas MSDS[24]
Intravenous LD_{50} (mg/kg)	2,131	Rat	4	Airgas MSDS24
Intraperitoneal LD_{50}	7,529	Rat	N/A	Airgas MSDS24
Developmental Toxicity	Negative	N/A	N/A	Methanol Toxicology Review[25]
Carcinogenicity	Negative	N/A	N/A	Methanol Toxicology Review25
Mutagenicity	Negative	N/A	N/A	Methanol Toxicology Review25
Reference Concentration (RfC) (mg/m^3)	20	N/A	24	IRIS[26]
Reference Dose (RfD) (mg/kg/day)	2.0	N/A	24	IRIS26
Octanol Water Partition Coefficient K_{ow}	-0.74	N/A	N/A	Thermo Fisher Scientific MSDS23
Biodegradability	readily biodegradable	N/A	N/A	EPA[27]
Soil Adsorption Coefficient, K_{oc} (L/kg)	9	N/A	N/A	EPA27
Estimated Bio-concentration Factor (BCF)	0.2	N/A	N/A	EPA27
Fish Toxicity LC_{50} (mg/L)	29,400	Pimephales promelas	96	Airgas MSDS24
Daphnia LC_{50} (mg/L)	23,400	Daphnia magna	48	Thermo Fisher Scientific MSDS23

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[23] http://www.fishersci.com/ecomm/servlet/msdsproxy?productName=A4134&productDescription=METHANOL+NF+4L&catNo=A413-4+%3Cimg+src%3D%22%2Fglyphs%2Fgsa_glyph.gif%22+width%3D%2230%22+height%3D%2213%22+alt%3D%22Available+on+GSA%2FVA+Contract+for+Federal+Government+customers+only.%22+title%3D%22Available+on+GSA%2FVA+Contract+for+Federal+Government+customers.%22++border%3D%220%22%3E%26%23160%3B&vendorId=VN00033897&storeId=10652

[24] http://www.airgas.com/documents/pdf/006043.pdf

[25] http://www.hpa.org.uk/webc/hpawebfile/hpaweb_c/1194947357226

[26] http://www.epa.gov/iris/subst/0305.htm

[27] http://www.epa.gov/chemfact/s_methan.txt

TEG (CAS# 112-27-6) Toxicological Data

Toxicological data shown in **Table 77** suggest that TEG is not very harmful. An inhalation value of >5.2 mg/kg suggests that proper ventilation or respiration protection equipment is needed when exposed to mists or vapors of TEG. The fish toxicity of 10-100 mg/L suggests that use of proper wastewater treatment techniques is needed before it can be released to the environment.

Table 77. TEG toxicological data

	Toxicity Test Result	Species	Time (hrs)	Resource
Ingestion LD_{50} (mg/kg)	17,000	Rat	N/A	Sigma Aldrich MSDS[28]
Inhalation LC_{50} (mg/kg)	>5.2	Rat	N/A	Raw Material Supplier Form
Dermal LD_{50} (mg/kg)	>22,500	Rabbit	N/A	Sigma Aldrich MSDS28
Skin Irritation	Mild Skin Irritation	Human	24	Sigma Aldrich MSDS28
Eye Irritation	Mild Eye Irritation	Rabbit	24	Sigma Aldrich MSDS28
Fish Toxicity LC_{50} (mg/L)	10-100	Fish	96	Raw Material Supplier Form
Daphnia LC_{50} (mg/L)	48,900	Daphnia magna	48	Dow MSDS[29]
Algae EC_{50} (mg/L)	>100	Pseudokirchneriella subcapitata	168	Dow MSDS29
Biodegradability	readily biodegradable	N/A	N/A	Dow MSDS29
Estimated Soil Adsorption Coefficient, K_{oc} (L/kg)	10	N/A	N/A	Dow MSDS29
Estimated Bio-concentration Factor (BCF)	<100	N/A	N/A	Dow MSDS29
Estimated Octanol Water Partition Coefficient K_{ow}	-1.75	N/A	N/A	Dow MSDS29
Carcinogenicity	Negative	Lab Animals	N/A	Dow MSDS29
Developmental Toxicity	Negative	Lab Animals	N/A	Dow MSDS29
Reproductive Toxicity	Negative	Lab Animals	N/A	Dow MSDS29
Genotoxicity	Negative	Lab Animals	N/A	Dow MSDS29

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[28] http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=90390&brand=FLUKA&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Ffluka%2F90390%3Flang%3Den

[29] http://aglayne.com/wp-content/uploads/2010/10/Triethylene-Glycol-MSDS.pdf

DDBSA (CAS # 27176-87-0) Toxicological Data

The toxicological data for DDBSA are provided in **Table 78**. The predicted fish toxicity LC_{50} and predicted Algae EC_{50} values are listed as no effects at saturation (NES). According to ECOSAR, no effects are expected if these values are greater than 10 times the solubility in water, which is predicted to be 0.7032 mg/L. Since these values were predicted to be above that limit, they are not included in the table. It should be noted that the other aquatic toxicity values listed in the table are also above the solubility of DDBSA in water, though below the 10X solubility limit required for NES classification.

Table 78. DDBSA toxicological data

	Toxicity Test Result	Species	Time (hrs)	Resource/Model Software
Ingestion LD_{50} (mg/kg)	650	Rat	N/A	MSDS[30]
Eye Irritation/Damage	Severe irritant	N/A	N/A	MSDS30
Skin Corrosion/Irritation	Severe irritant	N/A	N/A	MSDS30
Predicted Octanol Water Partition Coefficient, log K_{ow}	4.784	N/A	N/A	ECOSAR
Predicted Genotoxicity	Negative	N/A	N/A	Toxtree
Predicted Non-Cancer Toxicity	Negative	N/A	N/A	Toxtree
Predicted Mutagenicity	Negative	N/A	N/A	TEST
Predicted Fish Toxicity LC_{50} (ppm)	NES	N/A	96	ECOSAR
Predicted Fish Toxicity LC_{50} (ppm), Chronic	1.121	N/A	N/A	ECOSAR
Predicted Daphnia LC_{50} (ppm)	6.218	Daphnia	48	ECOSAR
Predicted Daphnia Toxicity LC_{50} (ppm), Chronic	1.24	Daphnia	N/A	ECOSAR
Predicted Algae EC_{50} (ppm)	NES	N/A	96	ECOSAR
Predicted Algae Toxicity (ppm), Chronic	6.225	N/A	N/A	ECOSAR
Predicted Biodegradability	Not readily biodegradable	N/A	N/A	EPIWIN
Predicted Soil Adsorption Coefficient, K_{oc} (L/kg)	3707	N/A	N/A	EPIWIN
Predicted Bioconcentration Factor (BCF)	71	N/A	N/A	EPIWIN

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[30] http://www.fishersci.com/ecomm/servlet/msdsproxy?productName=AC240885000&productDescription=DODECYLBENZENE+SULFONIC+500GR&catNo=AC240885000&vendorId=VN00032119&storeId=10652

The BCF is significantly below 5000, so very little bioaccumulation in fish is expected. DDBSA is a severe irritant and is known to cause burns to skin, eyes, the digestive tract, and respiratory system.

6.3. Physical Properties of the Materials in the CO_2 Capture Process

The volatility, flammability, chemical reactivity, corrosivity, and other physical property data were collected from various databases and included in Table 21 below. Data were collected for GAP-1_m, TEG, xylenes, methanol, and DDBSA. The information aids in the design and engineering of the CO_2 absorption/desorption system. It also helps in understanding how to handle and work with each chemical compound. The volatility and flash point data suggest that GAP-1m and TEG are not very volatile or flammable, but xylene and methanol are. All of the compounds react with oxidizing agents. GAP-1m and DDBSA are corrosive materials, but TEG, xylenes, and methanol are not. The storage and handling of these materials is discussed more fully in Section H.

Table 79. Physical properties of the CO_2 capture solution components

	GAP-1_m17 Stream 6	TEG[31] Stream 6	Xylenes[19] Stream 7	Methanol[23] Stream 4	DDBSA[30], Stream 4
Volatility (Evap. Rate)	<1 (butyl acetate = 1)	<0.001 (butyl acetate = 1)	0.86 (butyl acetate = 1)	4.6 (butyl acetate)[32]	Not available
Flash Point	>100 °C	177 °C	26.66 °C	12 °C	> 200°C
Lower Explosion Limit/Upper Explosion Limit	Not available[33]	0.9 % (V)/ 9.2 % (V)	1.0 % (V)/ 7.0 % (V)	6.0 % (V)/ 31.00 % (V)	Not available
Auto-Ignition Temperature	No data available	349 °C	527 °C	455 °C	Not available
Chemical Reactivity	May react with oxidizing agents	May react with oxidizing agents	May react with oxidizing agents	May react with oxidizing agents	May react with metals, strong oxidizing agents, strong bases
Corrosivity	Corrosive	Not Corrosive	Not Corrosive	Not Corrosive	Corrosive
State, STP	Liquid	Liquid	Liquid	Liquid	Liquid
Color	Brownish	Colorless	Colorless	Colorless	Brown
Odor	Amine-like	Odorless	Mild, aromatic	Alcohol-like	Sulfur dioxide odor
Melting Point	~ -90 °C	-7 °C	-47.00 °C	-98 °C	10°C
Boiling Point	>155 °C	288.0 °C	137-140 °C	64.7 °C	315°C
Vapor Pressure	<0.13 kPa @ 20 °C	<0.001kPa @ 20 °C	0.93 kPa @ 20 °C[34]	12.8 kPa @ 20 °C	Not available
Vapor Density	>1 (Air = 1.0)	5.2 (Air = 1.0)	3.66 (Air = 1.0)	1.11 (Air = 1.0)	Not available
Density	0.93 g/cm^3@ 20 °C	1.124 g/ cm^3 @ 20 °C	0.86 g/cm^3 @20 °C	0.791 g/ cm^3 @ 20 °C	1.2 g/cm^3
Water Solubility	Very slightly soluble in cold water	Soluble in water	Negligible (practically insoluble)	Soluble in water	Soluble in water
Solubility Properties	Soluble in chloroform, toluene, hexanes	Soluble in ethanol, benzene, ether	Ether; soluble in many organic liquids, alcohol	Ethanol, ether and many other organic solvents[35]	Not available

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[31] http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_004d/0901b8038004d042.pdf

[32] http://www.erowid.org/chemicals/alcohol/alcohol_data_sheet.shtml

[33] With the flash point being >100C, the material is considered to be non-flammable. The LEL and UEL have not been determined.

[34] http://www.ppci.com.ph/msds2k10/17_xylene.pdf

[35] http://oehha.ca.gov/air/chronic_rels/pdf/67561.pdf

6.4. U.S. EH&S Law Compliance and Regulation Implications for the CO_2 Capture Process

The compliance of the chemicals used in and potential emissions from the proposed continuous CO_2 absorption/desorption system to United States Environmental, Health, and Safety regulations is summarized below. The resulting implications on the proposed technology are also addressed. The applicable U.S. EH&S laws addressed include: Toxic Substances Control Act (TSCA), Comprehensive Environmental Response and Liability Act of 1980 (CERCLA), Clean Water Act (CWA), Clean Air Act (CAA), Superfund Amendments and Reauthorization Act (SARA) Title III, the Occupational Safety and Health Act (OSHA), and the Resource Conservation and Recovery Act (RCRA). **Table 80** summarizes the initial list of streams from the process (Figure 2) that were considered in preparing the regulatory review.

Table 80. Streams considered for regulatory review

Stream #	Components	Comments
1	Flue gas	This stream would come directly from the plant and is not included in the regulatory review of this specific process.
2	Clean flue gas – see Table 5	This process does not add any components to this stream. It is not discussed further in the regulatory review.
3	CO_2 product	This stream is not a concern for the regulatory review and is not discussed further in this section.
5	GAP-1m/SOx salts	--
6	GAP-1/TEG make-up stream, includes xylene and methanol	--
7	Xylene	--
12	GAP-1, DDBSA	--
13	Water, TEG, methanol, xylene	--

The following individual components are the primary focus of this review, based on the summary in **Table 80**:

- GAP-0
- GAP-1-4
- TEG

- Xylene
- DDBSA
- Methanol
- GAP-1m/SO_x salts

A summary of the applicable regulations for each of these components is provided in **Table 81**. Each regulation is discussed separately in the following sections. All substances are marked as being regulated by RCRA. This indicates that all of these materials are potential waste products of this process and would, therefore, be regulated under RCRA Subpart C or D. This table does not indicate hazardous or non-hazardous waste classification. For a detailed discussion of those classifications for each waste stream, see the RCRA section of this report.

Table 81. Regulatory overview for components of CO_2 capture system

	TSCA	CERCLA RQ (lbs.)	CWA	CAA HAP	CAA VOC	SARA 302 EHS	SARA 311/312	SARA 313	OSHA Regulated	RCRA
CAS#2469-55-8, GAP-0	Y	N	N	N	Y	N	Acute Fire	N	Y	Y
CAS#106214-84-0, GAP-1-4	Y	N	N	N	Y	N	Acute	N	Y	Y
CAS#1330-20-7, Xylene	Y	100	Y	Y	Y	N	Acute Chronic Fire	Y	Y	Y
CAS#67-65-1, Methanol	Y	5000	N	Y	Y	N	Acute Chronic Fire	Y	Y	Y
CAS#112-27-6, TEG	Y	N	N	N	Y	N	Acute	N	Y	Y
CAS#27176-87-0, DDBSA	Y	1000	Y	N	Y	N	Acute	N	Y	Y
GAP-1/SOx salts	N	N	N	N	N	N	N	N	Y	Y

TSCA

GAP-0, GAP-1-4, xylene, methanol, TEG, and DDBSA are all on EPA's TSCA Inventory allowing companies to manufacture and use the chemical commercially.

CERCLA

CERCLA hazardous substances are considered severely harmful to human health and the environment.[36] RQ is the minimum release quantity that must be reported.[37] CAS#2469-55-8 (GAP-0), CAS#106214-84-0 (GAP-1-4), and triethylene glycol are not listed as CERCLA hazardous substances, but xylene, methanol, and DDBSA are. The minimal reportable quantities are 100 lbs./day, 5000 lbs./day, and 1000 lbs./day for xylene, methanol, and DDBSA, respectively.

Xylene leaves this process through streams 7 and 13. The total amount of xylene leaving the process in both of these streams is estimated to be 1.2 lbs./day, which is expected to be the maximum potential quantity that could be released. This is below the reportable quantity so is unlikely to be a concern for this process.

Methanol leaves this process through stream 13. The estimated amount of methanol leaving this process is also 1.2 lbs./day, which is expected to be the maximum potential quantity that could be released. This is below the reportable quantity so is unlikely to be a concern for this process.

Though DDBSA leaves the process through stream 12, there is also the potential for spills of the pure material stored on-site for use in the process. This would need to be stored on-site in quantities greater than the reportable quantity. This emphasizes the importance of safe handling and storage of this material. In future, materials that could be substituted for DDBSA for treatment of stream 4 will also be investigated.

Clean Water Act

Xylene and DDBSA are designated as hazardous substances to the water supply in accordance with Section 311(b)(2)(A) of 40 CFR 116, the Clean Water Act (CWA).[38] As with CERCLA, the

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[36] http://www.epa.gov/oem/docs/er/302table01.pdf

[37] http://www.epa.gov/superfund/policy/release/rq/index.htm#levels

[38] EPA 2005b 40 CFR 116.4

minimum reportable quantities for xylene and DDBSA are 100 lbs./day and 1000 lbs./day (40 CFR § 117.3), respectively.

Clean Air Act

Xylene and methanol are also both regulated Hazardous Air Pollutants (HAPs) and Volatile Organic Compounds (VOCs) under the Clean Air Act (CAA).[39] GAP-1m, TEG, and DDBSA are also VOCs. VOCs are defined in this case as any compound of carbon that participates in atmospheric photochemical reactions. Certain exclusions are listed in the regulatory definition (40 CFR §51.100(s)). The potential release rate for these chemicals for a 550 MW power plant is lower than required for reporting.

SARA

None of these chemicals pose an immediate hazard to a community upon release as described by EPA's SARA 302 list. For Safety Data Sheet reporting (SARA 311/312), GAP-0, GAP-1-4, xylene, methanol, TEG, and DDBSA are considered as acute, immediate health hazards. Xylene and methanol are considered to be chronic, delayed health hazards, and GAP-0, xylene, and methanol are considered as fire hazards. SARA 313 rules require reporting chemical releases of xylene and methanol to public and government officials.[40]

OSHA

All of the chemicals are regulated by OSHA, requiring proper safety data sheet, handling, shipping, and storage equipment. Safe handling and storage are discussed in further detail in Section G of this report.

RCRA

The relevant sections of RCRA are Subparts C and D of 40 CFR Part 260.

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[39] EPA 2004b 42 USC 7412

[40] http://nepis.epa.gov/Exe/ZyNET.exe/100038G4.txt?ZyActionD=ZyDocument&Client=EPA&Index=1991%20Thru%201994&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C91THRU94%5CTXT%5C00000007%5C100038G4.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=p%7Cf&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=5

Subpart D deals with municipal solid waste and non-hazardous waste, including that generated by industry, such as power plants. Waste not categorized under Subpart C as a hazardous waste is disposed of under Subpart D. Specific requirements for disposal for Subpart D would depend on the power plant location and a detailed discussion of local requirements is outside the scope of this document. Specific disposal methods would need to be reviewed on a site-specific basis.

For the purpose of this review, only federal RCRA requirements are considered. These are the minimum requirements for RCRA. Some states administer their own programs, which are at least as stringent as the EPA's. This EH&S assessment does not include a detailed review of all the state programs. These requirements would vary based on power plant location and an extensive review of all state RCRA programs is considered to be outside the scope of this document.

To determine if Subpart C applies to a given stream, the following questions must be answered (in order):

1. Is the material in question a solid waste?
2. Is the material excluded from the definition of solid waste or hazardous waste?
3. Is the waste a listed or characteristic hazardous waste?
4. Is the waste delisted?

If a stream is excluded from RCRA's definition of a solid or hazardous waste by answering one of these questions, it is not necessary to proceed through the remaining questions.

Each of these questions is discussed in detail for the following streams ():

- Absorber: Streams 8, 9, and 10
- Desorber: Streams 5, 7, 12, 13, 14, 15, and 16

The overall conclusions for each stream are summarized at the end of this section in **Table 85**.

Absorber

Streams 8, 9 and 10

The flue gas in stream 8 goes through the water wash tower to remove GAP-1m, xylenes, and methanol. A stream containing GAP-1m, xylene, methanol, and water then undergoes a distillation step to separate into water (stream 9), which is recycled back to the wash tower, and GAP-1m, xylene, and methanol (stream 10), which is recycled back to the absorber.

Question 1: Is the material in question a solid waste?

Since these streams are involved in a distillation step before returning to the process and distillation is included in RCRA's definition of reclamation, streams 8, 9, and 10 would be considered solid waste.

Question 2: Is the material excluded from the definition of solid waste or hazardous waste?

An exclusion is provided by RCRA for Closed loop recycling (40 CFR § 261.4(a)(8)). This excludes materials from the definition of solid waste if they are being reclaimed and recycled to the process through an enclosed system of pipes and tanks. This exclusion would apply to streams 8, 9, and 10 since the material will be recycled back to the process. Therefore, all three streams are excluded from the RCRA definition of solid waste.

Desorber

Streams 5, 7, 15, and 16

To purge the GAP-1_m/SO_x salts from the system, stream 15 is removed from the desorber. It undergoes a vacuum distillation. This produces the GAP-1_m/SO_x salt stream (Stream 5), the xylene stream (stream 7), and the GAP-1m/TEG stream (stream 16). Stream 16 is recycled back to the desorber.

Question 1: Is the material in question a solid waste?

Streams 5, 7, 15, and 16 are considered to be solid wastes since a reclamation step is required before the GAP-1m/TEG can be recycled back to the desorber.

Question 2: Is the material excluded from the definition of solid or hazardous waste?

The GAP-1_m/TEG in streams 15 and 16 is excluded from the definition of solid waste by the Closed loop recycling exclusion, since the reclamation step will be fully enclosed and the GAP-1m/TEG stream (stream 16) will be returned directly to the desorber after reclamation.

Streams 5 and 7 will not return to the process and will require disposal and are, therefore, considered to be solid wastes.

Question 3: Is the material a listed or characteristic hazardous waste?

Stream 5 (GAP-1_m/SO_x salts) is not a listed waste. This stream also does not exhibit the characteristics listed in Table 24 so is not considered a characteristic waste. This waste will be disposed of under RCRA Subpart D as industrial, non-hazardous waste in accordance with local regulations at the plant in question.

Stream 7 contains primarily xylene. This is on the U list, but only if the xylene is pure, unspent solvent. It is also on the F list, but only if the solvent is being used in pure form or in a mixture with specifically named solvents. Xylene is present in low levels in the GAP-1m material and is not used in the process as a pure solvent or as a mixture with any of the other solvents listed under the F003 designation. In this process, xylene is not a listed waste. Xylene does exhibit the ignitability characteristic with a flashpoint below 60°C. Stream 7 is, therefore, a characteristic hazardous waste.

Table 82. Criteria to be considered characteristic waste under RCRA Subpart C

Characteristic	Criteria
Ignitability	Liquid wastes with flashpoints below 60 °C
Corrosivity	Aqueous with pH ≤ 2 or ≥ 12.5
Reactivity	Explode or cause violent reactions or react to release toxic gas or fumes when exposed to water or under normal handling conditions
Toxicity	Presence of chemical above TCLP regulatory levels

Question 4: Is the waste delisted?

Stream 7 is a characteristic hazardous waste, and not a listed hazardous waste. Therefore, question 4 does not apply. Stream 7 would need to be disposed of under Subpart C of RCRA as hazardous waste. The Subpart C requirements are discussed in more detail later in this section as they apply to this process.

Stream 12

Stream 12 is a GAP-1m/DDBSA stream produced from the treatment of stream 4 condensed out of the exit gas from the desorber.

Question 1: Is the material in question a solid waste?

Stream 12 is not returned to the process and would require disposal. It is, therefore, considered to be a solid waste.

Question 2: Is the material excluded from the definition of solid or hazardous waste?

Stream 12 is not excluded and is, therefore, considered to be solid waste.

Question 3: Is the material a listed or characteristic hazardous waste?

GAP-1m and DDBSA are not on the F, K, P, or U lists. They are not considered listed hazardous wastes.

The GAP-1m/DDBSA stream would not exhibit any of the criteria in **Table 82**. It is not a characteristic hazardous waste. This waste will be disposed of under RCRA Subpart D as industrial, non-hazardous waste in accordance with local regulations at the plant in question.

Stream 13

Stream 13 contains primarily water and TEG, with some methanol and xylene after treatment of stream 4.

Question 1: Is the material in question a solid waste?

Stream 13 is not returned to the process and would require disposal. It is, therefore, considered to be a solid waste.

Question 2: Is the material excluded from the definition of solid or hazardous waste?

Stream 13 is not excluded and is, therefore, considered to be solid waste.

Question 3: Is the material a listed or characteristic hazardous waste?

Methanol and xylene are on the U list, but this process does not use pure, unspent solvent so the designation would not apply in this case. Xylene is on the F list, but this process does not use the pure solvent and it is not mixed with the other solvents in the F003 definition so the designation would not apply. TEG is not on the F, K, U or P lists. Stream 13 is not considered to be a listed waste.

To be considered a characteristic waste, at least one of the criteria in Table 24 would need to apply. The flashpoints for pure xylene and pure methanol are below 60 °C. However, these chemicals are only present in trace amounts in Stream 13. Stream 13 would not cause an ignitability concern. The other criteria are not applicable to this stream either. Therefore, stream 13 would be considered industrial, non-hazardous solid waste under RCRA and would be disposed of under Subpart D in accordance with local regulations at the plant in question, which could include sending it to a wastewater treatment facility.

Stream 14

Stream 14 contains GAP-1m, TEG, xylenes, and some water that is condensed out of the gas exiting the desorber.

Question 1: Is the material in question a solid waste?

Since stream 14 is recycled directly back to the desorber and does not require reclamation, it is not considered solid waste.

An overall summary of the RCRA classifications for each of the streams discussed in this section is provided in **Table 83**.

Table 83. Summary of RCRA classifications

Stream Number	Materials	Classification and other relevant RCRA Information
Absorber		
8	Flue gas, GAP-1m, xylene and, methanol	Not solid waste under Closed loop recycling exclusion
9	Water	Not solid waste under Closed loop recycling exclusion
10	GAP-1m, xylene, and methanol	Not solid waste under Closed loop recycling exclusion
Desorber		
5	GAP-1m/SOx salts	Industrial, non-hazardous solid waste to be disposed of under Subpart D
7	Xylene	Characteristic hazardous waste based on ignitability to be disposed of under Subpart C
12	GAP-1m, DDBSA	Industrial, non-hazardous solid waste to be disposed of under Subpart D
13	Primarily water and TEG, with some xylene, and methanol	Industrial, non-hazardous solid waste to be disposed of under Subpart D
14	GAP-1m, TEG, xylene, and water	Not considered solid waste since directly recycled to desorber without reclamation
15	GAP-1m, TEG, xylene, GAP-1m/SOx salt	Not solid waste under Closed loop recycling exclusion
16	GAP-1m, TEG	Not solid waste under Closed loop recycling exclusion

RCRA Subpart C requirements

Generator requirements

Specific requirements for hazardous waste handling depend on the generator classification based on the quantity of hazardous waste generated per month. The only stream from this process for which the Subpart C requirements are relevant is stream 7.

The quantity of xylene generated based on the mass balance for stream 7 is estimated to be 28.4 lbs per month (calculated assuming 310.25 working days per year), or 12.9 kg per month. This would classify this process as a Conditionally Exempt Small Quantity Generator (CESQG) based on the RCRA definition and it would be exempt from RCRA requirements for this waste stream.

CESQG facilities are required to identify their hazardous waste, comply with storage limit requirements, and ensure waste treatment or disposal. Locations for disposal or waste treatment for CEQSG facilities include:[41]

- Permitted or interim status hazardous waste transport, storage, and disposal facilities (TSDFs)
- State hazardous waste facilities
- State permitted, licensed, or registered solid waste disposal facilities
- State municipal solid waste landfills
- Recycling facilities
- Universal waste facilities

Depending on the classification of the overall power plant, small quantity generator (SQG) requirements may be applicable since it would add to existing hazardous waste streams at the power plant. In general, SQGs need to do the following:

- Identify and count waste
- Obtain an EPA ID number
- Comply with accumulation and storage requirements
- Prepare the waste for transportation
- Track the shipment and receipt of such waste
- Meet recordkeeping and reporting requirements

Since the exact requirements for hazardous waste disposal would vary based on plant classification and plant location, they are not discussed in detail in this assessment but would need to be evaluated on a site-specific basis.

TSDF

RCRA excludes generators from the permit requirements for TSDFs as long as the generators accumulate waste on-site in accordance with the generator regulations. It is assumed that this process would comply with the necessary generator requirements and would, therefore, not be subject to TSDF regulations.

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[41] EPA 2011 RCRA Orientation Manual. http://www.epa.gov/osw/inforesources/pubs/orientat/

6.5. Engineering Analysis and Controls for the CO_2 Capture Process

The entire system requires some plant-wide engineering controls. Many of these are common in the chemical industry but might be new for a power plant facility. For example:

1) To protect groundwater, a double containment drain system is necessary. These keep rainwater separated from any chemical drainage system, not allowing them to mix. The containment system should be built with chemical resistant, high strength concrete.
2) A volatile vapor detection sampling and monitoring system is necessary to identify when leaks occur. This is especially important for VOCs like xylene and methanol.
3) A pressure/relief, vapor condensation/recovery system should be considered for all vessels. This prevents undesired backflow from one vessel to another, and it is required to minimize leaks and meet VOC release standards.
4) The equipment and piping arrangement chosen for the system should be designed to minimize leaks. For example, a shell & tube heat exchanger is much better than a plate & frame heat exchanger for minimizing leaks. The large number of gaskets in the plate & frame are all potential VOC emission points.
5) The gas streams, #2 and #3 in Figure 2, require a final gas polishing process like an activated carbon absorption bed. This removes any remaining VOCs, lowering potential emissions.
6) The thermal oxidizer equipment requires its own safety failure analysis. Equipment like detonation arrestors, back-flow valves, etc. is needed. Vendors of such equipment are well versed in the requirements and design of a specific unit, which is outside to scope of this task. [42]

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[42] http://www.oxidizerservice.com/ccs/; http://rto.american-environmental.us/Lower-Explosive-Limit.html

6.6. Handling and Storage for the CO2 Capture Process

This section describes the precautions necessary for safe handling and storage of the chemicals used in the CO_2 absorption/desorption system. The applicable rules and standards of the Occupational Safety and Health Act (OSHA) are summarized, including safe storage, incompatibilities with other materials, waste treatment and offsite disposal options, accidental release measures, and protective equipment suggestions. The following section provides handling and storage recommendations for GAP-1m, TEG, xylene, methanol, sulfur dioxide, and DDBSA. As discussed in Section C, the toxicity of GAP-1_m/SO_x is assumed to be less than or equal to its components, GAP-1_m and SO_x. Details of handling and storage of GAP-1m/SOx is not available but is assumed to be less rigorous than those needed for its components.

a) GAP-1_m (CAS# 106214-84-0 and 2469-55-8)

GAP-1_m is classified as a hazardous chemical by the OSHA Standard. It is regulated under both DOT and IATA as a corrosive liquid. Its NFPA Classification is a 3 for health hazard, 1 for flammability, and 0 for reactivity

1) Storage and Handling Recommendations

GAP-1m should be stored in a phenolic lined drum or pail and away from acids and oxidizers. When it is burned, it decomposes into carbon monoxide, carbon dioxide, nitrogen oxides, and silicone dioxide. The material should be used in an area with adequate ventilation.

2) Accidental Release Measures

When a spill occurs, one should evacuate the area and alert trained spill officials. Those trained to work with spills should wear a respirator when ventilation is not adequate and wear proper personal protect equipment. The spill team should keep those untrained and unprotected from entering the spill area. Also, they should prevent others from touching or walking through the contaminated area. For environmental protection, do not allow the material to be dispersed or come in contact with drains, sewers, soil or any water source. Use an absorbent barrier to prevent contamination into the environment. When or if the material comes in contact with the environment, notify the local authorities immediately.

3) Health Effects and Exposure limits

It is corrosive to the skin, eyes, digestive tract, and respiratory system and may cause burns. Use the material in a well-ventilated area.17 Overexposure to GAP-1m can cause respiratory irritation, coughing, stomach pains, skin redness, and watering or redness of the eyes. The PEL has not been established for this chemical. Since GAP-1m has a high boiling point, the amount that vaporizes at ambient conditions is very low.

4) Respiratory Protection Recommendation

If the vapor concentration of GAP-1m exceeds 2000 ppmv, a full-faced respirator with an olive cartridge is recommended. A cartridge designed for amines is recommended.

5) Hand and Eye Protection Recommendation

When using GAP-1m, chemical resistant gloves should be worn. Butyl rubber and neoprene are recommended. These gloves have an estimated breakthrough time of more than 8 hours. The recommended eye protection is splash goggles or a face shield.

6) Skin and Body Protection Recommendation

The risk of exposure for the production area needs to be evaluated to determine proper body protection. For low risk exposure of only hands, butyl or neoprene gloves are recommended. For high risk exposure, a rubberized acid suit is recommended.17,[43]

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[43] Carlton Dill, SiVance, LLC, personal communication, December 9, 2013.

b) *Triethylene Glycol (CAS# 112-27-6)*

Triethylene Glycol (TEG) is not known as an OSHA hazard. Its NFTP Classification is a 0 for health hazard, 1 for flammability and 0 for reactivity. It is not regulated by the Department of Transportation (DOT) or International Air Transport Association (IATA).

1) Storage and Handling Recommendations

It is recommended that the material be kept in a tightly closed container in a dry, well-ventilated area. Triethylene glycol is hygroscopic, requiring a storage container that minimizes exposure to moisture. Iron can contaminate the material. To avoid contamination from iron, the use of stainless steel, aluminum, phenolic or epoxy resin lined vessels is recommended.[44] Avoid storing this chemical near strong oxidizing agents, strong acids, or bases because triethylene glycol reacts with these materials. An exothermic reaction can take place when TEG mixes with strong acids and oxidizing agents. These reactions often produce a toxic, flammable gas and could lead to an explosion. Special examples of common chemicals that should be avoided are acetic acid and anhydrides.[45] In a fire, triethylene glycol can decompose to carbon monoxide and carbon dioxide.

2) Accidental Release Measures

In the case of a spill or accidental release, evacuate personnel to a safe area. Ensure adequate ventilation and inform trained clean-up professionals of the spill. Only allow these trained officials to enter the spill area wearing the proper protective equipment (including a respirator, if necessary).

Barriers should be placed around the spill to prevent TEG from entering drains or other water sources. Inert absorbent material should be used to cleanup and contain the spill. Contaminated material should be disposed as hazardous waste in closed containers.

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[44] http://www.huntsman.com/portal/page/portal/performance_products/Media%20Library/a_MC348531CFA3EA9A2E040EBCD2B6B7B06/Products_MC348531D0B9FA9A2E040EBCD2B6B7B06/Glycols_MC348531D11A3A9A2E040EBCD2B6B7B06/files/teg_triethylene_glycol_.pdf

[45] http://www.pttgcgroup.com/src/download/products/eo_based/TEG_MSDS.pdf

3) Health Effects and Exposure Limits

If triethylene glycol is inhaled, it may cause respiratory tract irritation. It may also cause skin and eye irritation. The material is not classified as hazardous under OSHA. No exposure limit data were available.

4)Respiratory Protection Recommendation

At room temperature, exposure to vapor is expected to be small due to low volatility, but at elevated temperatures, vapors may cause irritation of the upper respiratory tract (nose and throat). In such cases, respiratory protection should be worn when exposure to TEG vapors and mists are likely. In misty atmospheres, use an approved air purifying respirator with an organic vapor cartridge and a particulate pre-filter.[46]

5) Hand and Eye Protection Recommendation

Triethylene glycol should be handled with gloves. They should be inspected prior to use. If one is going to be in full contact with TEG, nitrile rubber gloves with a minimum layer thickness of 0.11 mm are recommended. The nitrile gloves have a break through time of >480 min. For splash protection when working with TEG, a nitrile rubber apron should also be worn. For eye protection, safety glasses with side shields are recommended.

6) Skin and Body Protection Recommendation

Prolonged skin contact is unlikely to result in absorption of harmful amounts. Massive contact with damaged skin or of material sufficiently hot to burn skin may result in absorption of potentially lethal amounts. Still, avoid contact with skin and clothing. Wash thoroughly after handling. Use protective clothing chemically resistant to this material, including such items as gloves, face-shields, boots, apron, or a full-body suit, depending upon the task. When handling hot material, protect skin from thermal burns as well as from skin absorption.

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[46] http://aglayne.com/wp-content/uploads/2010/10/Triethylene-Glycol-MSDS.pdf

c) *Xylene (CAS# 1330-20-7)*

Xylene is classified as a hazardous chemical by the OSHA Standard. It is regulated under both DOT and IATA as a flammable liquid (hazard class 3) with the proper shipping name xylenes. Its NFPA Classification is a 2 for health hazard, 3 for flammability, and 0 for reactivity.

1) Storage and Handling Recommendations

Xylene is a flammable liquid (flash point is 80oF/26.7oC). Handle material away from heat, flames, and sparks. When handling xylene, vessels need to be grounded before transfer or use of material. The material should be used in a cool, dry, and well ventilated area. Xylene should not be handled near alkalis, strong acids, and strong oxidizing agents.

2) Accidental Release Measures

When a spill occurs, spill team authorities should be alerted. All personnel should be evacuated to a safe area away from the spill. Unauthorized individuals should not be allowed to enter the area without proper protective equipment. Xylene is a flammable material; therefore, all sources of ignition (fire, electrical sparks, etc.) should be eliminated. Prevent vapors from building up by providing proper ventilation.

Xylene spills should be contained by non-combustible absorbent materials. Some examples of these materials are sand, vermiculite, and diatomaceous earth. The contaminated absorbent material should be disposed in accordance with national and local regulations pertaining to waste disposal. Xylene should be kept from entering drains and not flushed into the sewer system during the clean-up process. If the material is not able to be contained and gets into the environment, local authorities must be notified immediately.

3) Health Effects and Exposure Limits

Xylene may affect the central nervous system leading to dizziness, headache, or nausea. It may cause mild eye irritation with symptoms include stinging, tearing, or redness. It can also cause skin and respiratory tract irritation. Prolonged skin exposure may lead to burns, redness and cracking of the skin. Swallowing the material may lead to lung inflammation or other lung injury. Breathing small amounts (below the permissible exposure limits) of the material will not likely cause any harmful effects. Some symptoms from exposure to xylene include: nausea, vomiting, diarrhea, redness of the skin, inhalation irritation, chest discomfort, shortness and slowness of breath, lack of coordination and memory, irregular heartbeat, narcosis, coma, and central nervous system excitation followed by depression. Exposure to xylene may aggravate pre-existing medical issues relating to the lung, kidney, heart, skin, central nervous system, male reproductive system, and auditory system.

Overexposure to xylene by laboratory animals led to the following effects: testis damage, kidney and liver damage, effects on hearing, cardiac sensitization, and harm to animal fetuses. Also overexposure can lead to effects on the central nervous system. For xylenes, the PEL is 100 ppm or 435 mg/m^3 during 8 hrs. The Short Term Exposure Limit (STEL) is 150 ppm or 655 mg/m^3 over 15 minutes. The Immediately Dangerous to Life and Health (IDLH) limit is 900 ppm.

4) Respiratory Protection Recommendation

Typically, the PEL and IDLH are used to determine the threshold limit for implementation of respirators. From 100 to 900 ppm, an approved air-purifying respirator with an organic vapor cartridge is required. A full-faced respirator with organic cartridges is required when emptying a vessel of xylene, reducing the risk of exposure to vapors and in case of a flash fire. [47]

5) Hand and Eye Protection Recommendation

When working with xylene, one should wear butyl or neoprene gloves which should be inspected prior to use. Wash hands after glove removal. Either a face shield or splash goggles is recommended when working with xylene.

6) Skin and Body Protection Recommendation

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[47] http://www.ccohs.ca/oshanswers/chemicals/chem_profiles/xylene.html#_1_12

Since xylene is a flammable material, one should wear flame resistant protective clothing, especially when handling large quantities. The proper protective attire should be determined by the amount of the chemical being handled and the environment of the plant.

d) Methanol (CAS# 67-56-1)

Methanol is classified as a hazardous chemical by the OSHA Standard. It is regulated under both DOT and IATA as a flammable liquid (hazard class 3) with the proper shipping name methanol. Its NFPA Classification is a 2 for health hazard, 3 for flammability, and 0 for reactivity.

1) Storage and Handling Recommendations

Due to the flammability of methanol (flash point is 53.6°F/ 12°C), it should be handled away from hot surfaces, ignition sources, and open flames. When handling methanol, containers storing the material should be grounded or electrically bound before transfer or use of material. The material should be used in a cool, dry, and well ventilated area.

Methanol should not be handled near strong acids, acid anhydrides, acid chlorides, strong bases metals, peroxides, or strong oxidizing agents.

2) Accidental Release Measures

When a spill occurs, spill team authorities should be alerted. All personnel should be evacuated to a safe area away from the spill. Unauthorized individuals should not be allowed to enter the area without proper protective equipment. Methanol is a flammable material; therefore, all sources of ignition (fire, electrical sparks, etc.) should be eliminated. Prevent vapors from building up by providing proper ventilation.23 Methanol spills should be contained by inert absorbent materials. The contaminated absorbent material should be collected and stored in suitable containers for disposal. These containers shall be disposed of in accordance with national and local regulations pertaining to flammable waste disposal. Methanol should be kept from entering drains and not flushed into the sewer system during the clean-up process. If the material is not able to be contained and gets into the environment, local authorities must be notified immediately.23

3) Health Effects and Exposure Limits

The organs targeted by methanol are the central nervous system, eyes, skin, respiratory system, optic nerve, liver, kidney, spleen, blood, and the gastrointestinal tract (GI). The acute effects are irritation to eyes, skin, and respiratory tract. Research has shown, prolonged exposure (inhalation, dermal, and ingestion) can lead to serious irreversible effects. Methanol has been shown to cause liver and kidney problems along with reproductive toxicity effects. The PEL is 200 ppm or 260 mg/m^3 during 8 hrs. The Short Term Exposure Limit (STEL) is 250 ppm or 325 mg/m^3 over 15 minutes. The IDLH level is 6000 ppm.

4) Respiratory Protection Recommendation

A full-faced respirator with organic cartridges is recommended.

5) Hand and Eye Protection Recommendation

Methanol should be handled with butyl rubber or neoprene gloves. Wash hands after glove removal. Tightly fitting safety goggles or splash goggles are recommended.

6) Skin and Body Protection Recommendation

Since methanol is a flammable material, one should wear flame retardant or resistant antistatic protective clothing and boots, especially when handling large quantities. The proper protective attire should be determined by the amount of the chemical being handled. The Methanol Institute recommends the following:

> "For routine unloading of methanol where splashing or skin absorption is not anticipated, natural fiber clothing (cotton) is adequate. Avoid wearing synthetic fiber clothing when there is a risk of fire from handling methanol. A chemical resistant apron, butyl or nitrile rubber gloves, and rubber boots, and a full face-shield worn over goggles for additional protection, (but not as a substitute for goggles), may be needed where there is a risk of splashing, such as in coupling and uncoupling hoses or lines. Chemical-resistant clothing/materials should be worn if repeated or prolonged skin contact with methanol is expected. Respiratory protection should be selected based on hazards present and the likelihood of potential exposure. Air purifying respirators with organic vapor (OVA) cartridges are not appropriate protection against methanol vapors due to the very short service life of the OVA cartridge before it becomes saturated, and there are no means of knowing when the vapors break through and the cartridge is no longer offering protection. The use of a supplied air respirator with a full face piece operated in a pressure-demand or other positive-pressure mode is the recommended respiratory protection. Personal protection equipment for the responders should, at a minimum, include chemical splash goggles and face

shield, butyl or nitrile gloves, rubber boots, chemical resistance coveralls, and provision for supplied fresh breathing air, such as full face, positive pressure SCBA. Fire resistant clothing is only necessary when fighting a fire. For more information on methanol personal protective equipment consult Chapter 4.2.2 of the Methanol Institute's Methanol Safe Handling Manual."[48]

e) *DDBSA (CAS# 27176-87-0)*

DDBSA is classified as hazardous by the OSHA Standard based on corrosivity[49]. It is regulated under both DOT and IATA as a corrosive material. Its NFPA Classification is a 3 for health hazard, 0 for flammability, and 0 for reactivity.

1) Storage and Handling Recommendations

This material should be stored in a cool, dry place and the container kept closed when not in use. It should be kept away from oxidizing materials, metals, and alkaline substances. It should be used in a well-ventilated area.

2) Accidental Release Measures

In the case of a spill, personnel should be evacuated to a safe area and trained spill control officials should be notified. The area should be ventilated and the material absorbed with inert materials (e.g. vermiculite, sand or earth). For environmental protection, precautions should be taken to avoid any runoff into drains, storm sewers, or ditches.

3) Health Effects and Exposure Limits

DDBSA causes severe burns to skin and eyes and may cause irreversible eye injury. It is harmful to the digestive tract and respiratory system. The material should be used in a well-ventilated area. No OSHA PEL has been established for this chemical.

4) Respiratory Protection Recommendation

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[48] http://www.methanol.org/health-and-safety/frequently-asked-questions.aspx

[49] http://datasheets.scbt.com/sc-226619.pdf

No specific recommendations for exposure limits for respirator usage were available. When risk assessment indicates it is necessary, respirators should meet OSHA 29 CFR 1910.134 and ANSI Z88.2 requirements.

5) Hand and Eye Protection Recommendations

Appropriate gloves and safety glasses/splash goggles should be worn during use.

6) Skin and Body Protection Recommendation

At a minimum, gloves should be worn. The need for additional protective clothing should be evaluated based on the concentration and amount of chemical used.

6.7. Air, Water, and Solid Waste Identification for the Manufacturing Process of GAP-1_m

This section describes the potential ancillary or incidental air, water, and solid wastes and estimates their magnitude for the manufacturing process of GAP-1_m. In addition to the chemical inputs to the manufacturing process, the potential by-products and waste streams were considered.

The overall manufacturing process is shown in **Figure 129**. For the overall mass balance for the process, both the requirements for the initial fill for the CO_2-capture system on a 550 MW power plant (**Table 84**) and for the annual GAP-1m make-up stream were calculated (**Table 85**). The initial fill for the system used for the calculation was 1785 tons. Based on the mass balance completed for the CO_2-capture system (see Section B), the annual requirement for GAP-1m make-up is 359 tons/year, based on an assumption of 310.25 working days per year.

The first unit operation consists of the reaction of allyl chloride (stream M10) with potassium cyanate (stream M11) in a methanol solvent (stream M12) at elevated temperatures and under pressure to form methyl N-allylcarbamate and potassium chloride. The reaction mixture is cooled and the solid potassium chloride removed by filtration (stream M1). The crude product is stripped to remove methanol which is recycled (stream M5) back to the first step. The crude product is dissolved in xylene (stream M6) and any methylcarbamate by-product formed during the reaction is removed with a water wash (stream M2). The xylene layer is separated from the aqueous layer and the methyl N-allylcarbamate product is isolated by initially stripping off the xylene solvent for reuse (stream M6) and then distilling the product under reduced pressure.

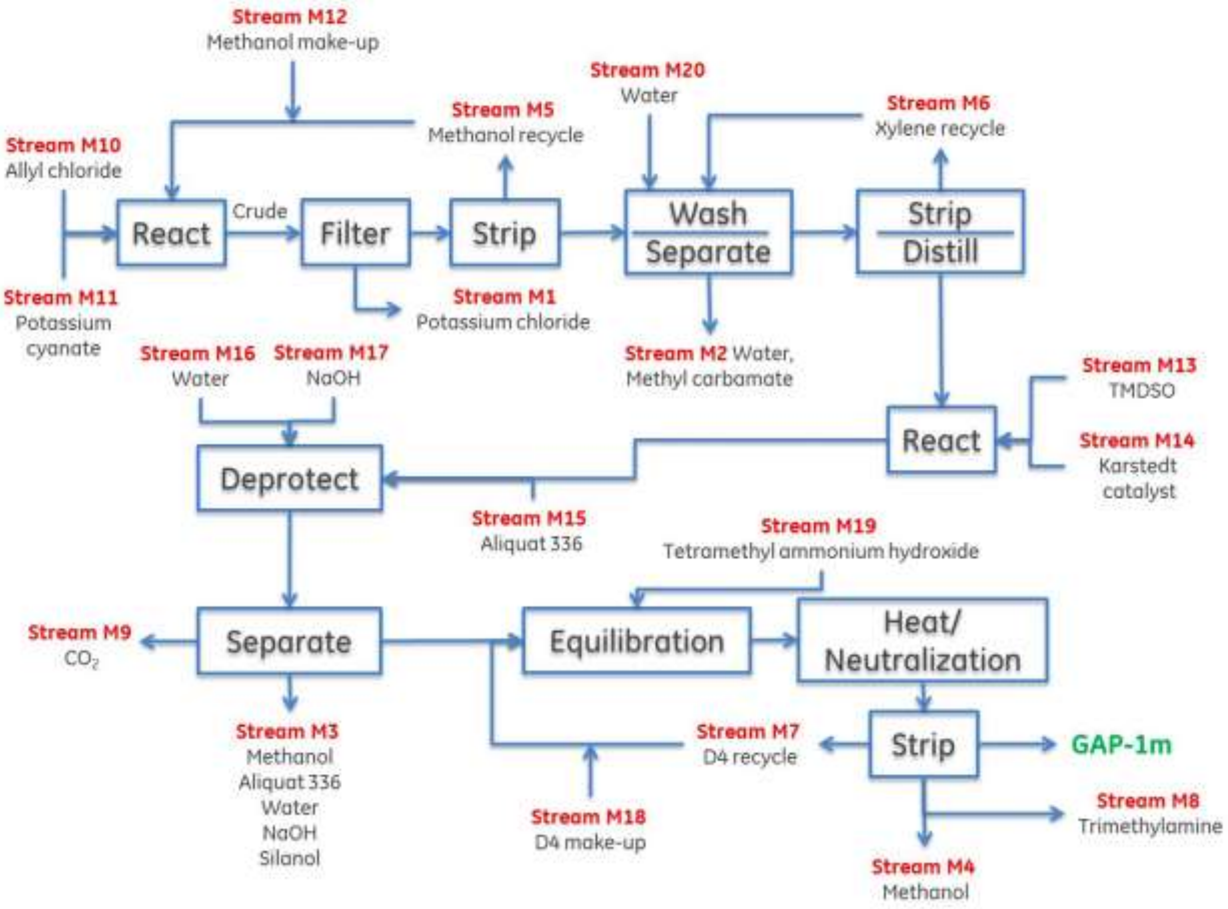

Figure 129. Manufacturing process for GAP-1_m

The methyl N-allylcarbamate is then contacted with TMSDO (stream M13) and a platinum catalyst (Karstedt's, stream M14) to effect a double hydrosilylation reaction in essentially quantitative yield to give 1,3-bis(3-methylcarbamatopropyl)-1,1,3,3-tetramethyldisiloxane. The carbamate protecting group is then removed by basic aqueous hydrolysis (streams M16 and

M17) under phase-transfer catalyst conditions (stream M15) at elevated temperature and pressure. The water layer is then separated (stream M3), the desorbed carbon dioxide vented (stream M9), and the GAP-0 product isolated. This intermediate product is added to D_4 (stream M18) and the mixture allowed to undergo an equilibration reaction catalyzed by tetramethylammonium hydroxide (stream M19). When equilibration is complete, the reaction mixture is heated to decompose the catalyst and neutralize the product. The more volatile components (methanol, stream M4 and trimethylamine, stream M8) are removed by scrubbers or condensation. The cyclic siloxanes that are formed during the equilibration reaction can be distilled off (stream M7) and recycled for further use in the equilibration reaction.

Table 84. Mass balance for manufacturing of GAP-1$_m$ for initial fill of system

Stream	Description	Total stream flowrate (lb/hr)	Total stream flowrate (lbmol/hr)	Component	Mol frac	lbmol/hr	MW	lb/hr
M1	Waste from filter	2.59E+02	3.47E+00	Potassium chloride	1.00E+00	3.47E+00	7.46E+01	2.59E+02
M2	Waste from Wash/ Separate step	2.00E+02	1.00E+01	Water	9.65E-01	9.65E+00	1.80E+01	1.74E+02
				Methyl carbamate	3.47E-02	3.47E-01	7.51E+01	2.61E+01
M3	Waste from Separate step	7.43E+02	3.58E+01	Water	9.02E-01	3.23E+01	1.80E+01	5.82E+02
				Methanol	8.72E-02	3.12E+00	3.20E+01	1.00E+02
				Aliquat 336	2.42E-03	8.68E-02	4.04E+02	3.51E+01
				NaOH	4.36E-03	1.56E-01	4.00E+01	6.25E+00
				Silanol	4.08E-03	1.46E-01	1.33E+02	1.95E+01
M4	Liquid Waste from Final Strip	1.74E+00	5.42E-02	Methanol	1.00E+00	5.42E-02	3.20E+01	1.74E+00
M5	Recycle stream	4.45E+02	1.39E+01	Methanol	1.00E+00	1.39E+01	3.20E+01	4.45E+02
M6	Recycle stream	1.74E+02	1.64E+00	Xylene	1.00E+00	1.64E+00	1.06E+02	1.74E+02
M7	Recycle stream	1.67E+01	5.62E-02	D4	1.00E+00	5.62E-02	2.97E+02	1.67E+01
M8	Gas waste stream from final strip	3.13E+00	5.29E-02	Trimethylamine	1.00E+00	5.29E-02	5.91E+01	3.13E+00
M9	Gas waste stream from separate step	1.38E+02	3.13E+00	CO2	1.00E+00	3.13E+00	4.40E+01	1.38E+02
M10	Allyl chloride input	2.66E+02	3.47E+00	Allyl chloride	1.00E+00	3.47E+00	7.65E+01	2.66E+02
M11	Potassium cyanate input	2.82E+02	3.47E+00	Potassium cyanate	1.00E+00	3.47E+00	8.11E+01	2.82E+02
M12	Methanol make-up stream	1.08E+02	3.38E+00	Methanol	1.00E+00	3.38E+00	3.20E+01	1.08E+02
M13	TMDSO input	2.10E+02	1.56E+00	TMDSO	1.00E+00	1.56E+00	1.34E+02	2.10E+02
M14	Karstedt catalyst input	8.69E-05	2.28E-07	Karstedt catalyst	1.00E+00	2.28E-07	3.81E+02	8.69E-05
M15	Aliquat 336 input	5.25E+01	1.30E-01	Aliquat 336	1.00E+00	1.30E-01	4.04E+02	5.25E+01
M16	Water input to deprotect step	5.25E+02	2.92E+01	Water	1.00E+00	2.92E+01	1.80E+01	5.25E+02
M17	NaOH input	1.31E+02	3.28E+00	NaOH	1.00E+00	3.28E+00	4.00E+01	1.31E+02
M18	D4 makeup stream	1.09E+02	3.69E-01	D4	1.00E+00	3.69E-01	2.97E+02	1.09E+02
M19	Tetramethyl ammonium hydroxide input	4.86E+00	5.34E-02	Tetramethyl ammonium hydroxide	1.00E+00	5.34E-02	9.12E+01	4.86E+00
M20	Water input to wash/ separate	1.74E+02	9.65E+00	Water	1.00E+00	9.65E+00	1.80E+01	1.74E+02

Table 85. Mass balance for manufacturing of GAP-1$_m$ for annual GAP-S make-up

Stream	Description	Total stream flowrate (lb/hr)	Total stream flowrate (lbmol/hr)	Component	Mol frac	lbmol/hr	MW	lb/hr
M1	Waste from filter	5.20E+01	6.98E-01	Potassium chloride	1.00E+00	6.98E-01	74.55	5.20E+01
M2	Waste from Wash/ Separate step	4.02E+01	2.01E+00	Water	9.65E-01	1.94E+00	18	3.49E+01
				Methyl carbamate	3.47E-02	6.98E-02	75.07	5.24E+00
M3	Waste from Separate step	1.49E+02	7.20E+00	Water	9.02E-01	6.50E+00	18	1.17E+02
				Methanol	8.72E-02	6.28E-01	32.04	2.01E+01
				Aliquat 336	2.42E-03	1.75E-02	404.16	7.06E+00
				NaOH	4.36E-03	3.14E-02	40	1.26E+00
				Silanol	4.08E-03	2.94E-02	133.1	3.91E+00
M4	Liquid Waste from Final Strip	3.49E-01	1.09E-02	Methanol	1.00E+00	1.09E-02	32.04	3.49E-01
M5	Recycle stream	8.94E+01	2.79E+00	Methanol	1.00E+00	2.79E+00	32.04	8.94E+01
M6	Recycle stream	3.49E+01	3.29E-01	Xylene	1.00E+00	3.29E-01	106.16	3.49E+01
M7	Recycle stream	3.35E+00	1.13E-02	D4	1.00E+00	1.13E-02	296.62	3.35E+00
M8	Gas waste stream from final strip	6.29E-01	1.06E-02	Trimethylamine	1.00E+00	1.06E-02	59.11	6.29E-01
M9	Gas waste stream from separate step	2.77E+01	6.29E-01	CO2	1.00E+00	6.29E-01	44	2.77E+01
M10	Allyl chloride input	5.34E+01	6.98E-01	Allyl chloride	1.00E+00	6.98E-01	76.52	5.34E+01
M11	Potassium cyanate input	5.67E+01	6.98E-01	Potassium cyanate	1.00E+00	6.98E-01	81.12	5.67E+01
M12	Methanol make-up stream	2.18E+01	6.80E-01	Methanol	1.00E+00	6.80E-01	32.04	2.18E+01
M13	TMDSO input	4.21E+01	3.14E-01	TMDSO	1.00E+00	3.14E-01	134.32	4.21E+01
M14	Karstedt catalyst input	1.75E-05	4.58E-08	Karstedt catalyst	1.00E+00	4.58E-08	381.48	1.75E-05
M15	Aliquat 336 input	1.05E+01	2.61E-02	Aliquat 336	1.00E+00	2.61E-02	404.16	1.05E+01
M16	Water input to deprotect step	1.06E+02	5.87E+00	Water	1.00E+00	5.87E+00	18	1.06E+02
M17	NaOH input	2.64E+01	6.60E-01	NaOH	1.00E+00	6.60E-01	40	2.64E+01
M18	D4 makeup stream	2.20E+01	7.42E-02	D4	1.00E+00	7.42E-02	296.62	2.20E+01
M19	Tetramethyl ammonium hydroxide input	9.78E-01	1.07E-02	Tetramethyl ammonium hydroxide	1.00E+00	1.07E-02	91.15	9.78E-01
M20	Water input to wash/ separate	3.49E+01	1.94E+00	Water	1.00E+00	1.94E+00	18	3.49E+01

6.8 Toxicological Effects of Components in the Manufacturing Process of GAP-1$_m$

Toxicological data for both methanol and xylene are provided in the toxicity section for the CO_2 capture system and are not included in this section.

In cases where data were not available for a specific endpoint, QSAR modeling with ECOSAR, EPIWIN, TEST, or Toxtree is included, where possible. Some chemicals also had read across data available for chemicals with a similar structure. In all cases where read across data are included, this has been noted in the summary tables. Several tables reference the QSAR Toolbox as the source of toxicological information. This is software resulting from the efforts of OECD countries and provides toxicological and physical property data from several databases.[50] According to the QSAR Toolbox website, the software is "intended to be used by governments, the chemical industry, and other stakeholders to fill gaps in (eco-)toxicity data needed for assessing the hazards of chemicals."

For the acute toxicity endpoints from animal testing (e.g. LD_{50} values), specific durations of the tests were not available for all values, but these tests typically include an observation period of less than or equal to 14 days after the initial dose.

Process Inputs

Allyl chloride (CAS # 107-05-1) Toxicological Data

The toxicological data for allyl chloride are summarized in **Table 86**. Several toxicological studies have been completed for allyl chloride, given that it is on the original HAP list under the Clean Air Act. Occupational exposures have been documented and effects have included eye/skin irritation, neurotoxicity, and reversible liver/kidney damage.[51,52]

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[50] http://www.qsartoolbox.org/

[51] EPA IRIS. http://www.epa.gov/iris

[52] OECD 1996. "SIDS Initial Assessment report for 3-Chloropropene." http://www.inchem.org/documents/sids/sids/Chloropropene.pdf

EPA provides an RfC value based on neurotoxicity in animal studies. EPA applied a 3000 fold uncertainty factor when calculating this value, which indicates that extreme caution should be used when applying the RfC when estimating potential human health risks.

Allyl chloride belongs to the class of compounds known as alkylating agents, which have the capability to interact directly with DNA to form adducts, cause mutations, and, presumably, initiate cancer. This mechanism of action is thought to be widely applicable to many species, including humans. However, species differences in pharmacokinetics and sensitivity can limit the ability to determine that there is a real risk for this endpoint in humans. *In vitro* genotoxicity testing results have been largely positive. This includes the Ames Test (with the exception of one study where the negative result was thought to be due to evaporation of the test article), E. coli reverse mutation, *A. nidulans* chromosome aberration, and yeast gene mutation. However, a cytogenetic assay was negative and two unscheduled DNA synthesis tests reported conflicting results.[53]

In the carcinogenicity evaluation in IRIS, EPA classifies allyl chloride as a Group C carcinogen and IARC classifies it as Group 3. Both of these classifications indicate that adequate data are not available to determine the carcinogenicity of this chemical. In animal testing, some effects on sperm have been observed in mice, but developmental effects have only been observed at maternally toxic doses. Bioconcentration factor testing was completed on *C. carpio* and the results indicated that there is a low risk for bioaccumulation of allyl chloride. The predicted K_{oc} value from the EPIWIN model indicates that high mobility in soils would be expected, since the value is significantly below 500 L/kg.

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[53] IUCLID database. http://iuclid.eu/index.php?fuseaction=home.iuclidHome

Table 86. Allyl chloride toxicological data

	Value	Species	Time	Resource
Reference concentration (mg/m^3)	1x10^{-3}	N/A	Chronic	EPA IRIS[51]
Ingestion LD$_{50}$ (mg/kg b.w.)	450 to 700	Rat	14 days observation after dose	IUCLID[53]
Inhalation LC$_{50}$ (mg/m^3)	3,200 to 11,800	Rat	2 to 6 hrs	IUCLID[53]
Dermal LD$_{50}$ (mg/kg b.w.)	2,066	Rabbit	N/A	TOXNET[54]
Eye irritation/ skin corrosion	Slightly irritating	Rabbit	N/A	IUCLID[53]
Inhalation NOAEL (mg/m^3)	17	Rabbit	90 days	Lu, et al 1982[55]
Inhalation LOAEL (mg/m^3)	206	Rabbit	90 days	Lu, et al 1982[55]
Reproductive toxicity	Sperm effects – 124 mg/kg	Mice, subcutaneous injection	39 days	IUCLID[53]
Developmental toxicity	Developmental effects only seen in animals at maternally-toxic doses	N/A	N/A	IUCLID[53]
Carcinogenicity	Data not adequate to allow for determination of cancer risks to humans, IARC group 3 and IRIS group C	N/A	N/A	IARC[56], IRIS[51]
Genotoxicity/ mutagenicity	See discussion of genotoxicity in this section			
Fish toxicity, acute, LC$_{50}$ (mg/L)	21	Carassius auratus (goldfish)	96 hr	IUCLID[53]
Fish toxicity, acute, LC$_{50}$ (mg/L)	51	Lebistus reticulates (guppy)	96 hr	IUCLID[53]

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[54] http://toxnet.nlm.nih.gov/

[55] Lu, B, D. Shuwei, Y. Airu, X. YinLin, G. Taibao and C. Tao. 1982. Studies on the toxicity of allyl chloride. *Ecotoxicol. Environ. Saf.* 6: 19-27.

[56] http://www.iarc.fr/

Fish toxicity, acute, LC$_{50}$ (mg/L)	42	Lepomis macrochirus (bluegill)	96 hr	IUCLID[53]
Fish toxicity, acute, LC$_{50}$ (mg/L)	20 to 24	Pimephales promelas (fathead minnow)	96 hr	IUCLID[53]
Fish toxicity, chronic LC$_{50}$ (mg/L)	1.2	Poecilia reticulate (guppy)	14 day	IUCLID[53]
Daphnid toxicity, acute EC$_{50}$ (mg/L)	250	Daphnia magna	24 hr	IUCLID[53]
Algae toxicity, chronic NOEC (mg/L)	8.2	Microcystis aeruginosa	8 day	IUCLID[53]
Algae toxicity, chronic NOEC (mg/L)	6.3	Scenedesmus quadricauda	8 day	IUCLID[53]
Octanol Water Partition Coefficient (log K$_{ow}$)	1.93	N/A	N/A	Yaws 2003[57]
Biodegradability	Readily biodegradable	N/A	N/A	QSAR Toolbox
Predicted soil adsorption coefficient, K$_{oc}$ (L/kg)	39.7	N/A	N/A	EPIWIN model
Bioconcentration factor (L/kg wet weight)	<5.6	C. carpio	42 days	QSAR Toolbox

Potassium cyanate (CAS# 590-28-3) Toxicological Data

The toxicological data for potassium cyanate are provided in **Table 87**. Genotoxicity test results for this chemical have been negative for the Ames test, chromosomal aberration, and mammalian gene mutation. No information was available for potassium cyanate on skin

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[57] Yaws, Carl L. (2003). Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds. Knovel. Online version available at: http://app.knovel.com/hotlink/toc/id:kpYHTPPCC4/yaws-handbook-thermodynamic/yaws-handbook-thermodynamic

sensitization, developmental toxicity, or acute algae toxicity. For these values, read-across data has been used for a similar chemical, sodium cyanate (CAS#917-61-3).

Potassium cyanate was found to not be corrosive to skin, but it is irritating to eyes based on rabbit testing. The low predicted K_{oc} value for this chemical indicates that it would have high mobility in subsurface environments. EPIWIN was also used to estimate the BCF, which indicated a low risk of bioaccumulation. ECOSAR modeling could not be completed for this chemical because it is not recommended to use the model for complex organic salts. However, some aquatic toxicity values have been compiled from other sources.

Table 87. Potassium cyanate toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	567	Rat	N/A	Sigma Aldrich MSDS[58]
Dermal LD_{50} (mg/kg b.w.)	>2000	Rat	N/A	Sigma Aldrich MSDS[58]
Eye irritation/ skin corrosion	No skin irritation, irritating to eyes	Rabbit	N/A	Sigma Aldrich MSDS[58]
Skin sensitization	Negative	Mouse (LLNA)	N/A	QSAR Toolbox, read across based on sodium cyanate
Developmental LOAEL (mg/kg/day in diet)	1500	Mouse	N/A	QSAR Toolbox, read across based on sodium cyanate
Genotoxicity/ mutagenicity	Negative for Ames test, chromosomal aberration, and mammalian cell gene mutation	N/A	N/A	QSAR Toolbox

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[58] Sigma Aldrich MSDS for potassium cyanate. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=215074&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F215074%3Flang%3Den

Fish toxicity, acute, LC$_{50}$ (mg/L)	15	Salmo gairdneri (Rainbow trout)	96 hr	Sigma Aldrich MSDS[58]
Fish toxicity, acute, LC$_{50}$ (mg/L)	24.3	Salmo gairdneri (Rainbow trout)	96 hr	TOXNET[54]
Daphnid toxicity, acute EC$_{50}$ (mg/L)	18	Daphnia magna	48 hr	Sigma Aldrich MSDS[58]
Algae toxicity, acute EC$_{50}$ (mg/L)	>100	D. subspicatus	72 hr	QSAR Toolbox, read across based on sodium cyanate
Predicted octanol Water Partition Coefficient (log K$_{ow}$)	-4.65	N/A	N/A	EPIWIN model
Predicted biodegradability	Readily biodegradable	N/A	N/A	EPIWIN model
Predicted soil adsorption coefficient, K$_{oc}$ (L/kg)	0.056	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K$_{ow}$ less than 1)	N/A	N/A	EPIWIN model

Sodium hydroxide (CAS #1310-73-2) Toxicological Data

The toxicological data for sodium hydroxide are summarized in **Table 88**.

Target organ toxicity data following systemic exposure for NaOH is not available or not considered to be reliable, and is considered “scientifically unjustified” by REACH, given its caustic nature. Results from two short term aquatic studies are reported in Table 30. The most likely impact of NaOH on the aquatic environment is expected to be due to pH effects, but available studies are not considered of a high enough quality for regulatory support.

The primary human health risk related to NaOH is the corrosive nature of the chemical and potential for severe burns to skin. ECOSAR modeling could not be completed for this compound since the model cannot be used for inorganic compounds. The EPIWIN models for log K_{ow}, biodegradability, and K_{oc} are also not valid for inorganic compounds.

Table 88. Sodium hydroxide toxicological data.

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	140 to 340	Rat	N/A	TOXNET[54]
Dermal LD_{50} (mg/kg b.w.)	1,350	Rabbit	N/A	TOXNET[54]
Eye irritation/ skin corrosion	Corrosive to eyes and causes severe burns to skin	Rabbit	N/A	Sigma Aldrich MSDS[59]
Fish toxicity, acute, LC_{50} (mg/L)	45.4	Oncorhynchus mykiss (rainbow trout)	96 hr	Sigma Aldrich MSDS[59]
Daphnid toxicity, acute EC_{50} (mg/L)	40.4	Daphnia magna	48 hr	Sigma Aldrich MSDS[59]

TMDSO (CAS# 3277-26-7) Toxicological Data

The toxicological data for TMDSO are summarized in **Table 89**. The results of three Ames tests are available which all provided negative results. Read across data is available for tetramethylcyclotetrasiloxane (CAS# 2370-88-9) for a chromosomal aberration assay in which negative results were obtained. Negative results were also obtained for a mammalian gene mutation chromosomal aberration and in vivo rodent bone marrow cytogenetic assays for a similar chemical, hexamethyldisiloxane (CAS#107-46-0).[50]

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[59] Sigma Aldrich Sodium Hydroxide MSDS. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=306576&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F306576%3Flang%3Den

Regarding the fate of TMDSO in aquatic environments, it has been shown that TMDSO is rapidly hydrolyzed to dimethylsilanediol (CAS#1066-42-8), with a half-life of 11 minutes at pH 7 and 25°C.[50] Therefore, any effects in an aquatic environment would be due to formation of the dimethylsilanediol and not to the parent compound, TMDSO. Therefore, modeling for environmental fate and transport and aquatic toxicity has been completed for dimethylsilanediol instead of TMDSO. The results are summarized in **Table 90**.

ECOSAR modeling resulted in relatively high LC_{50} and EC_{50} values for aquatic species, which would indicate a relatively low risk to aquatic environments. EPIWIN predicted a very low BCF value, which would indicate a low risk of bioaccumulation. The low predicted K_{oc} value indicates that this would have high mobility in soils.

Table 89. TMDSO toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	>2000	Rat	14 days observation after dose	QSAR Toolbox
Inhalation LC_{50} (mg/m^3)	>5,800	Rat	14 days observation after dose	QSAR Toolbox
Eye irritation/ skin corrosion	Not irritating to skin or eyes	Rabbits	N/A	QSAR Toolbox
Genotoxicity/ mutagenicity	Negative (See discussion in this section			
Predicted Octanol Water Partition Coefficient (log K_{ow})	4.154	N/A	N/A	ECOSAR model

Table 90. Dimethylsilanediol aquatic toxicity predicted data

	Value	Species	Time	Resource
Water solubility (mg/L)	1x10^6	N/A	N/A	ECOSAR model
Predicted fish toxicity, acute, LC_{50} (mg/L)	10,992	N/A	96 hr	ECOSAR model
Predicted fish toxicity, chronic LC_{50} (mg/L)	827	N/A	N/A	ECOSAR model
Predicted daphnid toxicity, acute LC_{50} (mg/L)	4,998	Daphnia magna	48 hr	ECOSAR model
Predicted daphnid toxicity, chronic LC_{50} (mg/L)	263	Daphnia magna	N/A	ECOSAR model
Predicted algae toxicity, acute EC_{50} (mg/L)	1,485	Green algae	96 hr	ECOSAR model
Predicted algae toxicity, chronic (mg/L)	237	Green algae	N/A	ECOSAR model
Predicted Octanol Water Partition Coefficient (log K_{ow})	-0.407	N/A	N/A	ECOSAR model
Predicted biodegradability	Not readily biodegradable	N/A	N/A	EPIWIN model
Predicted soil adsorption coefficient, K_{oc} (L/kg)	0.4403	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K_{ow} less than 1)	N/A	N/A	EPIWIN model

Tetramethyl ammonium hydroxide (CAS# 75-59-2) Toxicological Data

Toxicological data for tetramethyl ammonium hydroxide (TMAH) are provided in Table 33. Acute human exposure to TMAH solutions (25%) has resulted in severe chemical burns and some deaths.[60] Some aquatic studies have been completed for this material, but, similar to NaOH, the primary concern to aquatic life is expected to be related to pH effects. ECOSAR modeling was not completed for this chemical because it is not recommended to use the model for ammonium salts. TMAH was shown to be corrosive to skin in rabbit testing. Experimental results are available for K_{oc} values. The experiments were conducted for three different soil types and the K_{oc} value increased with increasing % of organic carbon, as expected. However, all measured values are still less than 500 L/kg and would indicate that the chemical would be mobile in a soil environment over a range of soil types. The low predicted BCF value would indicate that little bioaccumulation would be expected with this chemical. Genotoxicity testing has been completed for this chemical and results were negative for Ames test, chromosomal aberration, and mammalian cell gene mutation.

Table 91. TMAH toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	7.5 to 50	Rat	14 day observation after dose	QSAR Toolbox
Dermal LD_{50} (mg/kg b.w.)	12.5 to 50	Rat	14 day observation after dose	QSAR Toolbox, TOXNET[54]
Eye irritation/ skin corrosion	Corrosive to skin, eye testing not justified given high pH	Rabbit	N/A	QSAR Toolbox
Ingestion NOAEL (mg/kg/day)	5	Rat	28 day	QSAR Toolbox
Dermal NOAEL (mg/kg/day)	10	Rat	28 day	QSAR Toolbox
Reproductive/ developmental	≥20	Rat	14 day prior to mating male, 14 day prior to mating	QSAR toolbox

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[60] http://www.ncbi.nlm.nih.gov/pubmed/20230335

toxicity, NOAEL (mg/kg)			through 3 days after delivery female	
Genotoxicity/ mutagenicity	Negative for chromosomal aberration, Ames test, and mammalian cell gene mutation test	N/A	N/A	QSAR Toolbox
Fish toxicity, acute, LC_{50} (mg/L)	See discussion in this section of report			
Daphnid toxicity, acute EC_{50} (mg/L)	3	Daphnia magna	48 hr	Sigma Aldrich MSDS[61]
Algae toxicity, acute EC_{50} (mg/L)	>251	D. subspicatus	72 hr	QSAR Toolbox
Cyanobacteria toxicity, acute EC_{50} (mg/L)	96.3 (in 20% solution in water)	P. subcapitata	72 hr	QSAR Toolbox
Predicted Octanol Water Partition Coefficient (log K_{ow})	-2.47	N/A	N/A	EPIWIN model
Biodegradability	Readily biodegradable	N/A	N/A	QSAR Toolbox
Soil adsorption coefficient, K_{oc} (L/kg)	35 (loamy sand), 258 (sandy loam), 452 (clay)	N/A	N/A	QSAR Toolbox
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K_{ow} less than 1)	N/A	N/A	EPIWIN model

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[61] Sigma Aldrich MSDS for 25% tetramethylammonium hydroxide in water. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=331635&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F331635%3Flang%3Den

Karstedt catalyst (CAS # 68478-92-2) Toxicological Data

Relatively little toxicity data is available for the pure catalyst and QSAR modeling is not applicable to metal complexes and has not been completed (**Table 92**). This platinum catalyst uses zero valent platinum, which is considered inert and non-hazardous. Some irritation has been reported in occupational settings, but effects from other sources are very rare. This catalyst has been used in silicone breast implants and the FDA considers the Pt catalyst used in the implants not to be a risk,[62] and it has been approved for medical applications.

Since some agencies assume that the catalyst breaks down to platinum and divinyltetramethyldisiloxane (CAS# 2627-95-4) in the environment,[63] toxicological information for the siloxane component is provided in **Table 93**. Genotoxicity testing has been completed for the siloxane component and showed negative results for chromosomal aberration, Ames test, and mammalian cell gene mutation. Aquatic testing has been conducted and most tests showed no effects at the levels measured in the experiments, with the concentrations very close to the water solubility of the material. Experimental testing has shown the material not to be readily biodegradable. The high predicted K_{oc} value indicates that the mobility in a soil environment is expected to be low. The predicted BCF, while below the typical level of concern of 5000, is only a predicted value and is relatively high at 3962 so that could be a potential concern. However, it should be noted that the solubility of this chemical in water is very low.

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[62] http://www.fda.gov/MedicalDevices/ProductsandMedicalProcedures/ImplantsandProsthetics/BreastImplants/UCM064040?_sm_au_=iMVkM2SPDpk5SCkV

[63] Canada's Domestic Substances List, http://webnet.oecd.org/ccrweb/ChemicalDetails.aspx?ChemicalID=BFB59CA2-E5A5-4F74-9F5A-34655544D526

Table 92. Karstedt catalyst toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	500 to 5000	Rat	N/A	NuSil MSDS (inferred from ingredient hazards)[64]
Inhalation LC_{50} (mg/m^3)	2 to 20	Rat	N/A	NuSil MSDS (inferred from ingredient hazards)[64]
Dermal LD_{50} (mg/kg b.w.)	1000 to 2000	Rabbit	N/A	NuSil MSDS (inferred from ingredient hazards)[64]
Eye irritation/ skin corrosion	Moderate irritant	N/A	N/A	Costigan and Tinkler, 2004[65]
Genotoxicity/ mutagenicity	Negative in Ames Test	N/A	N/A	Costigan and Tinkler, 2004[65]
Predicted genotoxicity	Negative	N/A	N/A	Toxtree model
Predicted non-cancer toxicity	Negative	N/A	N/A	Toxtree model

Table 93. Divinyltetramethyldisiloxane toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	>5000	Rat	14 days observation after dose	QSAR Toolbox
Inhalation LC_{50} (mg/m^3)	>1875	Rat	14 days observation after dose	QSAR Toolbox
Oral NOAEL (mg/kg/day), liver effects	150 (males), 50 (females)	Rat	Up to 31 days for males and 34 days for females (14 day recovery for subgroup)	QSAR Toolbox
Eye irritation/ skin corrosion	Non-irritating to mild redness to skin, slight redness to eye	Rabbit	N/A	QSAR Toolbox

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[64] http://www.wpiinc.com/clientuploads/pdf/msds-100102-silicone-platinum-catalyst.pdf?_sm_au_=iMVZvJtsnS0V0ZVj

[65] Costigan, S. and J. Tinkler, 2004. "Long-term Platinum Catalyst Stability and Toxicity." http://www.mhra.gov.uk/home/groups/dts-bi/documents/websiteresources/con2032462.pdf

Genotoxicity/ mutagenicity	Negative for Ames test, mammalian cell gene mutation, and in vivo chromosomal aberration test	N/A	N/A	QSAR Toolbox
Reproductive oral NOAEL (mg/kg/day)	600	Rat	N/A	QSAR Toolbox
Neonatal oral NOAEL (mg/kg/day)	150	Rat	N/A	QSAR Toolbox
Fish toxicity, acute LC_{50} (mg/L)	>0.13	O. mykiss	96 hr	QSAR Toolbox
Daphnia toxicity, acute EC_{50} (mg/L)	>0.1	Daphnia magna	48 hr	QSAR Toolbox
Daphnia reproductive NOEC (mg/L)	0.12	Daphnia magna	21 day	QSAR Toolbox
Algae toxicity, EC_{50} (mg/L)	>0.12	P. subcapitata	72 hr	QSAR Toolbox
Predicted Octanol-Water Partition Coefficient, log K_{ow}	5.958	N/A	N/A	ECOSAR model
Water solubility	0.207 mg/L at 20°C	N/A	N/A	QSAR Toolbox
Biodegradability	Not readily biodegradable	N/A	N/A	QSAR Toolbox
Predicted soil adsorption coefficient, K_{oc} (L/kg)	1309	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight)	3962	N/A	N/A	EPIWIN model

Trioctylmethylammonium chloride (CAS# 63393-96-4) Toxicological Data

The toxicological data for trioctylmethylammonium chloride are summarized in **Table 94**. Very little toxicity information is available for this chemical, though some aquatic testing has been completed with LC_{50} values less than 1 mg/L for rainbow trout. Some ECOSAR modeling results are provided in the table. However, the results are not provided for acute fish or acute Daphnid effects because the predicted log K_{ow} is higher than the cutoff for these endpoints. The acute algae result is not provided because it was more than 10 times the solubility of this chemical in water. Based on the very high predicted K_{oc} value, the mobility of this chemical in soils is expected to be low. The low predicted BCF value would also indicate that the risk of bioaccumulation is low. Read across results for genotoxicity testing are provided in the table for didecyl dimethylammonium chloride (CAS#7173-51-5), which showed negative results for mammalian gene mutation, chromosome aberration, and Ames tests.

Table 94. Trioctylmethylammonium chloride toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	223	Rat	N/A	Sigma Aldrich MSDS[66]
Skin corrosion	Corrosive to skin	N/A	N/A	Sigma Aldrich MSDS[66]
Genotoxicity/ mutagenicity (read-across)	Negative for Ames test, mammalian cell gene mutation and chromosome aberration	N/A	N/A	QSAR Toolbox (read across for CAS#7173-51-5)
Fish toxicity, acute, LC_{50} (mg/L)	0.18 to 0.32	Oncorhynchus mykiss (rainbow trout)	96 hr	Sigma Aldrich MSDS[66]

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[66] Sigma Aldrich MSDS for trioctylmethylammonium chloride. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=91042&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F91042%3Flang%3Den

Predicted fish toxicity, chronic LC_{50} (mg/L)	0.01	N/A	N/A	ECOSAR model
Predicted daphnid toxicity, chronic (mg/L)	0.015	Daphnia magna	N/A	ECOSAR model
Predicted algae toxicity, chronic (mg/L)	0.119	Green algae	N/A	ECOSAR model
Predicted Octanol Water Partition Coefficient (log K_{ow})	6.131	N/A	N/A	ECOSAR model
Predicted biodegradability	Readily biodegradable	N/A	N/A	EPIWIN model
Predicted soil adsorption coefficient, K_{oc} (L/kg)	$1.69x10^4$	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight) (read-across)	70.79	N/A	N/A	EPIWIN model

1-octanol (CAS# 111-87-5) Toxicological Data

The toxicological data for 1-octanol are provided in Table 37. The high dermal and oral LD_{50} values would indicate a low risk for acute toxicity based on testing in rats and rabbits. The MSDS for this chemical indicates that it is not bioaccumulative, which is consistent with the low BCF value predicted by the EPIWIN model. Genotoxicity testing for this chemical was negative in the Ames test. The low predicted K_{oc} value from EPIWIN indicates that the expected mobility in a soil environment would be high. Experimental results indicate that this material is readily biodegradable.

Table 95. 1-octanol toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	>3,200	Rat	N/A	Sigma Aldrich MSDS[67]
Dermal LD_{50} (mg/kg b.w.)	>5,000	Rabbit	N/A	TOXNET[54]
Eye irritation/ skin corrosion	Skin irritant and moderate eye irritation	Rabbit	N/A	Sigma Aldrich MSDS[67]
Genotoxicity/ mutagenicity	Negative for Ames test	N/A	N/A	QSAR Toolbox
Fish toxicity, acute, LC_{50} (mg/L)	17.7	Oncorhynchus mykiss	96 hr	Sigma Aldrich MSDS[67]
Fish toxicity, acute, LC_{50} (mg/L)	13.3	Pimephales promelas	96 hr	Sigma Aldrich MSDS[67]
Fish toxicity, mortality LOEC (mg/L)	1.19	Pimephales promelas	7 day	Sigma Aldrich MSDS[67]
Daphnid toxicity, acute EC_{50} (mg/L)	20	Daphnia magna	48 hr	QSAR Toolbox
Daphnid toxicity, acute EC_{50} (mg/L)	26	Daphnia magna	24 hr	TOXNET[54]
Algae toxicity, acute EC_{50} (mg/L)	6.5 - 14	Desmodesmus subpicatus	48 hr	Sigma Aldrich MSDS[67]
Octanol Water Partition Coefficient (log K_{ow})	3	N/A	N/A	Yaws 2003[57]
Biodegradability, aerobic test	92%, readily biodegradable	N/A	28 day	Sigma Aldrich MSDS[67]
Predicted soil adsorption coefficient, K_{oc} (L/kg)	38.3	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight)	44.3	N/A	N/A	EPIWIN model

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[67] Sigma Aldrich MSDS for 1-octanol. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=297887&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F297887%3Flang%3Den

Trioctylamine (CAS# 1116-76-3) Toxicological Data

The toxicological data for trioctylamine are provided in **Table 96**. Little information is available on the toxicity of this chemical in literature. It is listed as a skin irritant. Predicted genotoxicity, non-cancer toxicity, and mutagenicity for this chemical were negative. ECOSAR modeling is not applicable to this chemical because the predicted log K_{ow} is higher than the log K_{ow} cutoffs for acute and chronic toxicity values for all species included in the model. The water solubility of this chemical is very low. Experimental results have shown that this chemical is not readily biodegradable. The very high predicted K_{oc} value would indicate that it would not be mobile in a soil environment.

Table 96. Trioctylamine toxicological data

	Value	Species	Time	Resource
Intraperitoneal LD_{50} (mg/kg b.w.)	1000	Rat	N/A	Sigma Aldrich MSDS[68]
Eye irritation/ skin corrosion	Irritant to skin	N/A	N/A	Sigma Aldrich MSDS[68]
Predicted genotoxicity	Negative	N/A	N/A	Toxtree model
Predicted non-cancer toxicity	Negative	N/A	N/A	Toxtree model
Predicted mutagenicity	Negative	N/A	N/A	TEST model
Predicted Octanol Water Partition Coefficient (log K_{ow})	10.362	N/A	N/A	ECOSAR model
Water solubility	0.05 mg/L at 25°C	N/A	N/A	TOXNET[54]
Biodegradability	Not readily biodegradable	N/A	N/A	QSAR Toolbox
Predicted soil adsorption coefficient, K_{oc}	2.5×10^6	N/A	N/A	EPIWIN model
Bioconcentration factor (L/kg wet)	101 to 143	C. carpio	N/A	QSAR Toolbox

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[68] Sigma Aldrich MSDS for trioctylamine. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=T81000&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2Ft81000%3Flang%3Den

D_4 (CAS# 556-67-2) Toxicological Data

The toxicological data for D_4 are summarized in **Table 97**. D_4 has been classified as PBT (persistent, bioaccumulative, and inherently toxic) by Canada.[69] This is consistent with the high BCF experimental values provided in the table. D_4 has been tested for chronic inhalation toxicity in rats and an increase in endometrial adenomas was noted at 700 ppm.[50] The high acute LD_{50} and LC_{50} values would indicate that D_4 is not an acute health hazard based on animal testing. Aquatic testing has been completed, which resulted in low chronic toxicity values for rainbow trout and *Daphnia magna*. Biodegradability testing has been completed and showed low biodegradation in sediments and sludge testing. The high measured K_{oc} value for D_4 indicates that it would have low mobility in a soil environment. Due the high volatility of D_4, it is expected to partition into the atmosphere where it would react with OH radicals to form silanols.[70] Estimated atmospheric lifetimes of approximately 11 days for D_4 have been calculated.[71]

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[69] http://webnet.oecd.org/ccrweb/ChemicalDetails.aspx?ChemicalID=99A53A15-9BA5-4F19-BA41-B63461B511BD

[70] Whelan, M.J., R. van Egmond, D. Gore, and D. Sanders. 2010. "Dynamic multi-phase partitioning of D_5 in river water". *Water Research*. 4: 3679-3686

[71] Navea, J.G., M.A. Young, S. Xu, V.H. Grassian, and C.O. Stanier. 2011. "The atmospheric lifetimes and concentrations of cyclic methylsiloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) and the influence of heterogeneous uptake" *Atmospheric Environment*. 45: 3181-3191

Table 97. D_4 toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	>4,800	Rat	14 day observation after dose	QSAR Toolbox
Inhalation LC_{50} (mg/m^3)	36,000	Rat	14 day observation after dose	QSAR Toolbox
Dermal LD_{50} (mg/kg b.w.)	>2,000	Rat	14 day observation after dose	QSAR Toolbox
Eye irritation/ skin corrosion	Not irritating to skin or eyes	Rabbit	N/A	QSAR Toolbox
Reproductive/ developmental NOAEL (ppm)	300	Rat	N/A	QSAR Toolbox
Carcinogenicity	See discussion in this section			QSAR Toolbox
Genotoxicity/ mutagenicity	Negative for Ames test, mammalian cell gene mutation, and chromosomal aberration test	N/A	N/A	QSAR Toolbox
Fish toxicity, acute, LC_{50} (mg/L)	>0.0063	C. variegatus	96 hr	QSAR Toolbox
Fish toxicity, chronic LC_{50} (mg/L)	0.01	O. mykiss	14 day	QSAR Toolbox
Daphnid toxicity, acute EC_{50} (mg/L)	>0.015	Daphnia magna	48 hr	QSAR Toolbox
Daphnia reproduction NOEC (mg/L)	0.0079	Daphnia magna	21 day	QSAR Toolbox
Daphnia toxicity, chronic (mg/L)	>0.015	Daphnia magna	21 day	QSAR Toolbox

Water solubility	0.07 mg/L at 25°C	N/A	N/A	Sigma Aldrich MSDS[72]
Octanol Water Partition Coefficient (log K_{ow})	6.49	N/A	N/A	QSAR Toolbox
Biodegradability	Sediment half-life of 365 days, 3.7% degradation in 29 days aerobic test, not readily biodegradable	N/A	N/A	QSAR Toolbox
Soil adsorption coefficient, K_{oc} (L/kg)	16,596	N/A	N/A	QSAR Toolbox
Bioconcentration factor (L/kg wet weight)	12,400 to 13,400	P. promelas	28 days	QSAR Toolbox

Potential Byproducts

Methyl carbamate (CAS# 598-55-0) Toxicological Data

The toxicological data for methyl carbamate are provided in Table 40. Genotoxicity testing has been completed for methyl carbamate, with negative results obtained for chromosome aberration and mammalian cell gene tests. Of the 38 test results provided for the Ames test from the QSAR toolbox databases, only two of the results were positive. NIH, EPA, and IARC do not classify the carcinogenicity of methyl carbamate given that limited testing has been conducted. However, California does list methyl carbamate as a known carcinogen under Prop 65 and it is listed as a concern in Maine and Minnesota. California provides a no significant risk level (NSRL) of 160 µg/day at a 10^{-5} cancer risk level and a cancer potency value of 0.0044 (mg/kg/day)$^{-1}$.[73]

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[72] Sigma Aldrich MSDS for D_4. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=235695&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F235695%3Flang%3Den

[73] http://oehha.ca.gov/tcdb/

No aquatic test results were found for this chemical so ECOSAR modeling was completed and is summarized in the table. The predicted BCF is very low, which would indicate that the risk of bioaccumulation should be low for this chemical. The low predicted K_{oc} value indicates a potential for high mobility in a soil environment.

Table 98. Methyl carbamate toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	2500	Rat	N/A	Sigma Aldrich MSDS[74]
Dermal LD_{50} (mg/kg b.w.)	>2000	Rabbit	N/A	Sigma Aldrich MSDS[74]
Eye irritation/ skin corrosion	Irritant to eyes and skin	Rabbit	N/A	Sigma Aldrich MSDS[74]
Genotoxicity/ mutagenicity	See discussion in this section			
Predicted Fish toxicity, acute, LC_{50} (mg/L)	293.4	N/A	96 hr	ECOSAR model
Predicted fish toxicity, chronic (mg/L)	37.4	N/A	N/A	ECOSAR model
Predicted daphnid toxicity, acute LC_{50} (mg/L)	798	Daphnia magna	48 hr	ECOSAR model
Predicted daphnid toxicity, chronic (mg/L)	1123	Daphnia magna	N/A	ECOSAR model
Predicted algae toxicity, acute EC_{50} (mg/L)	505.5	Green algae	96 hr	ECOSAR model
Predicted algae toxicity, chronic (mg/L)	57.4	Green algae	96 hr	ECOSAR model
Predicted Octanol Water Partition Coefficient (log K_{ow})	-0.51	N/A	N/A	ECOSAR model

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[74] Sigma Aldrich methyl carbamate MSDS. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=246352&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F246352%3Flang%3Den

Predicted biodegradability	Not readily biodegradable	N/A	N/A	EPIWIN model
Predicted soil adsorption coefficient, K_{oc} (L/kg)	3.003 L/kg	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K_{ow} less than 1)	N/A	N/A	EPIWIN model

Potassium chloride (CAS# 7447-40-7) Toxicological Data

The toxicological data for potassium chloride are summarized in Table 41. Potassium chloride is a gastrointestinal irritant in humans at high doses (greater than 31 mg/kg/day).[75] A 2 year oral chronic rat study yielded no tumors related to exposure up to 1820 mg/kg/day in food.[75] There have been mixed results from genotoxicity/mutagenicity testing, with positive results at high KCl concentrations and increased chromosomal aberrations in ovary cells.[75] EPIWIN modeling could not be completed for this compound because the modeling is not valid for inorganic compounds. The low predicted BCF value indicates that the risk of bioaccumulation is very low. Aquatic testing has been completed for potassium chloride and is summarized in the table.

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[75] OECD 2001. "SIDS Initial Assessment report for Potassium chloride." http://www.inchem.org/documents/sids/sids/KCHLORIDE.pdf

Table 99. Potassium chloride toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	2600 to 3020	Rat	N/A	TOXNET[54], OECD Report[75]
Repeated dose oral NOAEL (mg/kg/day)	1820	Rat	2 year	OECD Report[75]
Eye irritation	Not irritating			Sigma Aldrich MSDS[76]
Genotoxicity/ mutagenicity	See discussion in this section			
Developmental NOAEL (mg/kg/day)	235	Mouse	N/A	OECD Report[75]
Developmental NOAEL (mg/kg/day)	310	Rat	N/A	OECD Report[75]
Fish toxicity, acute, LC_{50} (mg/L)	880	Pimephales promelas (fathead minnow)	96 hr	OECD Report[75]
Fish toxicity, acute, LC_{50} (mg/L)	720	Ictalurus punctatus (catfish)	48 hr	OECD Report[75]
Fish toxicity, chronic, LC_{50} (mg/L)	700 to 1200	O. mykiss	7 days	QSAR Toolbox
Daphnid toxicity, acute EC_{50} (mg/L)	177 to 660	Daphnia magna	48 hr	OECD Report[75]
Daphnid toxicity, chronic EC_{50} (mg/L)	130	Daphnia magna	21 day	OECD Report[75]
Algae toxicity, acute EC_{50} (mg/L)	1337	Nitzschia linearis	120 hr	OECD Report[75]
Calculated Octanol Water Partition Coefficient (log K_{ow})	-0.46	N/A	N/A	OECD Report[75]
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K_{ow} less than 1)	N/A	N/A	EPIWIN model

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[76] Sigma Aldrich MSDS for potassium chloride. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=P3911&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2Fp3911%3Flang%3Den

Silanol, (3-aminopropyl)dimethyl- (CAS# 180051-45-0) Toxicological Data

No experimental toxicity data are available for this chemical so the QSAR modeling results are summarized in **Table 100**. It should be noted that this material will not be used as a pure chemical in the manufacturing process, but it will be present in very dilute concentrations in one waste stream that will be disposed of as non-hazardous waste under RCRA Subpart D (Section K). The predicted genotoxicity, non-cancer toxicity, and mutagenicity for this chemical were all negative. The modeled aquatic toxicity data are summarized in the table. The EPIWIN model predicts that this chemical would not be readily biodegradable. The very low predicted BCF value indicates a low potential for bioaccumulation and the low predicted K_{oc} value indicates a high potential for mobility in a soil environment.

Table 100. Silanol toxicological data

	Value	Species	Time	Resource
Predicted genotoxicity	Negative	N/A	N/A	Toxtree model
Predicted non-cancer toxicity	Negative	N/A	N/A	Toxtree model
Predicted mutagenicity	Negative	N/A	N/A	TEST model
Predicted fish toxicity, acute, LC_{50} (mg/L)	196.3	N/A	96 hr	ECOSAR model
Predicted fish toxicity, chronic, LC_{50} (mg/L)	18.4	N/A	N/A	ECOSAR model
Predicted daphnid toxicity, acute EC_{50} (mg/L)	20	Daphnia magna	48 hr	ECOSAR model
Predicted daphnid toxicity, chronic EC_{50} (mg/L)	1.4	Daphnia magna	N/A	ECOSAR model
Predicted algae toxicity, acute EC_{50} (mg/L)	22.5	Green algae	96 hr	ECOSAR model
Predicted algae toxicity, chronic EC_{50} (mg/L)	6.7	Green algae	96 hr	ECOSAR model

Predicted Octanol Water Partition Coefficient (log K_{ow})	0.654	N/A	N/A	ECOSAR model
Predicted biodegradability	Not readily biodegradable	N/A	N/A	EPIWIN model
Predicted soil adsorption coefficient, K_{oc} (L/kg)	18.32	N/A	N/A	EPIWIN model
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K_{ow} less than 1)	N/A	N/A	EPIWIN model

Trimethylamine (CAS# 75-50-3) Toxicological Data

The toxicological data for trimethylamine are provided in Table 43. At ambient temperature and pressure, trimethylamine is in the gas phase and is expected to be released in the gas phase from the manufacturing process, which will be handled with the proper engineering controls (Section L). Trimethylamine has been shown to be highly irritating to skin and destructive to eyes in rabbit testing. Genotoxicity testing has been completed and negative results were obtained for the Ames test, in vitro mammalian chromosomal aberration, and mammalian gene mutation tests. The very high acute inhalation LC_{50} value indicates that it is a low acute risk via this exposure pathway. Aquatic testing has been completed for trimethylamine in solution and the results are summarized in the table. The low predicted BCF value indicates a low risk for bioaccumulation and the low measured K_{oc} value would indicate a high potential for mobility in soil if this chemical were in a subsurface environment.

Table 101. Trimethylamine toxicological data

	Value	Species	Time	Resource
Ingestion LD_{50} (mg/kg b.w.)	397 to 766	Rat	14 days observation after dose	QSAR Toolbox, Sigma Aldrich MSDS[77]
Inhalation LC_{50} (mg/m^3)	>5,900	Rat	N/A	TOXNET[54]
Dermal LD_{50} (mg/kg b.w.)	>5,000	Rat	14 days observation after dose	QSAR Toolbox
Eye irritation/ skin corrosion	Highly irritating to skin and destructive to eyes	Rabbit	N/A	QSAR Toolbox
Reproductive/ developmental toxicity, NOAEL (mg/kg/day)	200	Rat	N/A	QSAR Toolbox
Genotoxicity/ mutagenicity	Negative in Ames test, in vitro mammalian chromosome aberration test, and mammalian gene mutation assay	N/A	N/A	QSAR Toolbox
Fish toxicity, acute, LC_{50} (mg/L)	1000	Oryzias latipes (Japanese rice fish)	48 hr	QSAR Toolbox
Fish toxicity, acute, LC_{50} (mg/L)	25	Leuciscus idus	48 hr (non-neutralized sample)	QSAR Toolbox
Fish toxicity, acute, LC_{50} (mg/L)	610	Leuciscus idus	48 hr (neutralized sample)	QSAR Toolbox
Daphnid toxicity, acute EC_{50} (mg/L)	140 (trimethylamine in 45% solution)	Daphnia magna	48 hr	QSAR Toolbox
Algae toxicity, acute, EC_{50} (mg/L)	90.6 to 150 (trimethylamine in 45% solution)	Scenedesmus subspicatus	72 hr	QSAR Toolbox
Octanol Water Partition Coefficient (log K_{ow})	0.16	N/A	N/A	Yaws 2003[57]
Biodegradability	Readily biodegradable	N/A	N/A	QSAR Toolbox
Soil adsorption coefficient, K_{oc} (L/kg)	2.4 to 4.7	N/A	N/A	QSAR Toolbox
Predicted bioconcentration factor (L/kg wet weight)	3.162 (default for compounds with log K_{ow} less than 1)	N/A	N/A	EPIWIN model

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[77] Sigma Aldrich trimethylamine MSDS. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=92251&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F92251%3Flang%3Den

6.9. Physical Properties of the Chemicals in the Manufacturing Process of GAP_{-1m}

The physical properties for the inputs to the manufacturing process are summarized in **Table 102** and **Table 103**. The physical properties for the potential by-products are summarized in **Table 104**. Since the physical properties for both methanol and xylene were summarized in the section on the CO_2 capture process (Section D), that information is not duplicated here.

Unfortunately, physical property data were not available for the silanol material. Some properties were modeled, so it should be noted that there is uncertainty around the properties listed in the table. This chemical is part of an aqueous waste stream in low concentrations (2.6 wt%) and will not be handled in pure form. Allyl chloride, TMDSO, D_4, 1-octanol, and trimethylamine are all classified as flammable chemicals. Of these, only trimethylamine has an NFPA rating of 4. Allyl chloride and TMDSO are rated as 3 and D_4 and 1-octanol are rated as 2.

Of the inputs and potential byproducts reviewed, allyl chloride, sodium hydroxide, tetramethyl ammonium hydroxide, and trioctylmethyl ammonium chloride are considered corrosive. Allyl chloride and TMDSO have high volatility. Though D_4 has a lower vapor pressure relative to allyl chloride and TMDSO, it is classified as a cyclic volatile methylsiloxane and is expected to volatilize under ambient temperature and pressure conditions. Information on volatility was not available for trioctylmethyl ammonium chloride or the silanol material so the vapor pressures were modeled for these two chemicals. In both cases, the predicted volatility is low, with trioctylmethyl ammonium chloride significantly lower. No volatility information was available for the Karstedt catalyst and no modeling could be completed for the metal complex.

Regarding reactivity of the chemicals, in all cases, strong oxidizing agents should be avoided and the MSDS for most chemicals also warn that strong acids should be avoided. The MSDS' for TMDSO, Karstedt catalyst, and D_4 all warn that strong bases should be avoided, so these chemicals need to be stored separately from such chemicals as sodium hydroxide and tetramethyl ammonium hydroxide.

The MSDS for trimethylamine lists certain types of metals that need to be avoided. These metals include brass, zinc, magnesium, copper, mercury and mercury oxides, and tin and tin oxides. This should be considered when handling the gaseous waste stream that includes this chemical.

Of the materials reviewed, only trimethylamine is a gas at ambient temperature and pressure. Given the concerns regarding flammability and corrosivity of this chemical, care needs to be taken that the control device for vapor containment for the waste stream that includes this chemical is always operational while the process is running.

Table 102. Physical properties for inputs to manufacturing process

	Allyl Chloride[57,78,79]	Potassium Cyanate[54,58]	NaOH[54,59,80]	TMDSO[81,82,83]	Tetramethyl ammonium hydroxide[54,61,84,85]
Volatility (evap. rate)	7	Not applicable	Not applicable	>1	Not available
Flash point	-32°C	Not flammable	Not applicable	-26°C	>100°C
Lower explosion limit/ upper explosion limit	3.2% (V)/ 11.2%(V)	Not flammable	Not combustible	0.8% (V)/ 62.9%(V)	Not available
Auto-ignition temperature	391°C	Not available	Not combustible	240°C	Not available
Chemical reactivity	Avoid strong oxidizing agents, boron trifluoride, sulfuric acid, nitric acid, ethylene diamine, ethyleneimine, oleum, chlorosulfonic acid	Avoid strong oxidizing agents	Avoid strong oxidizing agents, strong acids and organic materials	Avoid strong acids, strong bases and strong oxidizing agents	Avoid aluminium, alkali metals, strong oxidizing agents, acids, acid chlorides, acid anhydrides, halogens
Corrosivity	Corrosive	Not corrosive	Corrosive	Not corrosive	Corrosive
State, STP	Liquid	Powder, chunks	Pellets	Liquid	Liquid

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[78] CDC 1992. "Occupational Health Guidelines for Chemical Hazards for allyl chloride", http://www.cdc.gov/niosh/docs/81-123/pdfs/0018-rev.pdf

[79] Sigma Aldrich allyl chloride MSDS. http://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=US&brand=ALDRICH&productNumber=236306&PageToGoToURL=http://www.sigmaaldrich.com/catalog/product/aldrich/236306?lang=en&region=US

[80] CDC. 1978. "Occupational Health Guideline for sodium hydroxide." http://www.cdc.gov/niosh/docs/81-123/pdfs/0565.pdf

[81] SiBond TMDSO MSDS, http://www.sibond.com/msds/3277-26-7.pdf

[82] Alfa Aesar TMDSO MSDS, http://www.alfa.com/content/msds/USA/B23697.pdf

[83] Sigma Aldrich TMDSO MSDS http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=235733&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F235733%3Flang%3Den

[84] Alfa Aesar TMAH MSDS, http://www.alfa.com/content/msds/USA/A17724.pdf

[85] Fisher Scientific TMAH MSDS, http://www.fishersci.com/ecomm/servlet/msdsproxy?productName=O4643100&productDescription=TETMTLAMHYDRX+25%25%2FH20+R+100ML&catNo=O4643-100&vendorId=VN00033897&storeId=10652

Color	Colorless, yellow or purple	White	white	Colorless	Colorless to pale yellow
Odor	Garlic-like odor	Odorless	Odorless	Musty	Strong ammonia-like
Melting point	-134.5°C	315°C	318°C	< -78°C	63°C
Boiling point	44-45°C	Not applicable	1,390°C	70°C	102°C
Vapor pressure	295 mm Hg at 20°C	Not available	< 18 mmHg at 20°C	112.5 mmHg at 20°C	17.5 mmHg at 20°C
Vapor density	2.64 (Air = 1.0)	Not available	1.38 (Air = 1)	>1 (Air = 1)	3.14 (Air = 1)
Density	0.939 g/cm^3 at 25°C	2.056 g/cm^3 at 25°C	2.13 g/cm^3 at 25°C	0.76 g/mL at 25°C	1.014 g/cm^3 at 20°C
Water solubility	4000 mg/L at 25°C	6.3X10+5 mg/L @ 10 deg C	1260 g/L at 20°C	Insoluble	Fully miscible
Solubility properties	Miscible with alcohol, chloroform, ether and petroleum ether	Very slightly soluble in alcohol	Soluble in alcohol	Soluble in chloroform, THF, toluene, and acetone	Soluble in methanol
Viscosity, dynamic	0.32 cP at 25°C	Not applicable	4.0 cP at 350°C	0.5 cP	Not available

Table 103. Physical properties for inputs to manufacturing process (continued)

	Karstedt catalyst[86]	Trioctylmethylammonium chloride[66,87,88,89]	1-octanol [54,57,67,90,91,92]	Trioctylamine[54,57,68,93]	D_4[54,57,72,94]
Volatility (evap. rate)	Not available	Not available	0.007	Not available	<1
Flash point	>110°C	132°C	80°C	163°C	55°C
Lower explosion limit/ upper explosion limit	Not available	Not available	0.9% (V)/ 6.4% (V)	Not available	0.75%(V)/ 7.4%(V)
Auto-ignition temperature	Not available	Not available	270°C	315°	384°C
Chemical reactivity	Avoid oxidizing agents, acids and bases	Avoid strong oxidizing agents	Avoid Acids, acid chlorides, oxidizing agents	Avoid Strong oxidizing agents, acids, Acid chlorides,	Avoid strong oxidizing agents, acids, Bases
Corrosivity	Not corrosive	Corrosive	Not corrosive	Not corrosive	Not corrosive
State, STP	Liquid	Viscous liquid	Liquid	Liquid	Liquid
Color	Colorless	Amber	Colorless	Colorless	Colorless
Odor	Not available	Mild	Orange-rose odor	Amine-like	Odorless
Melting point	Not available	-20°C	-15°C	-34°C	17°C
Boiling point	>200°C	240°C	196°C	357°C	175°C
Vapor pressure	Not available	2E-12 mmHg (EPIWIN)	0.14 mmHg at 25°C	<0.01 hPa at 20°C	0.99 mmHg at 25°C
Vapor density	Not available	Not available	4.5 (air = 1)	Not available	10.24
Density (25 C)	0.98 g/cm^3	0.88 g/mL	0.827 g/cm^3 at 25°C	0.803 g/cm^3	0.956 g/mL
H2O solubility	Not available	10 g/L	540 mg/L at 25°C	0.05 mg/L	0.07 g/L at 25
Solubility properties	Not available	Not available	Miscible in ethanol, ether, chloroform and carbon tetrachloride,	Soluble in chloroform	Soluble in carbon tetrachloride

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[86] Sigma Aldrich MSDS for Karstedt catalyst. http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=479527&brand=ALDRICH&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F479527%3Flang%3Den

[87] Trioctylmethylammonium chloride Properties http://www.chemicalbook.com/ProductChemicalPropertiesCB4412612_EN.htm

[88] Fisher Scientific trioctylmethyl ammonium chloride MSDS https://www.fishersci.ca/viewmsds.do?catNo=AC194970025

[89] Alfa Aesar trioctylmethyl ammonium chloride MSDS http://www.alfa.com/content/msds/USA/A17247.pdf

[90] Fisher Scientific 1-octanol MSDS http://www.ar.cc.mn.us/chemistry/MSDS/Octanol.pdf

[91] Yaws, Carl L.. 2012. Yaws' Critical Property Data for Chemical Engineers and Chemists. Knovel. Online version available at: http://app.knovel.com/hotlink/toc/id:kpYCPDCECD/yaws-critical-property/yaws-critical-property

[92] Alfa Aesar 1-octanol MSDS, http://www.alfa.com/content/msds/USA/A15977.pdf

[93] Alfa Aesar trioctylamine MSDS http://www.alfa.com/content/msds/USA/A15067.pdf

[94] USPC D_4 MSDS http://www.usp.org/pdf/EN/referenceStandards/msds/1154707.pdf

Table 104. Physical properties for potential byproducts from manufacturing process

	Methyl carbamate[54,74]	Potassium chloride[54,76]	Silanol, (3-aminopropyl) dimethyl-	Trimethylamine[54,57,77,95,96]
Volatility (evap. rate)	Not available	Not available	Not available	>1
Flash point	Not available	Not available	Not available	-7°C
Lower explosion limit/ upper explosion limit	Not available	Not available	Not available	2%(V)/ 11.6%(V)
Auto-ignition temperature	Not available	Not available	Not available	190°C
Chemical reactivity	Avoid Strong oxidizing agents, Strong bases, Phosphorus halides	Avoid Strong acids, strong oxidizing agents	Not available	Avoid strong oxidizing agents, brass, magnesium, zinc, copper, mercury/mercury oxides., yin/tin oxides
Corrosivity	Not corrosive	Not corrosive	Not available	Corrosive
State, STP	Crystalline	Crystalline powder	liquid	Gas
Color	White	White	Not available	Colorless
Odor	Not available	Odorless	Not available	Fish-like
Melting point	56°C	770°C	Not available	-117°C
Boiling point	176°C	1500°C	178°C (modeled)[97]	3°C
Vapor pressure	Not available	Not available	0.045 to 0.064 mmHg at 25°C (modeled)[97,98]	1366 mmHg at 20°C
Vapor density	Not available	Not available	Not available	2.04 (Air = 1)
Density	1.1361 g/cm^3 at 25°C	1.98 g/mL at 25°C	0.89 g/mL at 25°C (modeled)[97]	0.63 g/cm^3 at 20°C
Water solubility	6.91X10+5 mg/l at 15.5 deg C	Soluble	Not available	8.9X10+5 mg/L at 30 deg C
Solubility properties	Soluble in ether	Soluble in glycerin, slightly soluble in alcohol, insoluble in ether and acetone	Not available	Readily absorbed by alcohol with which it is miscible; also soluble in ether, benzene, toluene, xylene, ethylbenzene, chloroform.
Viscosity, dynamic	Not available	Not available	Not available	0.185 cP at 25°C

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[95] Matheson trimethylamine MSDS https://www.mathesongas.com/pdfs/msds/MAT24180.pdf

[96] Alfa Aesar trimethylamine MSDS http://www.alfa.com/content/msds/USA/43282.pdf

[97] Modeled using TEST model

[98] Modeled using EPIWIN model

6.10. U.S. EH & S Law Compliance and Regulation Implications for the Manufacturing Process of GAP-$_{1m}$

The relevant regulations for the materials in the manufacturing process are summarized in Table 47. The applicable regulations that were considered are the same as those reviewed in Section E of this report for the CO_2 capture system. In the table, all entries are marked as being regulated by RCRA. This indicates that all materials in the process should be considered in the RCRA evaluation, but it does not indicate if these are considered hazardous or non-hazardous wastes. That classification will be discussed in detail in the RCRA section of this report for the manufacturing process. This section does not include a regulatory review of GAP-1m because this material is addressed in the section for the CO_2 capture system and it is not present in waste streams for the manufacturing process.

All materials reviewed have an MSDS available, with the exception of the silanol material. It should be noted that the silanol material will not be handled in pure form and will only be present in dilute concentrations in an aqueous waste stream. This waste stream is discussed in more detail within the RCRA section of the regulatory review.

Table 105. Regulatory overview for materials in manufacturing process

Chemical	TSCA	CERCLA RQ (lbs)	CWA	CAA HAP	CAA VOC	SARA 302 EHS	SARA 311/312	SARA 313	OSHA	RCRA
Methanol	Y	Yes – 5000 lb RQ	N	Y	Y	N	Acute Chronic Fire	Y	Y	Y
Xylene	Y	Yes – 100 lb RQ	Yes – 100 lb RQ	Y	Y	N	Acute Chronic Fire	Y	Y	Y
Allyl chloride	Y	Yes – 1000 lb RQ	Yes – 1000 lb RQ	Y	Y	N	Acute Chronic Fire	Y	Y	Y
KOCN	Y	N	N	N	Y	N	Acute	N	Y	Y
NaOH	Y	Yes – 1000 lb RQ	Yes – 1000 lb RQ	N	N	N	Acute	N	Y	Y
TMDSO	Y	N	N	N	Y	N	Fire	N	Y	Y
Tetramethyl ammonium hydroxide	Y	N	N	N	Y	N	Acute	N	Y	Y
Karstedt's catalyst	Y	N	N	N	Y	N	Acute	N	Y	Y
D4	Y	N	N	N	Y	N	Chronic Fire	N	Y	Y
Aliquat 336 components:										
Trioctylmethylammonium chloride	Y	N	N	N	Y	N	Acute Chronic	N	Y	Y
1-octanol	Y	N	N	N	Y	N	Acute Chronic Fire	N	Y	Y
trioctylamine	Y	N	N	N	Y	N	Acute	N	Y	Y
Potential byproducts:										
Methyl carbamate	Y	N	N	N	Y	N	Acute Chronic	N	Y	Y
Potassium chloride	Y	N	N	N	N	N	Chronic	N	Y	Y
Silanol, (3-aminopropyl)dimethyl-	Unknown	N	N	N	Y	N	Unknown	N	Y	Y
Trimethylamine	Y	Yes – 100 lb RQ	Yes – 100 lb RQ	N	Y	N	Acute Fire Sudden release of pressure	N	Y	Y

TSCA

With the exception of the silanol material, all chemical inputs to and potential byproducts from the manufacturing process are on EPA's TSCA inventory. However, it should be noted that only the non-confidential TSCA registrations could be searched to determine if the silanol material was TSCA registered.

CERCLA

Of the chemicals associated with the manufacturing process, methanol, xylene, allyl chloride, and sodium hydroxide are listed as CERCLA hazardous substances. The minimum reportable quantities are 5000 lbs/day, 100 lbs/day, 1000 lbs/day, and 1000 lbs/day for methanol, xylene, allyl chloride, and sodium hydroxide, respectively.

Clean Water Act

Xylene, allyl chloride, and sodium hydroxide are designed as hazardous substances to the water supply in accordance with CWA (40 CFR §116.4). The minimum reportable quantities for these chemicals are the same as those for CERCLA.

Clean Air Act

All chemicals associated with the manufacturing process, with the exception of potassium chloride and sodium hydroxide, are considered to be VOCs by EPA's definition. Methanol, xylene, and allyl chloride are also regulated HAPs.

Trimethylamine is also on the CAA 112r list with a limit of 10,000 lbs. The specific concern for this chemical is based on the high flammability. For this process, trimethylamine will not be stored onsite and is only present as a gaseous waste stream that will be handled with the proper engineering controls (Section L). The worst case release for this system would not approach 10,000 lbs and this material would not be stored in significant quantities on-site. Given the flammable and corrosive nature of trimethylamine, the manufacturing process should not be run if the necessary engineering controls are not in the proper working condition for this waste stream.

The manufacturer could also be subject to additional regulatory requirements under 40 CFR 63 Subpart FFFF National Emission Standards for Hazardous Air Pollutants: Miscellaneous Organic Chemical Manufacturing if the manufacturing units are located at or part of a major source of hazardous air pollutants as defined in section 112(a) of the CAA. Section 112(a) states that a major source has the potential to emit 10 tons per year or more of an individual hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants. Methanol, xylene, and allyl chloride would not be emitted above these levels under normal process conditions, but these regulations could still be relevant if the manufacturing process is part of a larger site that would be classified as a major source.

Different state regulatory agencies have different requirements for Title V air permits, so these requirements would need to be reviewed on a case by case basis. The determination of whether a site is considered a major source is dependent on the facility's potential to emit VOCs and HAPs under normal process conditions. Some states also require different types of permits for minor and major sources so the detailed requirements in the location of manufacturing would need to be consulted to determine what would be required. If the relevant jurisdiction calculates the potential to emit post-engineering controls and it is not co-located with a facility that is already classified as a major source, this is not expected to be classified as a major source.

SARA

None of the chemicals are on the SARA 302 list, which indicates that EPA does not consider these chemicals to pose an immediate hazard to a community upon release. With the exception of TMDSO, D_4, potassium chloride, and the silanol material, all of the chemicals are considered to be acute hazards under SARA 311/312. Methanol, xylene, allyl chloride, D_4, trioctylmethylammonium chloride, 1-octanol, methyl carbamate, and potassium chloride are all listed as chronic hazards. Methanol, xylene, allyl chloride, TMDSO, D_4, 1-octanol, and trimethylamine are listed as fire hazards. Trimethylamine is also listed as a hazard for sudden release of pressure when in its compressed gas state, which is not relevant for this process. Chemical releases of methanol, xylene, or allyl chloride would need to be reported to public and government officials under SARA 313.

OSHA

As was the case for the CO_2 capture process, all of the chemicals would be regulated by OSHA and require the MSDS and proper handling, shipping, and storage. These requirements are discussed in further detail in Section M of this report.

RCRA

A review of the RCRA requirements was provided in Section E of this report. As in Section E, this RCRA review focuses only on the federal regulations. A detailed review of state regulations was considered outside the scope of this document. Since regulations can vary depending on the relevant jurisdiction, this would need to be reviewed on a case-by-case basis to ensure that compliance is maintained. Streams M1 through M9 are discussed individually in the following section of the report and the results are summarized at the end of this section in Table 48. Streams M10 through M20 are not discussed in this section because they are inputs to the process and not potential waste streams.

Stream M1

Stream M1 contains potassium chloride from the filter after reaction of allyl chloride, potassium cyanate, and methanol.

Question 1: Is the material a solid waste?
Yes the material is solid waste because it will not be recycled back to the process and would require disposal.
Question 2: Is the material excluded from the definition of solid waste or hazardous waste?

No this material is not excluded from the definition of solid or hazardous waste.

Question 3: Is the material a listed or characteristic hazardous waste?
Potassium chloride is not a listed waste and does not exhibit any of the characteristics necessary to be considered a hazardous waste (Table 24). Therefore, this stream would be considered industrial, non-hazardous waste and would be disposed of under RCRA Subpart D.

Stream M2

Stream M2 contains primarily water with 13% methyl carbamate (by weight).

Question 1: Is the material a solid waste?
Yes the material is a solid waste because it will not be recycled back to the process and would require disposal.

Question 2: Is the material excluded from the definition of solid waste or hazardous waste?
No this material is not excluded from the definition of solid or hazardous waste.

Question 3: Is the material a listed or characteristic hazardous waste?
The materials in this stream are not listed wastes under RCRA. The mixture will also not exhibit any of the characteristics necessary to be considered a hazardous waste under RCRA. It would, therefore, be considered industrial, non-hazardous waste and be disposed of under Subpart D.

Stream M3

Stream M3 contains methanol (13% weight), Aliquot 336 (4.7% weight), water (78% weight), sodium hydroxide (0.8% weight), and silanol (2.6% weight).

Question 1: Is the material a solid waste?

Yes the material is a solid waste because it will not be recycled back to the process and would require disposal.

Question 2: Is the material excluded from the definition of solid waste or hazardous waste?
No this material is not excluded from the definition of solid or hazardous waste.

Question 3: Is the material a listed or characteristic hazardous waste?
Methanol is a listed waste under RCRA, with the designation of F003. However, F003 materials are only listed based on the characteristic of ignitability. According to RCRA, if the waste no longer exhibits the characteristic for which it was listed, it is no longer considered a listed hazardous waste. Aqueous wastes containing less than 24% alcohol by volume are not considered ignitable (40 CFR §261.21(a)(1)). Since methanol is approximately 16.3% by volume in this waste stream, the stream is not considered ignitable. Methanol is also on the U list, which is only relevant for unused chemicals and does not apply to this waste stream. The stream also does not exhibit any other characteristics that would classify the stream as hazardous. This stream would therefore not be a listed or characteristic hazardous waste and would be disposed of under Subpart D.

Stream M4

Stream M4 contains methanol from the final stripping step in the process.

Question 1: Is the material a solid waste?
Yes the material is a solid waste because it will not be recycled back to the process and would require disposal.

Question 2: Is the material excluded from the definition of solid or hazardous waste?
No this material is not excluded from the definition of solid or hazardous waste.

Question 3: Is the material a listed or characteristic hazardous waste?
Yes, methanol is a listed waste under RCRA with a F003 designation.

Question 4: Is the waste delisted?

No this waste is not delisted. This stream would therefore require disposal as a RCRA hazardous waste under Subpart C. The Subpart C requirements are discussed in more detail later in this section as they apply to this process.

Stream M5

Stream M5 is a methanol recycle stream.

Question 1: Is the material a solid waste?

No this material is not a solid waste because it is recycled directly back to the process without reclamation.

Stream M6

Stream M6 is the xylene recycle stream.

Question 1: Is the material a solid waste?
No this material is not a solid waste because it is recycled directly back to the process without reclamation.

Stream M7

Stream M7 is a D_4 recycle stream.

Question 1: Is the material a solid waste?
No this material is not a solid waste because it is recycled directly back to the process without reclamation.

Stream M8

Stream M8 is a gaseous trimethylamine amine stream from the final stripping step in the process.

Question 1: Is the material a solid waste?
Yes this material is a considered a solid waste because it is not returned to the process.

Question 2: Is the material excluded from the definition of solid waste or hazardous waste?
No this material is not excluded from the definition of solid or hazardous waste.

Question 3: Is the material a listed or characteristic hazardous waste?
No this material is not a listed waste under RCRA. It also does not exhibit the characteristics necessary to classify as a hazardous waste. It would therefore fall under Subpart D.

Stream M9

Stream M9 is a gaseous CO_2 stream from the separate step after the deprotect step.

Question 1: Is the material a solid waste?
Yes this material is considered a solid waste because it is not returned to the process.

Question 2: Is the material excluded from the definition of solid waste or hazardous waste?
No this material is not excluded from the definition of solid or hazardous waste.

Question 3: Is the material a listed or characteristic hazardous waste?
No this material is not a listed waste under RCRA. It also does not exhibit the characteristics necessary to classify as a hazardous waste. It would therefore fall under Subpart D.

Table 106. Summary of RCRA classifications

Stream Number	Materials	Classification and other relevant RCRA Information
M1	Potassium chloride	Industrial, non-hazardous solid waste to be disposed of under Subpart D
M2	Methyl carbamate and water	Industrial, non-hazardous solid waste to be disposed of under Subpart D
M3	Methanol, Aliquot 336, sodium hydroxide, silanol and water	Industrial, non-hazardous solid waste to be disposed of under Subpart D
M4	Methanol	Listed hazardous waste based on F003 designation to be disposed of under Subpart C
M5	Methanol	Not considered solid waste since directly recycled back to the process without reclamation
M6	Xylene	Not considered solid waste since directly recycled back to the process without reclamation
M7	D_4	Not considered solid waste since directly recycled back to the process without reclamation
M8	Trimethylamine (gas)	Industrial, non-hazardous solid waste in gas phase to be disposed of under Subpart D.
M9	CO_2 gas	Industrial, non-hazardous solid waste in gas phase to be disposed of under Subpart D.

RCRA Subpart C requirements

Generator requirements

Specific requirements for hazardous waste handling depend on the generator classification based on the quantity of hazardous waste generated per month. The only stream from this process for which the Subpart C requirements are relevant is stream M4. Requirements for CESQG, SQG, and LQG are summarized briefly in Section E of this report.

Classification for annual GAP-1$_m$ make-up

The quantity of methanol generated based on the mass balance for stream M4 is estimated to be 216.7 lbs per month (calculated based on 310.25 working days per year), or 98.5 kg per month for the manufacturing of GAP-1m to account for annual GAP-1m make-up for the system. This would classify this process as a CESQG based on the RCRA definition. However, it is very close to the cutoff for SQG classification (more than 100 kg per month).

Classification for initial fill of system

The quantity of methanol generated based on the mass balance for stream M4 is estimated to be 1078 lbs per month (calculated based on 310.25 working days per year), or 490 kg per month for the manufacturing of GAP-1m for the initial fill of the system. This would classify this process as a SQG based on the RCRA definition. If this manufacturing process is co-located with other processes that generate RCRA hazardous waste in sufficient quantities, it could potentially be subject to LQG requirements. A facility is classified as LQG if it generates greater than or equal to 1000 kg/month.

6.11. Engineering Analysis and Controls for the Manufacturing Process of GAP-1m

Controls of vapor emissions will be necessary in this process, given the use of three chemicals on the HAP list (methanol, xylene, and allyl chloride). In order to comply with 40 CFR 63, which regulates equipment leaks, all emissions from equipment leaks at this facility would be vented through a closed-vent system to a control device, in accordance with the requirements of 40 CFR §63.172. These requirements are summarized briefly in this section.

If a closed-vent system is not in place at the facility in question, then the specific requirements outlined in 40 CFR §63.163 through §63.171, §63.173, and §63.174 would apply in order to ensure compliance with equipment leak regulations. These requirements are not summarized in detail in this report.

Requirements for the closed-vent systems and control devices (40 CFR §63.172) include:

- Recovery or recapture devices (such as condensers or absorbers) need to operate with an efficiency of 95% or greater, or to an exit concentration of 20 ppm_v, whichever is less stringent.

- Enclosed combustion devices also need to operate with an efficiency of 95% or greater, or to an exit concentration of 20 ppm_v, whichever is less stringent, or to provide a minimum residence time of 0.5 seconds at a minimum temperature of 760°C. In this case, the 20 ppm_v is on a dry basis and is corrected to 3% oxygen.
- Control devices need to be monitored, including an initial inspection and annual inspections. Specific requirements for these inspections are detailed in the regulations.
- Leaks are indicated by either an instrument reading greater than 500 ppm_v or by visual inspections and need to be repaired as soon as practicable.

A control device should also be designed that will reduce trimethylamine emissions from waste stream M8. Though this chemical is not on the HAP list, it is a corrosive and flammable gas and the need for safe handling of this stream should be considered in designing a vapor mitigation and control strategy for the facility.

6.12. Handling and Storage for the Manufacturing Process of GAP_{-1m}

The following section provides handling and storage recommendations for allyl chloride, potassium cyanate, sodium hydroxide, TMDSO, tetramethylammonium hydroxide, Karstedt's catalyst, D_4, trioxtylmethylammonium chloride, 1-octanol, trioctylamine, methyl carbamate, potassium chloride, and trimethylamine. There is no MSDS with safety and handling information for the silanol material. However, this material will only be present as part of a waste stream that will be handled safely in accordance with RCRA Subpart D regulations. Methanol and xylene were discussed earlier in this report for the CO_2 capture system (Section G) and the information is not duplicated here.

a) Allyl chloride (CAS # 107-05-1)[79]

Allyl chloride is classified as a hazardous chemical by the OSHA standard. It is regulated under both DOT and IATA as a flammable liquid. The NFPA rating for allyl chloride is 2 for health hazard, 3 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Allyl chloride needs to be stored in a closed container in a dry area with adequate ventilation. The recommended storage temperature is 2-8°C. It should be used in explosion proof equipment and kept away from ignition sources. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. Allyl chloride should be stored separately from strong oxidizing agents. Additional chemicals that should be stored separately from allyl chloride are listed in Section J of this report.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to a safe area and all sources of ignition removed. PPE should be worn, including respiratory protection to avoid breathing vapors. Precautions should be taken due to the high volatility, corrosivity, and flammability of allyl chloride. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. The spill should be contained and the material collected with an electrically protected vacuum cleaner or by wet-brushing.

3) Health Effects and Exposure Limits

ACGIH provides TLV-TWA (threshold limit value – time weighted average) of 1 ppm_v and a TLV-STEL (threshold limit value – short-term exposure limit) of 2 ppm_v. Both of these exposure limits are based on eye and upper respiratory tract irritation and liver and kidney damage. Both NIOSH and OSHA provide a TWA of 1 ppm_v (3 mg/m^3) and a STEL of 2 ppm_v (6 mg/m^3). OSHA classifies this chemical as being harmful by ingestion and skin absorption, an irritant, a carcinogen, and a mutagen. Symptoms of exposure to allyl chloride include spasm, inflammation and edema of the larynx and bronchi, pneumonitis, pulmonary edema, burning sensation, coughing, headache, nausea, and vomiting.

4) Respiratory Protection Recommendation

If the risk assessment indicates that a respirator is necessary, use a full-face respirator with either multi-purpose combination or type ABEK (EN 14387) respirator cartridges in addition to engineering controls. If the respirator is the only protection available, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Fluorinated rubber gloves with a minimum layer thickness of 0.7 mm are recommended. Face shield and safety glasses are the recommended eye protection. Eye protection must be approved under appropriate government standards, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

When complete suit protection is required, wear flame retardant antistatic protective clothing. The need for this type of protection is determined based on the concentration and amount of material in the workplace in question.

b) Potassium Cyanate (CAS# 590-28-3)[58]

Potassium cyanate is classified as a hazardous chemical by the OSHA standard. It is not regulated by either DOT or IATA as dangerous goods. The NFPA rating for potassium cyanate is 2 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Potassium cyanate should be kept in a closed container in a dry area with adequate ventilation. Contact with skin and eyes should be avoided. The formation of dust and aerosols can also pose a risk and may result in the formation of combustible dusts. Potassium cyanate should be stored separately from strong oxidizing agents.

2) Accidental Release Measures

Proper PPE should be worn when dealing with spills of this material. Dust formation should be avoided and proper ventilation should be provided in the area of the spill. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. The spill should be cleaned in such a way so as to avoid the creation of dust and the material kept in suitable, closed containers for disposal.

3) Health Effects and Exposure Limits

OSHA classifies potassium cyanate as an acute toxicity hazard in the case of ingestion and an eye irritant. No OSHA, ACGIH, or WEEL (Workplace Environmental Exposure Levels) exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

Use type P95 or type P1 particle respirator for nuisance exposures. Use type OV/AG/P99 or ABEK-P2 respirator cartridges for higher level exposures.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Nitrile rubber gloves with a minimum layer thickness of 0.11 mm are recommended. Safety glasses and side-shields should be worn for eye protection. Eye protection needs to be approved under such standards as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

The need for complete suit protective clothing against chemicals should be determined based on the concentration and amount of the substance in the workplace in question.

c) Sodium hydroxide (CAS# 1310-73-2)[59]

Sodium hydroxide is classified as a hazardous chemical by the OSHA standard. It is regulated under both DOT and IATA as a corrosive material. The NFPA rating for sodium hydroxide is 3 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Sodium hydroxide should be kept in a closed container in a dry area with adequate ventilation. The formation of dusts and aerosols should be avoided. This material is a strong base and should not be stored with certain types of incompatible chemicals, including strong acids and organic materials. Specific chemicals involved in this process that should be stored separately include TMDSO, Karstedt catalyst, and D4.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to safe areas. The use of proper PPE is necessary when dealing with a spill of this material, including respiratory protection. When handling this material, the corrosivity should be considered and contact with skin avoided. Dust formation should be avoided and adequate ventilation provided in the location of the spill. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. The spill should be cleaned in such a way so as to avoid the creation of dust and the material kept in suitable, closed containers for disposal.

3) Health Effects and Exposure Limits

Sodium hydroxide is extremely corrosive and will cause damage to skin and eyes. ACGIH provides a TLV-C (threshold limit value – ceiling limit) value of 2 mg/m^3. OSHA also provides TWA and C (ceiling limit) values of 2 mg/m^3. These values are based on eye, skin, and upper respiratory tract irritation.

4) Respiratory Protection Recommendation

If the risk assessment determines that a respirator is necessary, use a full-face particle respirator with type N100 or type P3 cartridges in addition to engineering controls. If the respirator is the only means of protection, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material needs to be handled with gloves. Nitrile rubber gloves with a minimum layer thickness of 0.11 mm are recommended. A face shield and safety glasses are recommended. All eye protection needs to be approved under such standards or NIOSH or EN 166.

6) Skin and Body Protection Recommendation

The need for complete suit protective clothing against chemicals should be determined based on the concentration and amount of the substance in the workplace in question.

d) TMDSO (CAS# 3277-26-7)[83]

TMDSO is classified as a hazardous chemical by the OSHA standard. It is regulated under both DOT and IATA as a flammable liquid. The NFPA rating for TMDSO is 0 for health hazard, 3 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

TMDSO should be stored in a closed container in a dry area with adequate ventilation. It should also be stored under inert gas given its moisture sensitivity. It should be used in explosion proof equipment and kept away from ignition sources. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. TMDSO should be stored separately from strong acids, bases, and oxidizing agents.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to a safe area and all sources of ignition removed. PPE should be worn, including respiratory protection to avoid breathing vapors. Precautions should be taken due to the flammability of TMDSO. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. The spill should be contained and the material collected with an electrically protected vacuum cleaner or by wet-brushing.

3) Health Effects and Exposure Limits

This material may form a siloxane polymer when in contact with skin, eyes, or in the lungs and may cause irritation, dizziness, or headache. No specific information on target organ effects was available. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that respiratory protection is necessary, a full-face respirator with multi-purpose combination of type ABEK respirator cartridges should be used in addition to engineering controls. If a respirator is the only means of protection, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material needs to be handled with gloves. Nitrile rubber gloves with a minimum thickness of 0.11 mm are recommended. A face shield and safety glasses are recommended for eye protection. All equipment used for eye protection needs to be approved under the appropriate standard such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

Impervious, flame retardant, antistatic protective clothing is recommended. The type of protective clothing necessary would be determined based on the concentration and amount of the material in the workplace in question.

e) Tetramethyl ammonium hydroxide (CAS# 75-59-2)[61]

Tetramethyl ammonium hydroxide is classified as a hazardous chemical by the OSHA standard. It is regulated under both DOT and IATA as a corrosive liquid. The NFPA rating for tetramethylammonium hydroxide is 3 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Tetramethyl ammonium hydroxide needs to be stored in a closed container in a dry area with adequate ventilation. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. Tetramethyl ammonium hydroxide should be stored separately from alkali metals, strong oxidizing agents, acids, acid chlorides, acid anhydrides, and halogens.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to safe areas. Proper PPE should be worn when dealing with the spill, including respiratory protection, given the corrosive nature of this material. Adequate ventilation should be provided. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. To clean the spill, soak with an inert absorbent material and dispose of as hazardous waste.

3) Health Effects and Exposure Limits

OSHA classifies this chemical as hazardous based on acute oral toxicity, acute dermal toxicity, skin corrosion, and eye damage. It is listed as being fatal if swallowed or if in contact with skin. It is destructive to mucous membranes and upper respiratory tract, eyes, and skin. Symptoms of exposure include burning sensation, coughing, shortness of breath, headache, nausea, and vomiting. Symptoms of inhalation exposure may include pulmonary edema, spasm, inflammation, and edema of bronchi and larynx. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that respiratory protection is needed, use a full-face respirator with multi-purpose combination or type ABEK cartridges in addition to engineering controls. If a respirator is the only means of protection, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Nitrile rubber gloves with a minimum layer thickness of 0.11 mm are recommended. Tightly fitting safety goggles and an 8” minimum faceshield are recommended eye protection. All eye protection equipment needs to be approved by the appropriate standards, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

The need for complete suit protective clothing against chemicals should be determined based on the concentration and amount of the substance in the workplace in question.

f) Karstedt catalyst (CAS# 68478-92-2)[86]

Karstedt catalyst when prepared in vinyl terminated polydimethylsiloxane (PDMS) is not classified as a hazardous chemical by the OSHA standard. It is not regulated by either DOT or IATA as dangerous goods. The NFPA rating for Karstedt catalyst is 2 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Karstedt catalyst needs to be stored in a closed container in a dry area with adequate ventilation. It should be stored separately from oxidizing agents, acids, and bases, such as NaOH and tetramethyl ammonium hydroxide.

2) Accidental Release Measures

In the event of a spill, proper PPE should be worn. Adequate ventilation should be provided. To clean the spill, soak with an inert absorbent material and dispose of as hazardous waste.

3) Health Effects and Exposure Limits

No specific data on target organs or health effects is available on the MSDS. It should be noted that this catalyst has been approved by the FDA for use in medical applications (Section I). No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that respiratory protection is required, use a full-face respirator with multi-purpose combination or type ABEK cartridges in addition to engineering controls. If the respirator is the only means of protection, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Safety glasses with side-shields are recommended for eye protection. Any eye protection equipment needs to be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

Impervious clothing should be worn if protective clothing is necessary. The need for protective clothing would be determined based on the concentration and amount of the material in the workplace in question.

g) D_4 (CAS# 556-67-2)[72]

D_4 is classified as a hazardous chemical by the OSHA Standard. It is regulated under both DOT and IATA as a flammable liquid. The NFPA rating for D4 is 1 for health hazard, 2 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

D_4 should be stored in a closed container in a dry area with adequate ventilation away from ignition sources. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. It should be stored separately from strong oxidizing agents, acids, and bases, such as NaOH and tetramethyl ammonium hydroxide.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to a safe area and all sources of ignition removed. PPE should be worn, including respiratory protection to avoid breathing vapors. Precautions should be taken due to the flammability of D_4. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. The spill should be contained and the material collected with an electrically protected vacuum cleaner or by wet-brushing.

3) Health Effects and Exposure Limits

D_4 is classified as hazardous by OSHA based on reproductive toxicity (category 2), it is suspected of potentially damaging fertility or the unborn child based on testing in rats. It does not cause skin or eye irritation. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that a respirator is necessary, a full-face respirator with multi-purpose combination or type ABEK cartridges should be used in addition to engineering controls. If the respirator is the only protection, a full-face supplied air respirator should be used.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Nitrile gloves with a minimum thickness of 0.11 mm are recommended for splash contact. If there is potential for full contact with the chemical, nitrile gloves with a minimum layer thickness of 0.4 mm should be used. A face shield and safety glasses are the recommended eye protection. All eye protection equipment needs to be approved under the appropriate standards, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

If protective clothing is needed, it should be impervious, flame retardant, and anti-static. The need for protective clothing would be determined based on the concentration and amount of the material in the workplace in question.

h) Trioctylmethylammonium chloride (CAS# 63393-96-4)[66]

Trioctylmethylammonium chloride is classified as a hazardous chemical by the OSHA Standard. It is regulated under both DOT and IATA as a toxic substance. The NFPA rating for trioctylmethylammonium chloride is 2 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Trioctylmethylammonium chloride should be stored in a closed container in a dry area with adequate ventilation. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. This material is hygroscopic so care should be taken to limit exposure to moisture. It should be stored separately from strong oxidizing agents.

2) Accidental Release Measures

In the event of a spill, evacuate personnel to safe areas. When dealing with the spill, proper PPE needs to be worn, including respiratory protection and adequate ventilation provided. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. To clean the spill, soak up with inert absorbent material and dispose of as a hazardous waste.

3) Health Effects and Exposure Limits

OSHA classifies this as hazardous based on acute oral toxicity, skin corrosion, and serious eye damage. Potential effects upon exposure include burning sensation, cough, shortness of breath, headache, nausea, vomiting, and narcosis. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that a respirator would be necessary, wear a full-face respirator with multi-purpose combination or type ABEK cartridges in addition to engineering controls. If the respirator is the only source of protection, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material needs to be handled with gloves. Nitrile gloves with a minimum layer thickness of 0.11 mm are recommended. Tightly fitting safety goggles and an 8” minimum faceshield are the recommended eye protection. All eye protection equipment needs to be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

The need for protective clothing would be determined based on the concentration and amount of the material in the workplace in question.

i) <u>1-octanol (CAS# 111-87-5)</u>[67]

1-octanol is classified as a hazardous chemical by the OSHA Standard. It is not regulated under DOT or IATA as dangerous goods. The NFPA rating for 1-octanol is 2 for health hazard, 2 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

1-octanol should be stored in a closed container in a dry area with adequate ventilation away from ignition sources. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. It should be noted that this material is a component of Aliquat 336 and would not be present on-site in its pure form.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to a safe area and all sources of ignition removed. PPE should be worn, including respiratory protection to avoid breathing vapors. Precautions should be taken due to the flammability of 1-octanol. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. The spill should be contained and the material collected with an electrically protected vacuum cleaner or by wet-brushing.

3) Health Effects and Exposure Limits

OSHA classifies this chemical as hazardous based on skin and eye irritation. It can cause central nervous system depression, nausea, headache, vomiting, and narcosis. WEEL provides a TWA of 50 ppm_v for this chemical.

4) Respiratory Protection Recommendation

If the risk assessment indicates that a respirator is necessary, use a full-face respirator with multi-purpose combination or type ABEK cartridges in addition to engineering controls. If the respirator is the only source of protection, use a full-face supplied air respirator.

5) Hand and Eye Protection Recommendation

This material needs to be handled with gloves. For splash contact, nitrile gloves with a minimum layer thickness of 0.11 mm are recommended. For full contact, nitrile gloves with a minimum layer thickness of 0.4 mm are recommended. Safety glasses with side-shields are the recommended eye protection. All eye protection equipment needs to be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

If protective clothing is necessary, it should be impervious. The need for protective clothing would be determined based on the concentration and amount of material in the workplace.

j) Trioctylamine (CAS# 1116-76-3)[68]

Trioctylamine is classified as a hazardous chemical by the OSHA Standard. It is not regulated under DOT or IATA as dangerous goods. The NFPA rating for trioctylamine is 2 for health hazard, 1 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Trioctylamine needs to be stored in a closed container in a dry area with adequate ventilation. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. It should be noted that this material is a component of Aliquat 336 and would not be present on-site in its pure form.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to safe areas. When dealing with the spill, proper PPE should be worn and adequate ventilation provided to avoid breathing vapors. To clean the material, soak up with inert absorbent material and dispose of as hazardous waste.

3) Health Effects and Exposure Limits

OSHA classifies this chemical as hazardous based on skin and eye irritation and for respiratory irritation. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that a respirator is needed, a full-face respirator with multi-purpose combination or type ABEK cartridge should be used in addition to engineering controls. If the respirator is the only means of protection, a full-face supplied air respirator should be used.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Nitrile gloves with a minimum layer thickness of 0.11 mm are recommended. Safety glasses with side-shields are the recommended eye protection. All eye protection equipment needs to be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

If protective clothing is necessary, it should be impervious. The need for protective clothing would be determined based on the concentration and amount of material in the workplace.

k) Methyl carbamate (CAS# 598-55-0)[74]

Methyl carbamate is classified as a hazardous chemical by the OSHA Standard. It is not regulated under DOT or IATA as dangerous goods. The NFPA rating for methyl carbamate is 2 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Methyl carbamate needs to be stored in a closed container in a dry area with adequate ventilation. Contact with skin and eyes needs to be avoided. The formation of dust and aerosols should also be avoided. This material should be stored separately from strong oxidizing agents, strong bases, and phosphorous halides.

2) Accidental Release Measures

In the event of a spill, evacuate personnel to safe areas. When dealing with the spill, proper PPE should be worn and adequate ventilation provided to avoid breathing vapors. Dust formation should be avoided. If it is safe to do so, further leakage or spillage should be prevented. When cleaning, the creation of dust should be avoided and the material stored in closed containers for disposal.

3) Health Effects and Exposure Limits

OSHA classifies this chemical as hazardous based on eye irritation and carcinogenicity. For carcinogenicity, it is category 2, which means they suspect it causes cancer. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

If the risk assessment indicates that a respirator is necessary, a full-face particle respirator with type N100 or P3 cartridge should be used in addition to engineering controls. If the respirator is the only means of protection, a full-face supplied air respirator should be used.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Safety glasses with side-shields are the recommended eye protection. All eye protection must be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

If protective clothing is needed, it should be impervious. The need for protective clothing would be determined based on the concentration and amount of material in the workplace in question.

l) Potassium chloride (CAS# 7447-40-7)[76]

Potassium chloride is classified as a hazardous chemical by the OSHA Standard. It is not regulated under DOT or IATA as dangerous goods. The NFPA rating for potassium chloride is 0 for health hazard, 0 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Potassium chloride should be stored in a closed container in a dry area with adequate ventilation. Formation of dusts and aerosols should be avoided. This material is hygroscopic so care should be taken to limit exposure to moisture. It should be stored separately from strong acids and oxidizing agents.

2) Accidental Release Measures

In the event of a spill, proper PPE should be worn and adequate ventilation provided to avoid breathing vapors. Dust formation should be avoided. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided. When cleaning, the creation of dust should be avoided and the material stored in closed containers for disposal.

3) Health Effects and Exposure Limits

Potassium chloride is a gastrointestinal irritant after ingestion of high doses.[75] Potential symptoms of exposure include hyperkalemia, nausea, vomiting, abdominal pain, diarrhea, constipation, thirst, dizziness, rash, weakness, and muscle cramps. No OSHA, ACGIH, or WEEL exposure limit values are provided for this material.

4) Respiratory Protection Recommendation

Respiratory protection for this chemical is not required. If protection from nuisance levels is desired, use type N95 or P1 dust masks.

5) Hand and Eye Protection Recommendation

This material should be handled with gloves. Nitrile gloves with a minimum layer thickness of 0.11 mm are recommended. No specific eye protection is recommended on the MSDS for this material, but, if eye protection is used, it should be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

The need for protective clothing would be determined based on the concentration and amount of material in the workplace in question. No specific requirements are listed on the MSDS.

m) <u>Trimethylamine (CAS# 75-50-3)</u>[77]

Trimethylamine is classified as a hazardous chemical by the OSHA Standard. It is regulated under both DOT and IATA as a flammable gas. The NFPA rating for trimethylamine is 2 for health hazard, 4 for flammability, and a 0 for reactivity.

1) Storage and Handling Recommendations

Trimethylamine needs to be stored in a closed container in a dry area with adequate ventilation. The recommended storage temperature is 2-8°C. It should be used in explosion proof equipment and kept away from ignition sources. Contact with skin and eyes and inhalation of vapors or mist need to be avoided. It should be stored separately from oxidizing agents. Specific metals that should be avoided when storing or handling this chemical are listed in Section J of this report.

2) Accidental Release Measures

In the event of a spill, personnel should be evacuated to a safe area and all sources of ignition removed. PPE should be worn, including respiratory protection to avoid breathing vapors, given the corrosive nature of the material. Precautions should be taken due to the flammability of trimethylamine. If it is safe to do so, further leakage or spillage should be prevented and discharge to the environment avoided.

3) Health Effects and Exposure Limits

OSHA classifies this chemical as hazardous based on acute oral toxicity, acute inhalation toxicity, skin irritation, eye damage, and respiratory irritation. It is destructive to mucous membranes and the upper respiratory tract, eyes, and skin. Potential symptoms of exposure include cough, shortness of breath, headache, and nausea. ACGIH provides a TWA of 5 ppm$_v$ and a STEL of 15 ppm$_v$. These levels are based on respiratory tract irritation. Both OSHA and NIOSH provide a TWA of 10 ppm$_v$. OSHA provides a STEL of 15 ppm$_v$. NIOSH provides a ST (short-term) value of 15 ppm$_v$. WEEL provides a TWA of 1 ppm$_v$.

4) Respiratory Protection Recommendation

If the risk assessment indicates that respiratory protection is necessary, a full-face respirator with multi-purpose combination or type ABEK cartridge should be used in addition to engineering controls. If the respirator is the only source of protection, a full-face supplied air respirator should be used.

5) Hand and Eye Protection Recommendation

This material needs to be handled with gloves. Fluorinated rubber gloves with a minimum layer thickness of 0.7 mm are recommended. Tightly fitting safety goggles and an 8” minimum face shield are the recommended eye protection. All eye protection equipment needs to be approved under the appropriate standard, such as NIOSH or EN 166.

6) Skin and Body Protection Recommendation

If protective clothing is necessary, it should be flame retardant and anti-static. The need for protective clothing would be determined based on the concentration and amount of material in the workplace in question.

7. Summary

Performance of the GAP-1_m/TEG non-aqueous solvent was demonstrated at 0.5 MW_e at NCCC for over 900 hrs using two desorber technologies: continuous stirred reactor (CSTR) and steam stripper column (SSC).

GAP-1_m/TEG

GAP-1_m/TEG is a non-aqueous post combustion CO_2 capture system with lower vapor pressure, lower corrosity and improved working capacity vs. aqueous amines solvents. Formation of urea under desorber conditions and hydrothermal equilibration are major pathways in thermal degradation. Solvent management can be improved by implementing low temperature desorption processes and/or by developing Gen 2 solvent systems with reduced thermal degradation.

CSTR Campaign

A CSTR desorber system was designed, fabricated and integrated with the PSTU at NCCC. The CSTR is a one-stage separation unit with reduced space requirements, and capital cost. GAP-1_m/TEG performance with CSTR was tested for over 500 hrs. Solvent carry-over in the CSTR overhead was controlled by limiting the water content to less than 5 wt.%. 65 % CO_2 capture efficiency was achieved at 0.5 MWe with the CSTR desorber. Solvent degradation was dominated by the thermal formation of urea under desorber conditions. To take advantage of the low capital cost / low reduced space requirement of the CSTR, one needs to develop and scale-up the Gen 2 aminosilicone solvents with improved thermal stability.

Steam Stripping Column Campaign

Controlled water addition to GAP-1_m/TEG and steam stripping desorption were developed to mitigate thermal degradation. The concepts were first tested in a glass stripping column (GE GRC), optimized in a continuous bench scale system (2 kW_e, GE GRC), and demonstrated in a 0.5

MW_e pilot (NCCC). Small amounts of water in the working solution were found to be an effective way to enable steam stripping, lower desorption temperature, and hence reduce thermal degradation. Steam stripping also increased working capacity by 30% due to a more efficient desorption. No special system modifications were required to the PSTU to accommodate the testing of the non-aqueous GAP-1_m solvent with the regenerator column. 90 – 95% CO_2 capture efficiency was achieved under stoichiometric conditions at 0.5 MW_e (235 ^oF desorption, 2 psig and 19 wt. % H_2O). Both CO_2 capture efficiency and specific duty reached optimum conditions at 18 wt.% H_2O. Low amine degradation (< 0.05 wt.%/day) was recorded over 350 hrs of operation. GAP-1_m/TEG solvent exhibited a 25% increased working capacity, and 10% reduction in specific steam duty vs. MEA, at 10 ^oF lower desorption temperature. Further improvements in specific steam utilization can be achieved by optimizing water loading and implementing an advanced process scheme with staged steam injection.

Techno-economic Analysis

An ASPEN process model was developed for the GAP-1_m/TEG solvent. Techno-economical analysis developed for a 550 MW supercritical coal plant[1] showed a 20 – 30 % improvements in both CAPEX and CO_2 removal cost vs. aqueous amine systems. The 1st year CO_2 removal cost for the aminosilicone-based carbon-capture process was evaluated at \$48/ton CO_2 using the steam stripper column. CO_2 cost using the CSTR desorber is dominated by the economics of the solvent make-up. The steam stripper desorber is the preferred unit operation due to a more efficient desorption, and reduced solvent make-up rate. Improved economics can be achieved by implementing Gen 2 aminosilicone solvents and advanced process schemes.