

# **CO<sub>2</sub>-Reactive Amines in SCOT\* Solvent: Operating Insights from Norco's SCOT Units**

Jim Critchfield, Consultant

Farhang Abdollahi, Technology Manager, Gas Processing & Decarb – Shell Catalysts and Technologies

Ganesh Kidambi, Subject Matter Expert, Sulfur and Tail Gas Treating – Shell Projects and Technology

Jason Lowry, Shell Norco Sulfur Production Specialist

Claus Sulfur Units must respond to often-changing air demand, and SO<sub>2</sub> breakthrough to the downstream Shell Claus Off-gas Treating (SCOT\*) process solvent may occur when that response is imperfect. In 1999, a publication<sup>1</sup> demonstrated that such events result in partial degradation of Methyldiethanolamine (MDEA), creating CO<sub>2</sub>-reactive secondary (2') amines in the SCOT solvent.

Buildup of CO<sub>2</sub>-reactive 2' amines in the solvent can increase absorption of CO<sub>2</sub>, which opposes the SCOT process requirement of slipping the majority of CO<sub>2</sub>. Academic studies demonstrate that blends of 2' amines with MDEA enhance CO<sub>2</sub> reaction kinetics. However, the design and operation of SCOT units minimizes CO<sub>2</sub> absorption, so reaction kinetics alone do not fully describe the practical impact of accumulating 2' amines on process performance. Notably, the SCOT process was originally developed to employ a CO<sub>2</sub>-reactive 2' amine (Diisopropanolamine, (DIPA)) as the H<sub>2</sub>S-selective solvent.

Shell's operating experience, both as the SCOT process licensor and as an operator of commercial SCOT units, can provide perspective on the practical impact of accumulating 2' amines in SCOT solvent. This paper presents solvent analysis from two dozen operating MDEA solvent inventories. The data demonstrate the prevalence of 2' amines in successfully-operating commercial applications.

A more in-depth perspective is illustrated with operating experience and solvent analysis history from the SCOT units at Shell Energy and Chemicals Park – Norco in Louisiana, USA. This site has been operating SCOT units for more than 4 decades and has monitored the solvent composition closely for more than 20 years. During that time, several large SO<sub>2</sub>-breakthrough events have occurred, resulting in operation with varying composition of solvent. Matching operating data with the changing solvent composition provides insight into the practical effect of accumulating 2' amines on the SCOT unit's performance.

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<sup>1</sup> Critchfield, J., and J. Jenkins, "Evidence of MDEA degradation in tail gas treating plants", Petroleum Technology Quarterly, 2Q 1999.

\* SCOT is a Trademark of Shell

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# 1. The SCOT Process

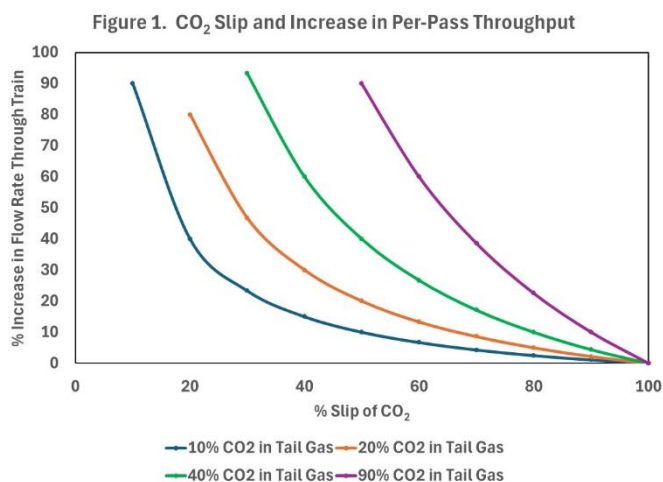
The Shell Claus Offgas Treating (SCOT) Process was announced by Shell in 1972 and was deployed less than 9 months later in California in two small skidded units. In 1973, a world-scale SCOT unit was installed in the Foothills of Canada at the Waterton Gas Plant. Since that time, the process has become the premier choice in Claus offgas treatment, with more than 200 SCOT units licensed, in addition to numerous units deployed inside Shell equity assets.

The SCOT Process has three major process steps:

- 1) A hydrogenation reactor, to convert Claus Tail Gas  $\text{SO}_2$ , sulfur, COS and  $\text{CS}_2$  to  $\text{H}_2\text{S}$
- 2) A heat recovery/removal section, to remove heat and excess water from converted tail gas
- 3) An amine solvent section, to selectively remove  $\text{H}_2\text{S}$  from the tail gas, and then recycle the  $\text{H}_2\text{S}$  to the front of the Claus unit.

Selective  $\text{H}_2\text{S}$  removal is key to the function of the amine solvent. Nearly complete removal of  $\text{H}_2\text{S}$  is necessary in the application, along with the simultaneous ability of the solvent to \*not\* remove much  $\text{CO}_2$ . This lack of  $\text{CO}_2$  removal is commonly referred to as 'slipping'  $\text{CO}_2$ .

Acid gases processed in Claus units almost always contain some amount of  $\text{CO}_2$ , and that concentration of  $\text{CO}_2$  may be significant. Hydrocarbons that may exist in the acid gas also are burnt in the Claus unit; co-firing and reheat of the process gas by burning fuel / natural gas also contribute to  $\text{CO}_2$  in the tail gas. The preferred operation of a SCOT unit requires a high level of 'slip' to limit the degree of recycle of  $\text{CO}_2$ ; typically 80% or more of the  $\text{CO}_2$  present in the tail gas is slipped in normal operation, preventing  $\text{CO}_2$  from building up in the train due to excessive recycle. For a typical refinery tail gas unit with less than 20%  $\text{CO}_2$  in tail gas,  $\text{CO}_2$  recycle resulting from 80% slip increases per-pass flow in the train by less than 10% (Figure 1).



Residual traces of sulfur compounds still present in Tail Gas after amine treating are normally incinerated and then vented as  $\text{SO}_2$  in a manner compliant with environmental requirements.

## 1.1 The SCOT Amine Section

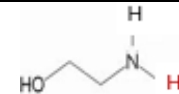
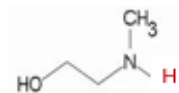
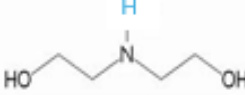
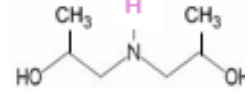
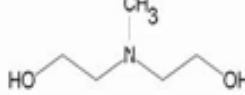
The focus of this paper is on the performance of the SCOT amine section.

Since its inception, the SCOT Process has employed generic and 'designer' amine solvents for selective removal of  $\text{H}_2\text{S}$  from the Claus tail gas. All of these solvents preferentially remove  $\text{H}_2\text{S}$  from Claus Tail Gas while slipping a majority of the  $\text{CO}_2$ , subject to the individual solvent's properties/nature and to the design and operating conditions in the application. It is useful to

understand the reaction of CO<sub>2</sub> with these solvents, in order to gain perspective on how the SCOT process ‘slips’ CO<sub>2</sub>.

## 1.2 Amines Differentiated by CO<sub>2</sub> Reaction with the Solvent

The basic nitrogen atom in amines can support up to three substitutions. Amines which have 1 or 2 carbon arms attached to the nitrogen are described as primary (1') or secondary (2'), respectively. These 1' or 2' amines undergo a direct reaction with CO<sub>2</sub>.<sup>2</sup> Amines which have 3 carbon arms are tertiary (3'). Tertiary amines react with CO<sub>2</sub> only indirectly, by acting as a buffer to raise the pH of aqueous solutions and by base-catalysis of the reaction of CO<sub>2</sub> with water. Table 1 shows common amines relevant to this paper:

Table 1. Properties of Common Amines			MW	pKa, 25°C	nBP, °F <sup>3</sup>
	1'	MEA Monoethanolamine	61.08	9.51 <sup>4</sup>	338
	2'	MMEA Methyl Monoethanolamine	75.11	9.8	316
	2'	DEA Diethanolamine	105.14	8.88 <sup>5</sup>	516
	2'	DIPA Diisopropanolamine	133.19	8.89 <sup>6</sup>	480
	3'	MDEA Methyl Diethanolamine	119.16	8.52 <sup>7</sup>	477

<sup>2</sup> unless structural effects suppress (hinder) the reaction

<sup>3</sup> National Toxicology Program, Institute of Environmental Health Sciences, National Institutes of Health (NTP). 1992. National Toxicology Program Chemical Repository Database. Research Triangle Park, North Carolina

<sup>4</sup> S. P. Datta and A. K. Grzybowski. J. Chem. Soc. 1959, 1091.

<sup>5</sup> Littel, R. J., Selective Carbonyl Sulfide Removal in Acid Gas Treating Processes, Dissertation University of Twente, 1991, Table 1, p 172

<sup>6</sup> Littel, R. J., Selective Carbonyl Sulfide Removal in Acid Gas Treating Processes, Dissertation University of Twente, 1991, Table 1, p 172

<sup>7</sup> Perrin DD; Dissociation constants of organic bases in aqueous solution. IUPAC Chem Data Ser, Butterworth, London (1965)

## 2. Development of Amines for SCOT Solvent

The original 1960's R&D for the SCOT process studied the then-commercially relevant amines for their ability to remove H<sub>2</sub>S while providing adequate CO<sub>2</sub> slip. At the time, the available amines were MEA, DEA, TEA, and DIPA. MEA was found to be too-fast reacting to achieve sufficient slip of CO<sub>2</sub> (a critical process requirement). TEA was found to perform poorly with respect to H<sub>2</sub>S absorption.

The 2' amine DEA was found to slip about 30-50% of the CO<sub>2</sub> in the tail gas. DIPA, a CO<sub>2</sub>-reactive 2' amine which reacts more slowly with CO<sub>2</sub> than DEA does, showed about 70-80% CO<sub>2</sub> slip in that research. DIPA became the first amine to be commercially deployed in SCOT in the 1970's.

Later in the 1980's, MDEA became widely commercial as a gas treating solvent, as a 3' amine MDEA is not directly CO<sub>2</sub>-reactive. MDEA provided the potential for high levels of CO<sub>2</sub> slip, and it became the popular choice of SCOT solvent.

Appendix C provides more information on the history of amine deployment in SCOT.

## 3. SO<sub>2</sub> Intrusion in SCOT Units

### 3.1 Effect of heat stable salts on H<sub>2</sub>S performance

From the first deployments in the 1970's, it was recognized that Claus plant upsets were capable of contaminating SCOT solvent with SO<sub>2</sub>. The original process guide from the era included analytical methods for measuring acid concentration (often expressed as "heat stable salts").<sup>8</sup> Folk wisdom from that time recognized 'aged solvent works better than fresh solvent' even if the exact cause of that wasn't yet known.

Later pilot plant studies in the 1980's and early 1990's demonstrated the powerful effect that acids had in the solvent on depth of H<sub>2</sub>S treating. The effect was due to improvement in depth of regeneration: a little bit of acid contamination resulted in deeper H<sub>2</sub>S removal by driving H<sub>2</sub>S out of the lean solvent in the Regenerator. It was also recognized that too much acid consumed solvent capacity.

Figure 2 shows pilot plant performance data which demonstrate this acid-aided-regeneration effect, and the corresponding improvement in H<sub>2</sub>S treating performance.<sup>9</sup>

The knowledge of this effect became widespread in the late 1980's, and the effect was incorporated into the solution chemistry in design/simulation tools.

However, the consequence of SO<sub>2</sub> intrusion on degradation of the solvent, and potentially CO<sub>2</sub> slip, was not well-recognized at the time. In that era it was common to hear statements such as "MDEA does not degrade" spoken at technical venues.

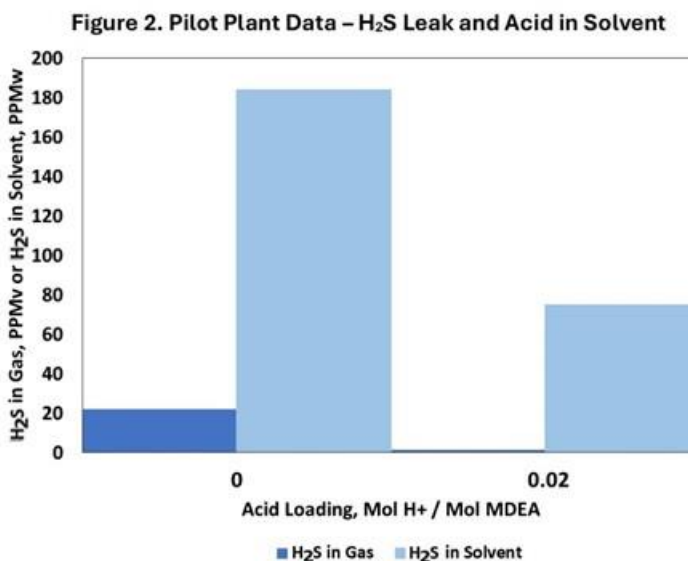
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<sup>8</sup> Shell internal document (SCOT Process Guide)

<sup>9</sup> "Low Leak Solvents for SCOT Application", Shell internal research report, Critchfield et al, 1990

A 1999 publication showed that SO<sub>2</sub> intrusion events did partially degrade MDEA into 2' amines, organic acids, and aminoacids.<sup>10</sup>

Appendix D presents more information on that degradation, and on past comments about the impact of degradation on CO<sub>2</sub> slip in SCOT application. The Appendix also presents evidence that CO<sub>2</sub>-reactive amines may be present as impurities in fresh MDEA, resulting in increased reactivity of impure MDEA. And the Appendix shows evidence from academic research that intentional blends of MDEA with small amounts CO<sub>2</sub>-reactive amines results in faster rates of reaction.



## 4. Operating Experiences

### 4.1 24 Operating Units

Since the early deployments of the SCOT Process, Shell has operated dozens of SCOT units, and designed/supported many more. Experience gained in those activities validates the ubiquity of 2' amines in operating inventories of tail gas MDEA solvents.

Table 2 presents summary results of solvent analysis of two dozen operating MDEA solvent inventories. From the grand average of those unit's analysis, a typical SCOT MDEA solvent would be expected to contain about 0.8% DEA, 0.3% MMEA, and 0.8% HSS.

It should be noted that the min and max values shown in the Table represent operating solvent inventories at all stages of their life: including fresh or gently used solvent, and also solvent subjected

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<sup>10</sup> Critchfield, J., and J. Jenkins, "Evidence of MDEA degradation in tail gas treating plants", Petroleum Technology Quarterly, 2Q 1999

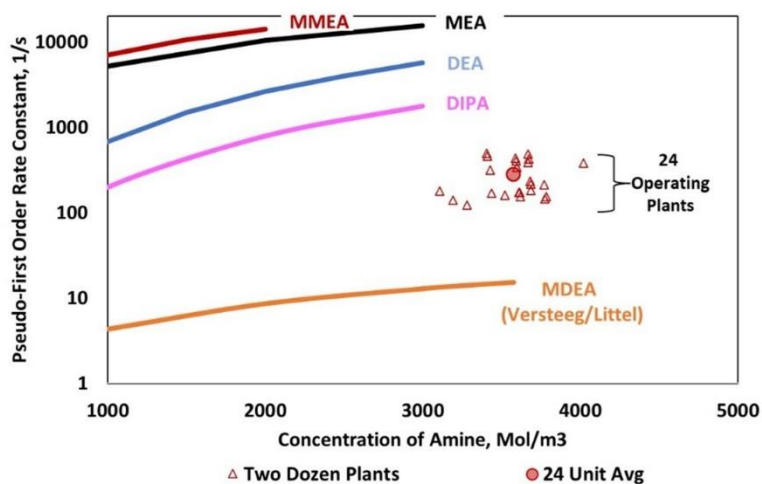
**Table 2. Composition of MDEA Solvent in 24 Operating Tail Gas Units**

Plant ID	year start	year stop	Duration, yrs	# Samples	Amine Str	DEA			MMEA			2' Amines			HSAS %wt as Amine		
						Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
1	1995	2012	17	75	45	0.41	0.01	1.46	0.11	0.00	0.64	0.50	0.03	1.99	0.27	0.00	1.55
2	1997	2010	13	45	44	0.89	0.30	1.39	0.44	0.09	1.05	1.42	0.87	2.22	1.13	0.10	4.55
3	1996	2009	13	58	41	1.06	0.12	2.23	0.54	0.00	1.40	1.59	0.21	3.38	1.17	0.09	8.66
4	1999	2020	21	222	48	1.14	0.30	2.52	0.34	0.01	0.94	1.48	0.53	2.81	0.85	0.05	6.94
5	1996	2010	14	50	38	0.74	0.42	1.14	0.09	0.03	0.15	0.83	0.49	1.24	0.51	0.26	0.75
6	1996	2010	14	62	39	0.80	0.28	1.24	0.06	0.00	0.17	0.85	0.31	1.27	0.60	0.27	1.23
7	2005	2012	7	63	41	0.47	0.00	1.36	0.14	0.00	0.44	0.55	0.08	2.00	0.32	0.01	1.31
8	2008	2014	6	21	45	0.56	0.05	0.92	0.23	0.00	0.36	0.79	0.09	1.19	1.11	0.00	0.30
9	1996	2012	16	132	43	0.92	0.00	1.85	0.12	0.00	0.99	1.03	0.04	2.80	0.98	0.04	5.70
10	1998	2010	12	47	42	0.42	0.04	1.00	0.13	0.00	0.47	0.55	0.10	1.19	0.28	0.04	1.79
11	1998	2010	12	35	37	0.97	0.03	2.88	0.14	0.00	0.55	0.75	0.00	3.02	0.93	0.12	5.40
12	1998	2012	14	56	43	0.96	0.05	1.66	0.07	0.00	0.26	1.03	0.05	1.66	0.43	0.06	0.95
13	1998	2010	12	49	45	0.73	0.07	1.47	0.09	0.00	0.59	0.82	0.11	1.83	0.43	0.07	2.89
14	2000	2010	10	37	43	0.56	0.00	1.27	0.13	0.00	0.72	0.69	0.03	1.81	0.32	0.03	1.11
15	1995	2009	14	45	43	0.91	0.14	1.79	0.39	0.11	1.26	1.30	0.36	2.18	0.54	0.13	2.03
16	1995	2010	15	56	44	1.09	0.04	2.18	0.51	0.00	1.79	1.59	0.04	3.19	0.82	0.02	3.49
17	1995	2009	14	47	43	1.22	0.06	2.51	0.36	0.06	0.74	1.58	0.17	2.59	1.34	0.13	5.87
18	1995	2012	17	59	43	1.22	0.11	2.44	0.49	0.00	1.19	1.71	0.17	3.32	1.23	0.16	7.35
19	1995	2012	17	54	44	1.24	0.29	3.15	0.47	0.08	1.24	1.71	0.51	3.87	1.29	0.35	9.13
20	1999	2012	13	137	41	0.91	0.12	1.98	0.33	0.04	1.34	1.24	0.24	2.88	0.97	0.01	2.03
21	1999	2012	13	135	41	0.95	0.06	2.29	0.61	0.07	1.52	1.56	0.12	2.97	1.16	0.04	7.40
22	2012	2014	2	17	44	0.43	0.20	0.73	0.17	0.10	0.34	0.60	0.32	0.96	0.59	0.20	2.07
23	2012	2014	2	8	44	0.41	0.19	0.90	0.27	0.10	0.57	0.68	0.31	1.46	0.95	0.12	1.04
24	2012	2014	2	20	44	0.52	0.20	0.81	0.23	0.00	0.62	0.74	0.32	1.31	0.92	0.44	2.64
Total			290	1530													
Grand Average			12.1	64	43	0.81			0.27			1.07			0.80		
STDDEV					2.4	0.28			0.17			0.42			0.35		
Min					37.0	0.41			0.06			0.50			0.27		
Max					48.0	1.24			0.61			1.71			1.34		

to big SO<sub>2</sub> events. For instance, Plant #19 shows a maximum heat stable salt value of over 9%wt; intervention clearly was required in such a large SO<sub>2</sub> event, and so that extreme value doesn't represent sustained operation.

The values in Table 2 were used to calculate rate constants for each plant's average composition using the rate expression from literature.<sup>11</sup> Those values are shown in Figure 3, which also presents rate constants for other amines of interest. The average composition results in a rate constant that is about 18X

**Figure 3. 24 Operating Plants – CO<sub>2</sub> Rate Constants**



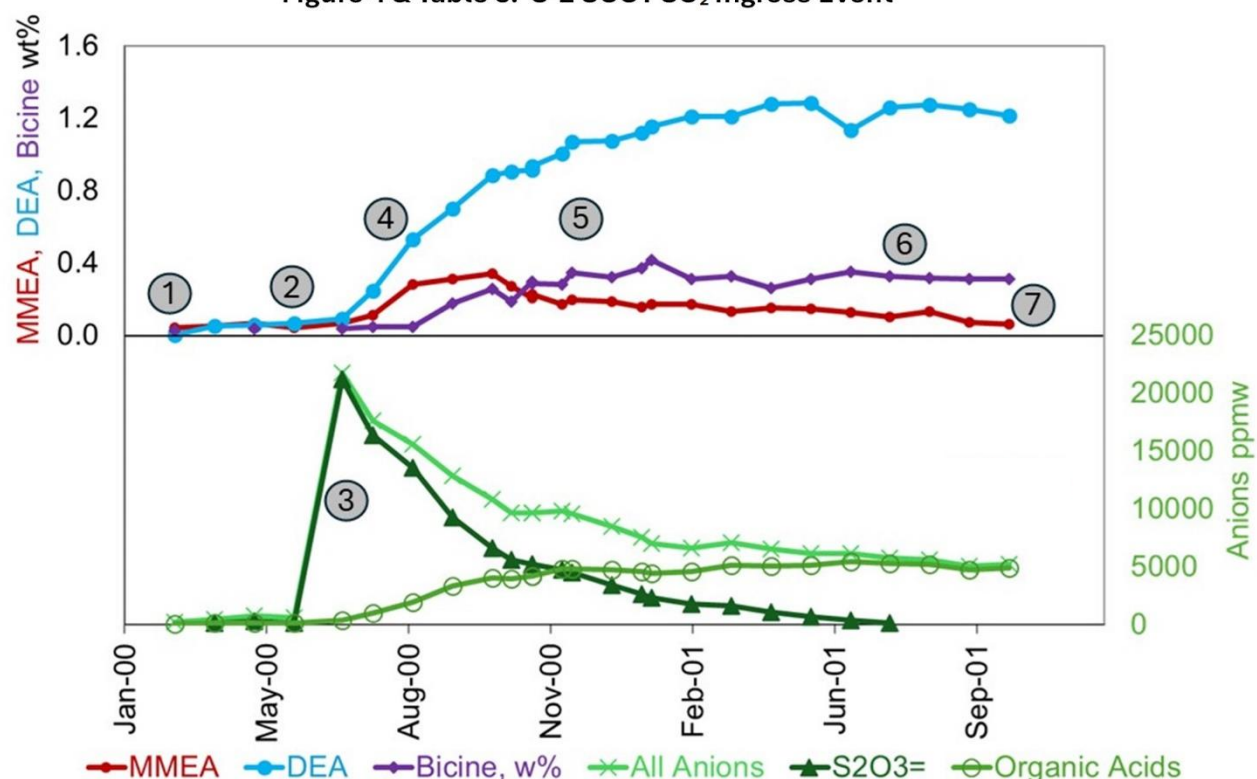
<sup>11</sup> Littell, R. J., Selective Carbonyl Sulfide Removal in Acid Gas Treating Processes, Dissertation University of Twente, 1991, Eq 4, p 139

higher than that of MDEA alone. All the plants display rate constants intermediate to those of pure MDEA and that of DIPA.

## 4.2 Norco S-2 SCOT - An Example of a Major SO<sub>2</sub> Intrusion Event

The Norco Refinery operates two MDEA-based SCOT units, S-2 and S-3 SCOT.<sup>12</sup> S-2 SCOT has a history of SO<sub>2</sub> intrusion events dating back into the 1980's. A major SO<sub>2</sub> intrusion event in 2000 was documented with frequent solvent sampling/analysis; no significant solvent purging or replacement occurred during that event. The changing solvent composition during the event demonstrates how degradation progresses with prolonged operation of SO<sub>2</sub>-contaminated solvent. The compositions are presented in Figure 4 and Table 3.

Figure 4 & Table 3. S-2 SCOT SO<sub>2</sub> Ingress Event



	1	2	3	4	5	6	7
Date	29-Feb-00	23-May-00	26-Jun-00	15-Aug-00	10-Oct-00	17-Jul-01	9-Oct-01
S2O3=	<100	112	21234	13521	6592	120	<100 ppmw
All Anions	<500	591	21587	15601	10848	5741	5232 ppmw
Organic Acids	72	167	353	1942	4060	5298	4873 ppmw
DEA	<0.05	0.07	0.09	0.53	0.88	1.26	1.22 %wt
MMEA	0.043	0.044	0.068	0.28	0.34	0.10	0.060 %wt
Bicine	<0.05	<0.05	<0.05	0.05	0.25	0.32	0.31 %wt

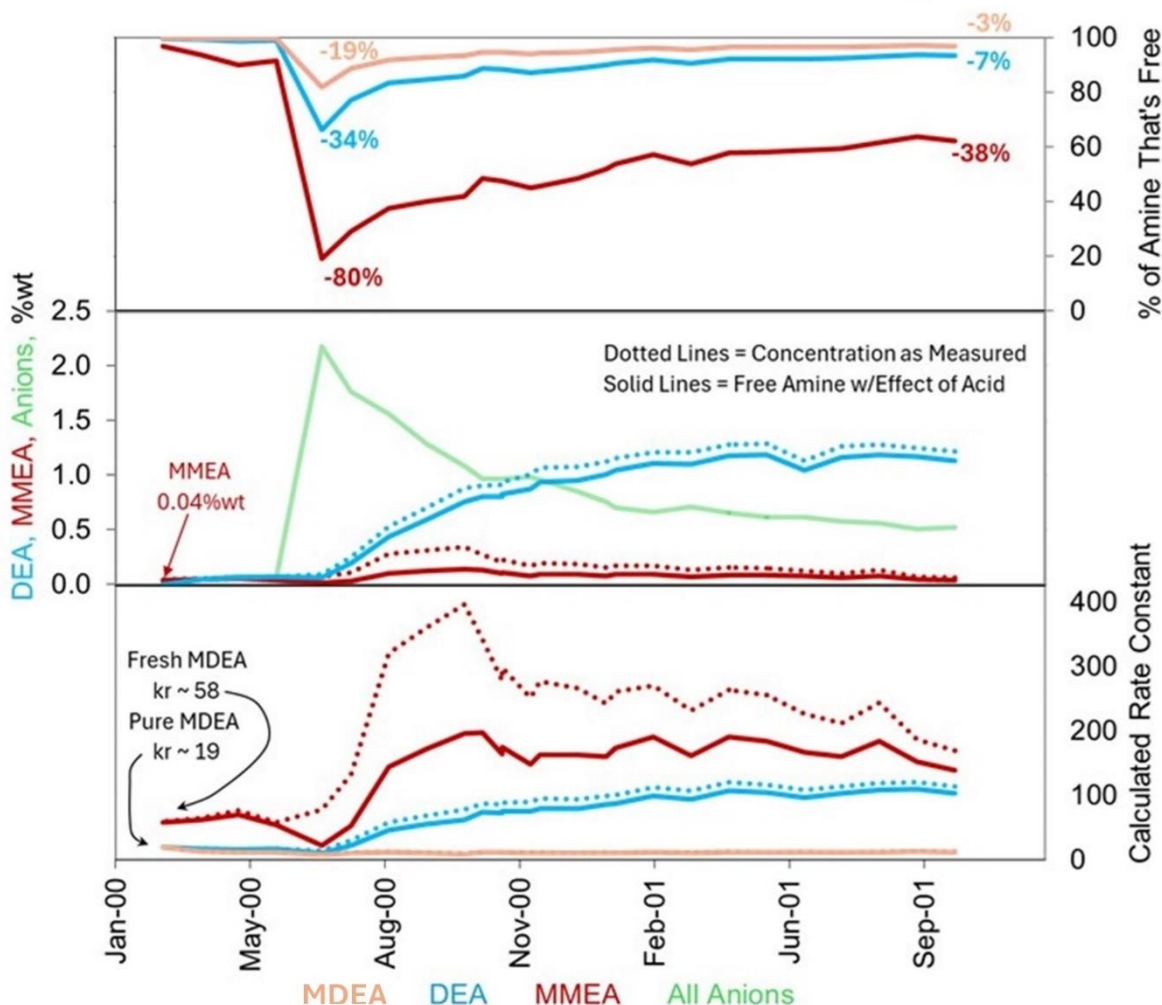
<sup>1,3</sup> MMEA is a known impurity in MDEA, and an intermediary in the manufacture of MDEA from ethylene oxide and methyl amine. Due to its volatility, MMEA separates from the MDEA product via distillation. Shell has a required specification for minimum purity of MDEA for the application; the MDEA in S-2 SCOT met that specification.



One can use solution equilibria to estimate the distribution of species; the easy way to do that is to rely on process simulation tools that employ sophisticated activity models to speciate solvents. Or one can combine pH equilibria calculations with material balance manually, and estimate that distribution of species (with or without an activity model). In this work the latter approach was taken.

Because the 2' amines are stronger bases, when considering the kinetic contributions of DEA and MMEA in SCOT MDEA, it's especially important to estimate the neutralization of the CO<sub>2</sub>-reactive

**Figure 5. S-2 SCOT Event: Neutralization and Rate Constant**



amines. Figure 5 demonstrates the importance of considering thiosulfate and organic acids neutralization of 2' amines in the S-2 SCOT example. MMEA is the strongest base in the mix; the presence of acids has the greatest effect on its “free” concentration. DEA is next most affected, and MDEA is much less so (the top graph in Figure 5).

The bottom graph in Figure 5 presents calculated rate constants with CO<sub>2</sub> based on the analyzed compositions. Dotted lines represent rate constants based on total amine concentration, without considering neutralization effects. Solid lines include the effect of neutralization on the calculated

rate constant. Note that the rate constants shown in the Figure are stacked; the amber line is the contribution of MDEA alone. The blue line is the contributions of DEA+MDEA, and the red line is the full rate constant, with the contributions of all three amines included.

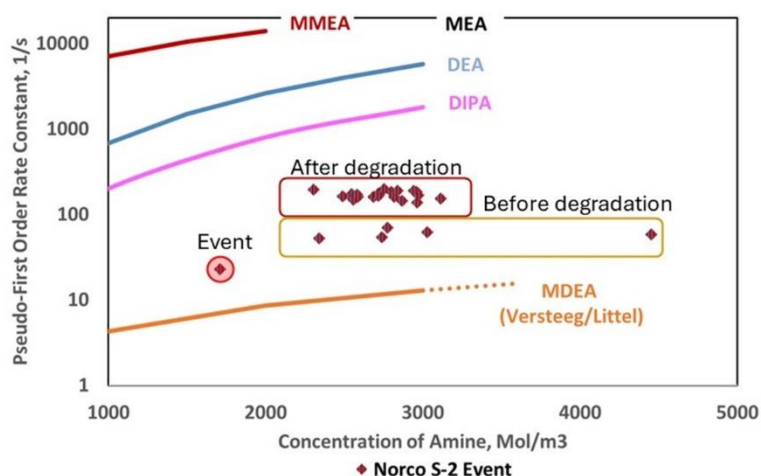
At the highest concentration of acids in the system, the overall rate constant is decreased by about 50% by neutralization. Interestingly, in this example, the combined effects of neutralization and MMEA concentration change result in an approximately stable value of reaction rate constant after the initial SO<sub>2</sub> contamination, despite the wide composition variation experienced.

#### 4.2.2 Comparing Rate Constants – S-2 SCOT SO<sub>2</sub> Event

Figure 5 showed that building MMEA and DEA in the solvent increased the calculated rate constant by an order of magnitude compared to MDEA-only.

To provide some perspective, Figure 6 presents the calculated rate constants (based on free amine) compared to literature values for other amines. Even in the very-degraded condition during the SO<sub>2</sub> event, the rate constants were intermediate between those of MDEA and those of DIPA (the original solvent in SCOT application).

**Figure 6. S-2 SO<sub>2</sub> Event – CO<sub>2</sub> Rate Constants**



The Norco S-2 SCOT event demonstrated that the CO<sub>2</sub> reaction rate constant increased, and that co-occurring heat stable salts minimized the size of the potential increase during the event. MMEA ‘weathered’ away after being created in the event. Over the course time in service, a SCOT solvent may experience considerable variation of composition due to such events, and due to solvent loss and/or solvent replacement as operators manage solvent quality.

### 4.3 Norco S-3 SCOT: Solvent Composition and Process Data

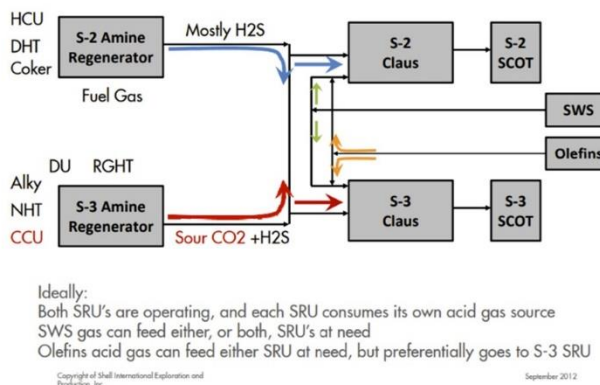
#### 4.3.1 Norco S-3 Claus + SCOT

Norco’s S-3 Claus + SCOT train was commissioned in the 1990’s, and shares the sulfur load of the refinery with the older S-2 train. Each SCOT unit is dedicated to its own Claus; acid gas is routed to (and between) the Claus units via a header system. Figure 7 is a simple sketch of how H<sub>2</sub>S-producing

refinery units send acid gas to the two Claus+SCOT trains. The operation of this acid gas header, and more information on the two trains, was presented in a paper at 2012 Vail Sulfur Symposium.<sup>14</sup>

An important feature of the acid gas header system is that the primary source of CO<sub>2</sub> in acid gas, the CCU, preferentially flows to the S-3 Claus+SCOT train. As refinery production varies in the upstream units, the composition of combined acid gas may change. And as the total acid gas and SWS gas flow is divided between the two units, the resulting composition of the acid gas to each unit can change. When acid gas rates are low in S-3, that train sees the majority of CO<sub>2</sub>-rich acid gas. As rates in S-3 increase, more low-CO<sub>2</sub> acid gas from the hydrotreating-concentrated side of the system improves the quality of the acid gas to S-3. That fact adds complexity to simulation of the train at different degrees of turndown and it highlights the importance of flexibility in the design of S-3 SCOT.

**Figure 7. Norco's Amine/Claus/SCOT System**



#### 4.3.2 S-3 SCOT Design Intent

These are refinery SRU's, therefore variability of flow and composition is their reality. That fact was well-recognized in the design phase of S-3 SCOT; the design took on learnings from S-2 SCOT's history of operation as well.

S-3 Claus was the first 2-bed unit in Shell's USA refinery system; the designer recognized the implications of end-of-run Claus catalyst activity decline on SCOT capacity requirements. Additionally, S-3 employed the first high pressure steam generator and SRU catalyst steam reheaters in the Shell USA refinery system. Discussions in design also included risk for bed 2 dewpoint deactivation and difficulty with catalyst heat-soak using only steam reheat...with the resulting potential increased load on SCOT. A future SRU conversion to O<sub>2</sub> enrichment was also premised.

With consideration of this broad design envelope, the design team emphasized operating flexibility instead of optimizing for maximum CO<sub>2</sub> slip.<sup>15</sup> The SCOT unit which resulted provided performance under a wide range of conditions, in exchange for somewhat lower CO<sub>2</sub> slip than might otherwise be achieved with a different design intention.

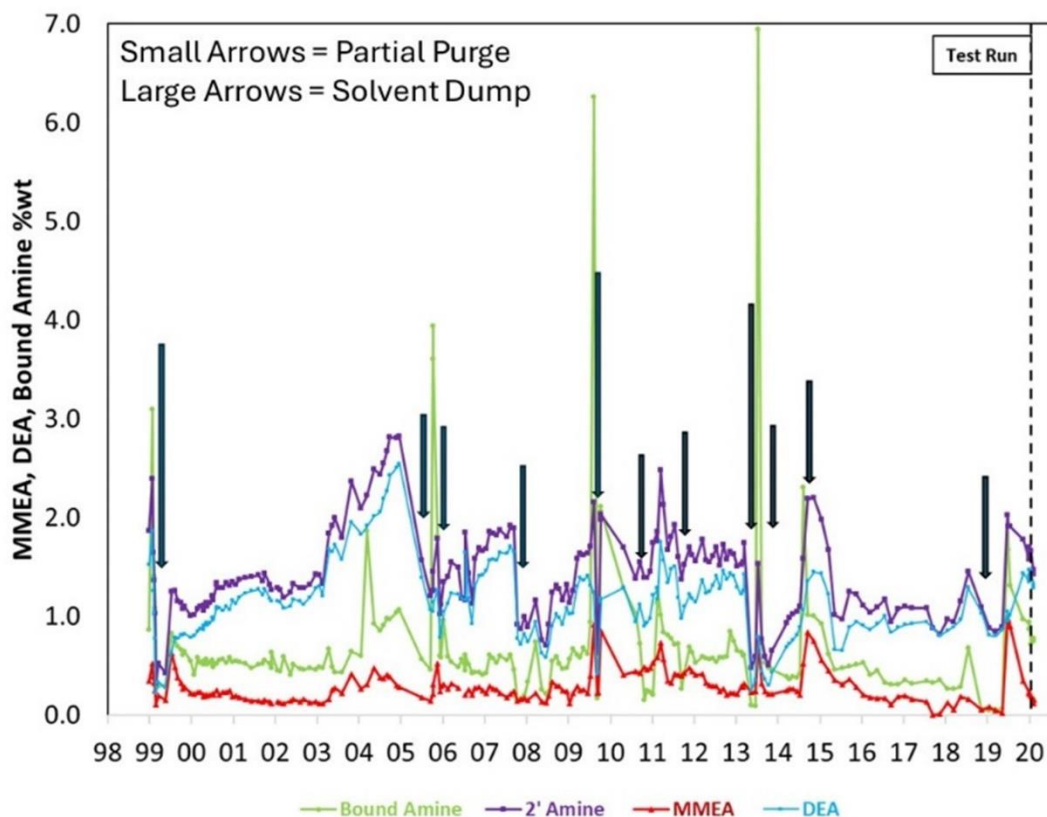
<sup>14</sup> R. Clark and J. Critchfield, "Experiences with Norco's SRU+SCOT Trains", Brimstone Conference, Sept 10-14, 2012

<sup>15</sup> Discussions with Lon Stern, Shell's Refinery Sulfur expert / S3 SRU Train technical lead, 1990-94

#### 4.3.3 S-3 SCOT Solvent Analysis History

One lesson obtained from prior experiences with S-2 SCOT was that SO<sub>2</sub> intrusion events happen, and therefore it was necessary to monitor the solvent composition and proactively manage solvent quality. S-3 SCOT solvent has been analyzed as frequently as monthly, starting in the mid 1990's, totalling over 200 detailed analyses.<sup>16</sup> That analytical history documents a number of significant SO<sub>2</sub>

**Figure 8. Solvent Analysis History, S-3 SCOT**



intrusion events, including full or partial solvent changeouts in response to the larger of those events (Figure 8). And at turnaround, depending on solvent quality, a decision was sometimes justified to replace the solvent so as to start a multi-year run with uncontaminated solvent.

An outcome of the SO<sub>2</sub> events and interventions is that Norco's S-3 SCOT solvent has seen wide variation in composition over the long-term history of operation. Figure 8 shows that history; the solvent has contained varying concentrations of heat stable salts, DEA, and MMEA over time. That fact makes the S-3 SCOT history interesting for the present topic – effect of solvent composition on process performance.

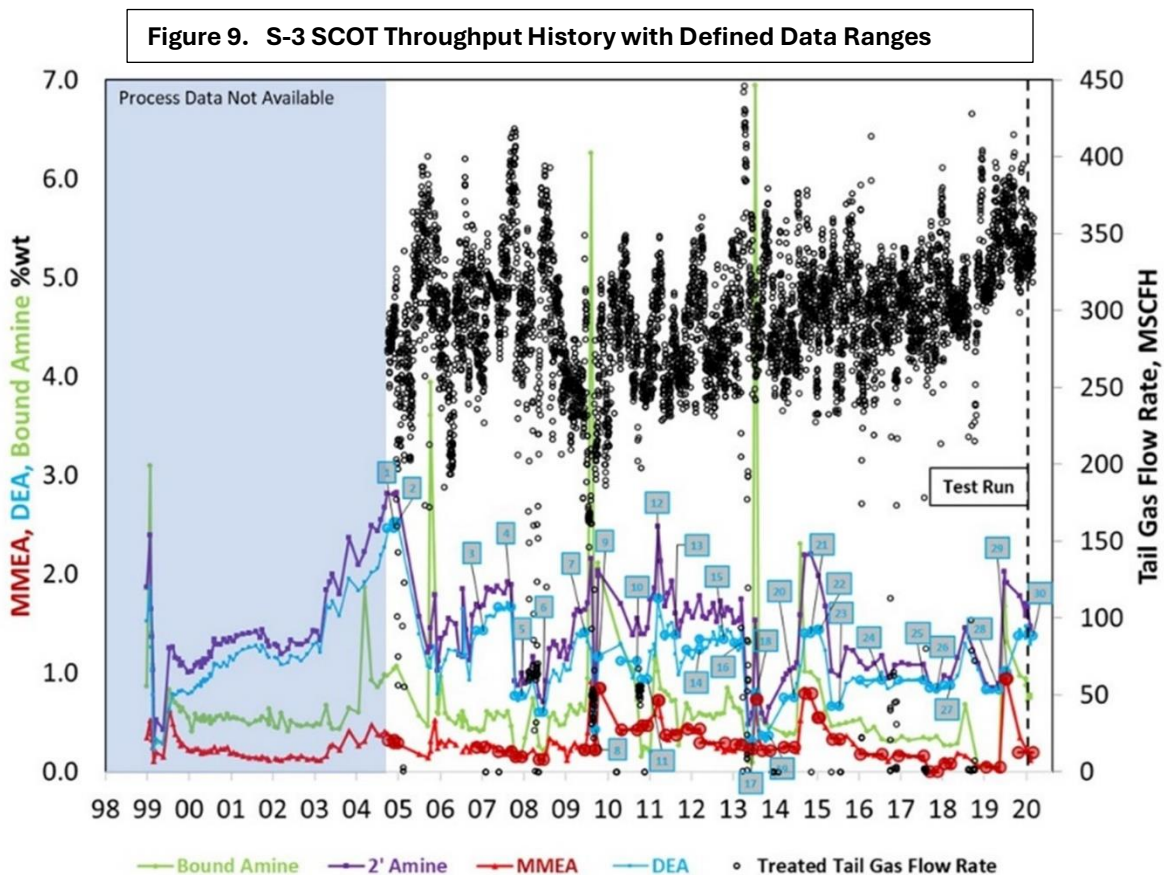
<sup>16</sup> Norco S-3 SCOT is Plant #4 in Table 2

#### 4.3.4 S-3 SCOT Operating Data History

Norco's data system S-3 SCOT retained operating data as far back as 2005 for some variables and only as far back as 2009 to 2012 for others. Those operating data were collected and correlated with the composition history in the plant. To create a consistent basis to compare the data sets, extended periods of relative stable solvent composition were defined – along with some shorter periods where composition was especially interesting. Those defined time periods are shown in Figure 9, and represent an average composition of 51%wt MDEA, 1.1%wt DEA, 0.34%wt MMEA, and 0.85%wt Heat Stable Salts.<sup>17</sup>

##### 4.3.4a Throughput

Throughput in the plant varies substantially. Figure 9 shows that throughput (as indicated by tail gas flowrate), varies by a factor of about 2 over the course of time and even in short periods. Maximum practical throughput has historically been around 400 MSCFH, and throughput has been as low as 200 MSCFH. Minimum rates in the unit are limited by turndown issues, notably with the SCOT unit reheater burner.



<sup>17</sup> Norco's S-3 SCOT operates with higher amine strength than many other SCOT plants. As mentioned in the 2012 Brimstone paper, S-3 SCOT has a history of occasional absorber foaming, which is unusual for a SCOT unit. Norco's operators have found that higher amine strength minimizes foaming episodes in their unit.



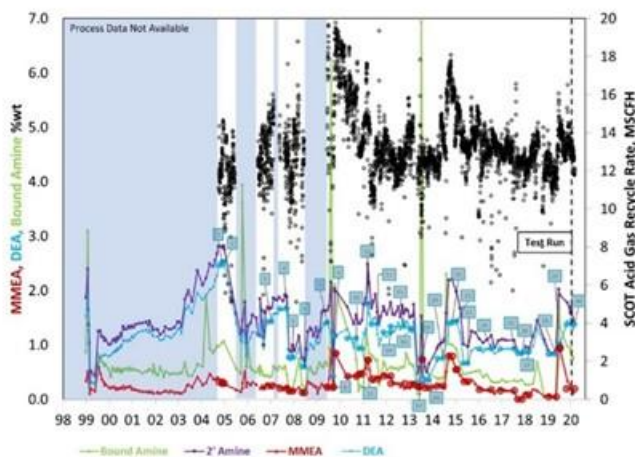
#### 4.3.4b Recycle Rate

The recycle of SCOT acid gas indicates something about CO<sub>2</sub> slip: If more CO<sub>2</sub> is removed from the tail gas, that CO<sub>2</sub> will recycle to the front end of the Claus unit with the SCOT acid gas (Recycle Rate). S-3 has a flow meter on that stream; values of Recycle Rate are available going back to 2005. Recycle Rates have varied in normal operation from values as low as 10-11 MSCFH to peak values of 18+ (Figure 10).

#### 4.3.4c Turndown Effect on Recycle Rate

Turndown in selective amine applications is a factor in CO<sub>2</sub> slip; increasing CO<sub>2</sub> removal occurs with increased holdup on trays. Also in S-3, the SRU Acid Gas composition is known to change with turndown. Since the defined data ranges based on solvent composition correspond to different ranges of throughput, consistency in data analysis requires removing bias from turndown effects from the evaluation. For this work, turndown effects were empirically removed by comparing recycle rates at fixed throughput: 280 MSCFH was chosen as the value most common to the data sets. Figure 11 provides an example of turndown trends in different data sets.

Figure 10. S-3 SCOT Recycle Rate



#### 4.3.4d Stack SO<sub>2</sub>

Stack SO<sub>2</sub> data are available back to 2009. SO<sub>2</sub> values are consistently below the 250 ppm SO<sub>2</sub> permit limit for units such as this (Appendix E).

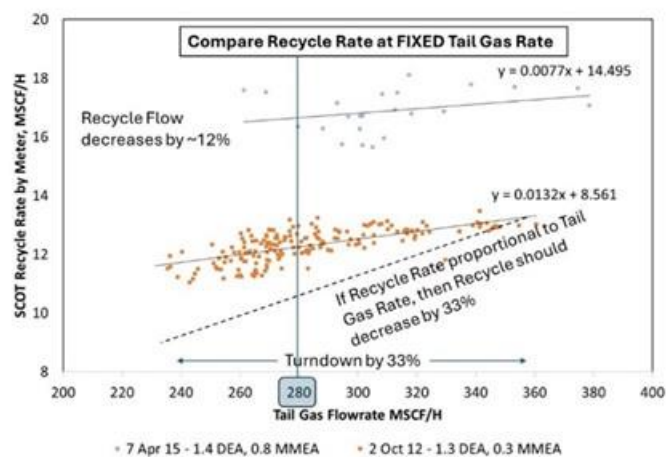
#### 4.3.4e Reboiler Steam

Data for steam supplied to the reboiler are available back to 2005 (Appendix E). Steam rates in this unit are especially low, however deep regeneration is often obtained with low steam rates. The operators adjust steam rate in order to manage lean solvent sulfide concentration within boundaries established with Shell's corrosion control guidance.

#### 4.3.4f Lean Solvent H<sub>2</sub>S

Lean solvent H<sub>2</sub>S (or rather, sulfide in lean solvent) is measured locally, and rapidly, with a silver nitrate method. Experience shows that local approach is more trustworthy than results obtained

Figure 11. Recycle at Turndown: 2 Compositions



from offsite analysis, which often involves significant time elapsed. Sulfide history is available back to 2012 (Appendix E).

#### 4.3.4g Differential Pressure

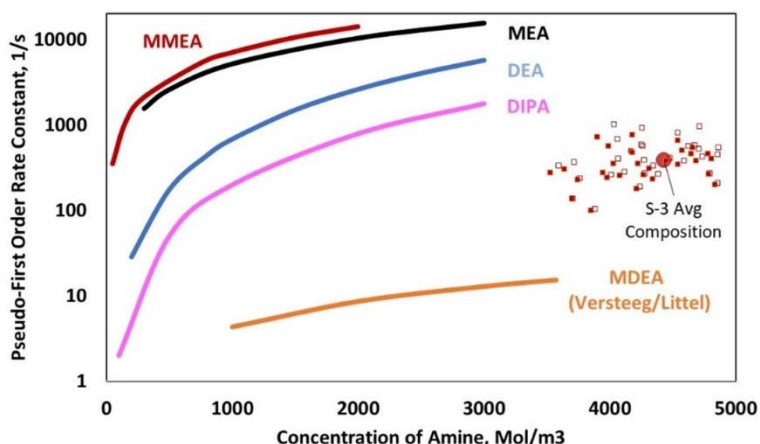
Differential pressure data are available back to 2005, but normalization prior to 2011 gave artificially high train DP. Those earlier values are not considered. DP is taken from Claus front end pressure, and so represents the combined Claus+SCOT train. DP is typically stable in the unit except when specific problems develop, such as SCOT Quench fouling (Appendix E).

#### 4.3.5 Connecting Operating and Analytical Data

##### 4.3.5a Rate Constants for Each Composition

All the rate constants calculated for the 24 plant average compositions were intermediate between those of MDEA and DIPA. The same is the case for the rate constants corresponding to the S-3 SCOT MDEA data periods. Those data periods also include compositions containing peak concentration of 2' amines. The closed points in Figure 12 are rate constants calculated including the effect of neutralization; the open points do not consider that. On average, Norco's solvent composition yields a rate constant that is 21X than that of pure MDEA.

Figure 12. Norco S-3 Data Period – Rate Constants



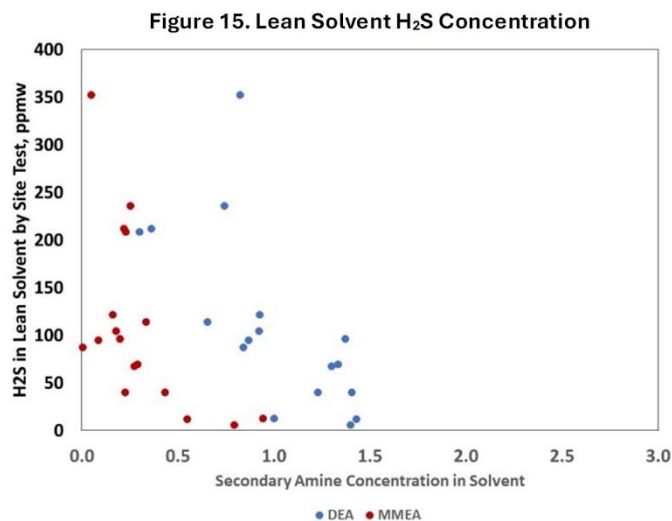
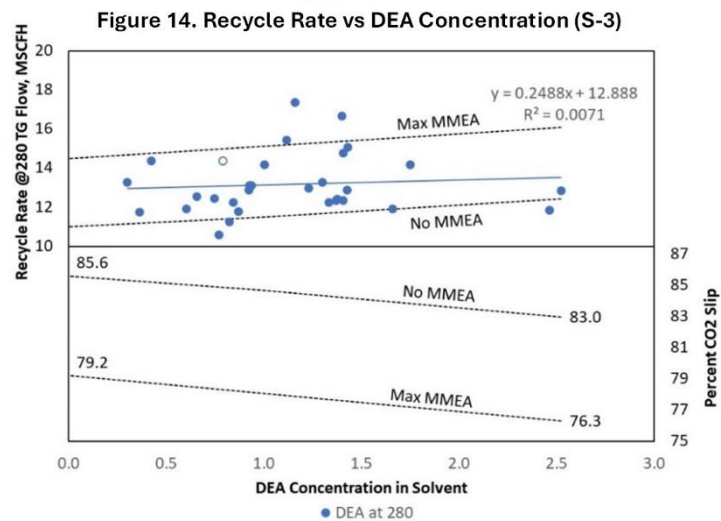
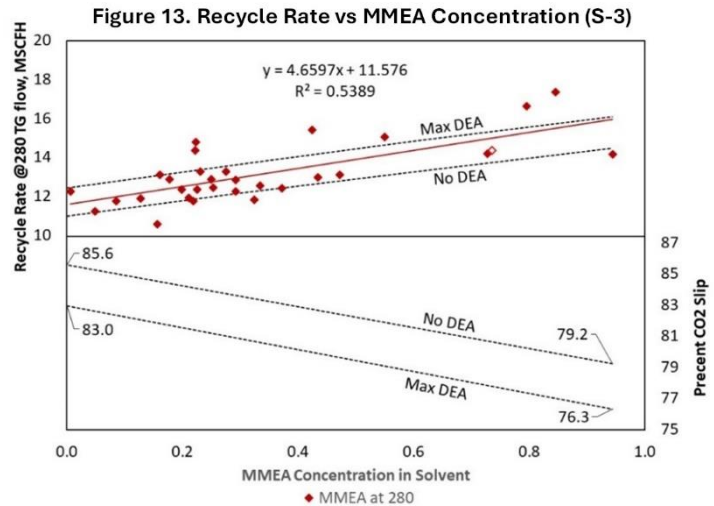
#### 4.3.5b Impact on Acid Gas Recycle Rate

There is a correlation between Recycle Rate and the concentration of MMEA in the solvent (Figure 13). At maximum MMEA concentration, the recycle rate increases about 40%. The average value of MMEA results in an increase of about 15%. Simulated trends with ProMax® are in very good agreement with plant trend.<sup>18</sup>

Figure 14 shows that increasing DEA in the solvent does not result in obvious trends in the Recycle Rate. Simulation predicts a smaller effect than with MMEA: the maximum value of DEA would be expected to increase the recycle rate by about 20%; that would be smaller than the noise in the data.

The Figures show the recycle rate corresponding to a fixed value of unit throughput (280 MSCFH) in order to eliminate potential bias in the correlation from turndown effects.

MMEA reacts much more quickly with CO<sub>2</sub> than DEA does. The fact that Recycle Rate correlates with MMEA concentration makes sense; mole-for-mole, MMEA is a more powerful accelerator of CO<sub>2</sub> reaction.



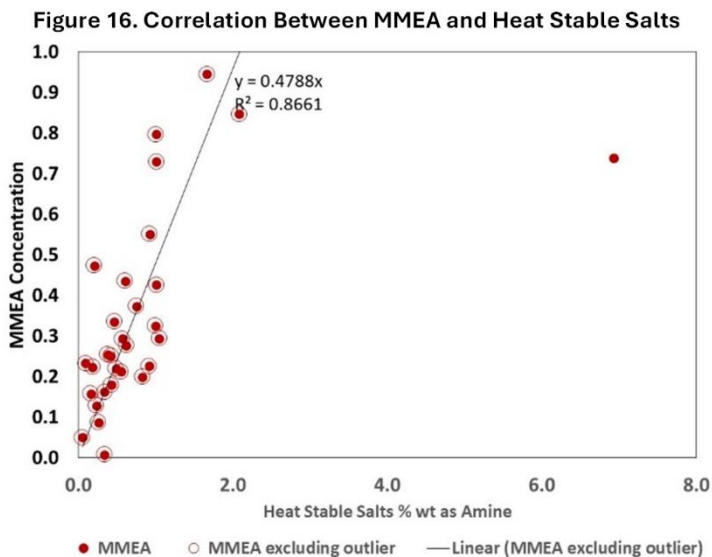
<sup>18</sup> ProMax® is a trademark of Bryan Research & Engineering, LLC



#### 4.3.5c Lean Solvent H<sub>2</sub>S Concentration

There is a clear effect of buildup of MMEA on depth of regeneration of H<sub>2</sub>S: deeper stripping occurs at higher concentration of MMEA (Figure 15). This is contrary to what one might expect; MMEA is a stronger amine than MDEA, and so the MMEA- H<sub>2</sub>S salt would take more energy to reverse.

In the data sets, there is a strong correlation between MMEA concentration and the concentration of heat stable salts (Figure 16). Buildup of heat stable salts improves the depth of regeneration; likely that is the governing effect.



#### 4.3.5e Other Process Variables

A number of other process variables were considered for effect of 2' amine concentration on unit performance.

The following process variables displayed no obvious correlation with 2' amine concentration in the solvent:

- SO<sub>2</sub> in the Incinerator Stack
- Claus+SCOT Train Differential Pressure
- Reboiler Steam
- Lean Solvent CO<sub>2</sub> Concentration
- Solvent Circulation<sup>19</sup>

For brevity, Figures presenting most of those data are in Appendix F.

## 5. How Does Higher Reaction Rate Affect CO<sub>2</sub> Slip?

An increase in reaction rate constant of 18X or 21X compared to pure MDEA may seem to be very substantial, but how that increase translates into CO<sub>2</sub> absorption rate is complex. When reaction rates are very slow, reaction does little to accelerate CO<sub>2</sub> absorption. A slow reaction may occur as CO<sub>2</sub>-saturated solvent sits for a relatively long time (for instance, on a tray) with some small contribution to CO<sub>2</sub> absorption. In that range of slow reaction rates, relatively large changes in rate constant have minor effect on the overall amount of CO<sub>2</sub> slip.

<sup>19</sup> Solvent circulation is manually controlled at a value close to the design value.

When reactions become very fast, the reaction will start to occur in the mass transfer boundary layer. At that point, the speed of reaction has a strong effect on CO<sub>2</sub> slip and changes in the speed of reaction make a big difference.

Figure 17 shows the results of ProMax simulation employing Norco SCOT conditions, and using various amines with very different rate constants. Hypothetically converting a SCOT plant from pure MDEA to other amines changes the predicted CO<sub>2</sub> slip. CO<sub>2</sub> removal rates increase with reaction rate constant, but in a nuanced manner.

Moving from a very slow reacting amine like MDEA to an amine that reacts 10 times faster (such as DEEA)<sup>20</sup> changes the CO<sub>2</sub> slip only a small amount. For this set of conditions, DEEA still behaves as slow-reacting amine. Changing DEEA to DIPA, which reacts 170 times faster than DEEA, decreases slip a lot more, but slip is still about 74%.

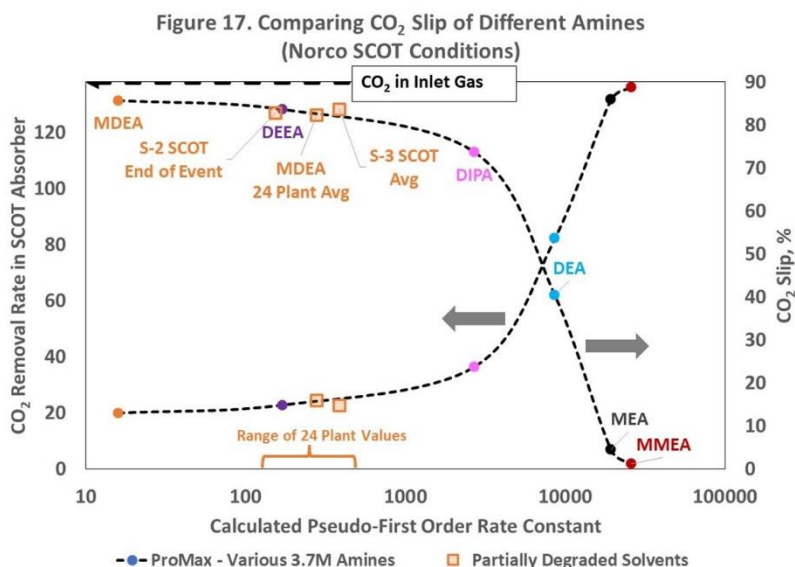


Table 4. Rate of Change of CO <sub>2</sub> Removal with Increasing Reaction Rate						
Amine Swap	Starting Rate Constant	Rate Constant Increase	SQRT Rate Constant Increase	CO <sub>2</sub> Removal Rate Increase	Removal Rate Increase / Rate Const Increase	Removal Rate Increase / SQRT(Rate Const Increase)
MDEA → DEEA	16	11X	3.3X	1.1X	0.1	0.34
DEEA → DIPA	170	16X	4.0X	1.6X	0.1	0.40
DIPA → DEA	2700	3.2X	1.8X	2.3X	0.72	1.3

Above the rate constant of DIPA (in the 1000's), CO<sub>2</sub> slip is strongly affected by reaction rate; CO<sub>2</sub> slip rapidly decreases when DEA is simulated. DEA only slips less than half the tail gas CO<sub>2</sub>.<sup>21</sup> MEA and MMEA slip very little CO<sub>2</sub>.

<sup>20</sup> DEEA, Diethylethanolamine, is a high pKa 3' amine studied by Littell (1991) and implemented in ProMax

<sup>21</sup> It is interesting (and gratifying) to see the slip values predicted for DIPA and DEA match up well with those found in the SCOT R&D from the 1960's (Appendix C).

Table 4 presents the ratio of increased removal rate to that of increased rate constant in the simulation of these hypothetical conversions. When fast reaction rates control the performance of an absorber, the rate of absorption is proportional to the square root of the rate constant. That condition corresponds to values in the right-hand column of Table 4 of approximately 1. For rate constants slower than DIPA, those predicted values are much lower than 1, suggesting that reaction rate is not fully controlling the rate of CO<sub>2</sub> absorption.

Changing the simulation from MDEA to the average composition of 24 plant population decreased the predicted CO<sub>2</sub> slip from about 85.6 to 82.3; a relatively small change considering that the rate constant increased by about 18X. For S-3 SCOT, the average composition results in a simulated slip of about 83.5%.

Because the SCOT Absorber operates in a regime where reaction rate doesn't strongly affect absorption rate, increases in rate constant such as those corresponding to the solvent compositions in the Norco SCOT units, and in the population of the 24 Plant solvent systems, have comparatively minor effect on CO<sub>2</sub> slip.

## **6. MMEA Volatility Loss - Is Water Wash in SCOT a Good Idea?**

### **6.1 Estimated Loss Rates**

Considering the volatility of MMEA and the observed trends over time in the S-2 SCOT SO<sub>2</sub> event, volatility losses of MMEA are more pronounced. Simulation was performed with BR&E's ProMax with 1%wt MMEA and 1%wt DEA added to the simulation. At maximum throughput the Norco S-3 SCOT, predicted volatility losses

Table 5. Simulated Amine Losses Due To Volatility

	<u>Vapor Flow, lb/d</u>
MDEA	8
DEA	0.02
MMEA	18

The predicted MMEA loss rate was more than twice that of MDEA, despite MMEA's much lower concentration in the solvent.

In the simulated case, the inventory of the working solvent contains about 24,000 lb MDEA and 480 lb MMEA. At the predicted initial loss rates, it would take about 3 days to lose 10% of the system MMEA and 300 days to lose 10% of the MDEA. The daily loss rate of MMEA is approximately 3-4% of the inventory of MMEA. Of course, as the reservoir of MMEA is depleted from loss, the rate of loss would decline, but the point is clear: MMEA vapor loss from the system is large. Without a way to keep MMEA in solution, in the absence of active degradation of MDEA, very high values of MMEA concentration are not sustained over time.

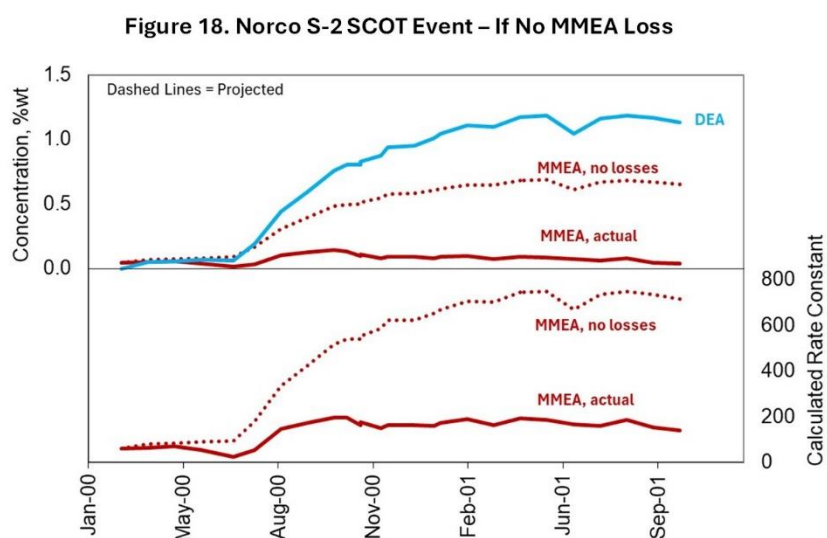
## 6.2 Is Water Wash in SCOT a Good Idea?

Water wash of treated SCOT gas is not common in North America. However water wash is often considered for large applications, sometimes with justification of saving on solvent losses. Experience shows that solvent losses in MDEA-based SCOT application are typically low, despite the low pressure of the application. Simulation of the Norco SCOT units at maximum rates suggests that volatility losses of MDEA would be approximately 10-15% of the working inventory per year.<sup>22</sup>

Figure 18 shows the result of a thought experiment: what might happen to the reactivity of the S-2 SCOT Solvent, if volatility loss of MMEA was suppressed? To illustrate the potential impact, it was assumed that water wash was completely effective, and that MMEA's make-rate continued in proportion to that of DEA during the SO<sub>2</sub> event.

Without MMEA loss, the calculated CO<sub>2</sub> reaction rate constant at the end of the event was five times higher than the value based on the actual composition.

Applications that are focused on achieving the highest values of CO<sub>2</sub> slip should consider that volatility losses of MMEA minimize the impact of degradation of MDEA on CO<sub>2</sub> slip performance.



## 7. Conclusions

The paper presented supporting information on the following conclusions / perspectives:

### 7.1 Partial Degradation is Common

Some perspective has been presented on the ubiquity of the partial degradation of SCOT MDEA into CO<sub>2</sub>-reactive amines. The average composition obtained from monitoring 24 operating tail gas units was presented: the grand average composition was 0.8 % DEA, 0.3% MMEA, and 0.8 % HSS (as amine).

### 7.2 Partially Degraded Solvents React Faster with CO<sub>2</sub>

A large SO<sub>2</sub> intrusion event in Norco's S-2 SCOT unit provided an example of how CO<sub>2</sub>-reactivity changes throughout that sort of event. MDEA degradation into CO<sub>2</sub>-reactive amines increased the calculated rate constant. When the neutralizing effect of heat stable salts was incorporated into the

<sup>22</sup> Entrainment losses were not considered in the simulation.

calculation of reaction rate constant, the changing composition throughout the event resulted in an approximately stable value of rate constant.

Based on calculated rate constants, the average composition of each of 24 solvent inventories shows reaction rates intermediate between those of pure MDEA and DIPA -- the previously successful SCOT solvent prior to MDEA's popularity. On average, the CO<sub>2</sub> rate constant was 18X that of only MDEA.

Norco's S-3 SCOT demonstrated a correlation between CO<sub>2</sub> slip (Acid Gas Recycle) and the concentration of MMEA in partially degraded solution. A similar correlation with DEA was not observed. The average composition in the unit yielded a CO<sub>2</sub> rate constant 21X that of only MDEA.

### **7.3 Large Increase in CO<sub>2</sub> Reaction Rate Doesn't Translate to Large Decrease in CO<sub>2</sub> slip, at SCOT conditions**

The relationship between reaction rate constant and CO<sub>2</sub> slip was demonstrated through simulation with different amines, each having their own very different rate constants. CO<sub>2</sub> slip did not suffer much when rate constants increased in the range of those of MDEA and somewhat degraded MDEA solvents. CO<sub>2</sub> slip was strong function of increasing rate constants when the rate constant was much higher than that of DIPA.

### **7.4 The Effect on Process Variables Other than CO<sub>2</sub> Slip Was Not Observed In S-3's Operating History SCOT ... With The Notable Exception of H<sub>2</sub>S in the Lean Solvent**

H<sub>2</sub>S stripping improved as the concentration of 2' amine increased in the data periods, due to co-occurring heat stable salts.

### **7.5 MMEA Volatility Loss from the Partially Degraded Solvent Limits the Impact of Partial Degradation on CO<sub>2</sub> Slip**

As shown in the S-2 SO<sub>2</sub> event, as MMEA creation slowed and then stopped, MMEA 'weathered' away over time to a value similar to that seen in fresh MDEA prior to the event. The potential for water wash to retain MMEA in solution should be examined if water wash is considered in SCOT application.

## Appendix A. Calculation of Pseudo-First Order Kinetic Constants

Employing the rate expressions of Littel (1991), one can calculate rate constants for the blended compositions from the S-2 SCOT SO<sub>2</sub> ingress event.

### MMEA

For MMEA/water systems, Littel found simple kinetics, first order in MMEA concentration.<sup>23</sup> For blend systems, no special interaction kinetics is considered.

$$k_{app,MMEA} = k_{2,MMEA} * [MMEA]$$

### DEA

For DEA/water system, the reaction is more complex, with DEA reaction order between first and second. Littel found that kinetics of blends of DEA/MDEA displayed synergy, with the rate constant expressed as:<sup>24</sup>

$$k_{app,DEA} = \frac{[DEA]}{1/k_2 + 1/(k_{H_2O}*[H_2O] + k_{DEA}*[DEA] + k_{MDEA}*[MDEA])}$$

Littel demonstrated that all amines could contribute to the complex DEA kinetics, and further that the contribution correlated with the pKa of the amine. Therefore, the potential for MMEA to contribute to DEA reaction was estimated with Littel's Eq. 15:

$$k_{AM} = \exp(1.69 * pKa - 22.7)$$

MMEA at pKa = 9.8 at 298°K

$$k_{MMEA} = 0.0216$$

So for a blend of DEA/MMEA/MDEA the expression becomes:

$$k_{app,DEA'} = \frac{[DEA]}{1/k_2 + 1/(k_{H_2O}*[H_2O] + k_{DEA}*[DEA] + k_{MDEA}*[MDEA] + k_{MMEA}*[MMEA])}$$

### MDEA

MDEA itself has slow reaction with CO<sub>2</sub>, with a rate constant expressed as:

$$k_{app,MDEA} = k_{2,MDEA} * [MDEA]$$

### OVERALL

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<sup>23</sup> Littel, R. J., Selective Carbonyl Sulfide Removal in Acid Gas Treating Processes, Dissertation University of Twente, 1991, Table 1 p 172

<sup>24</sup> Littel, R. J., Selective Carbonyl Sulfide Removal in Acid Gas Treating Processes, Dissertation University of Twente, 1991, Eq 4, p 139

Combining these into a single expression yields a combined reaction rate constant that accounts for CO<sub>2</sub>-reactive amines in MDEA solvent:

$$k_{app,OV} = k_{app,MMEA} + k_{app,DEA} + k_{app,MDEA}$$

The values for rate constants employed in this expression are shown in the Table below, with concentration expressed as mol/m<sup>3</sup>, yielding pseudo-first-order rate constants in units of 1/s:

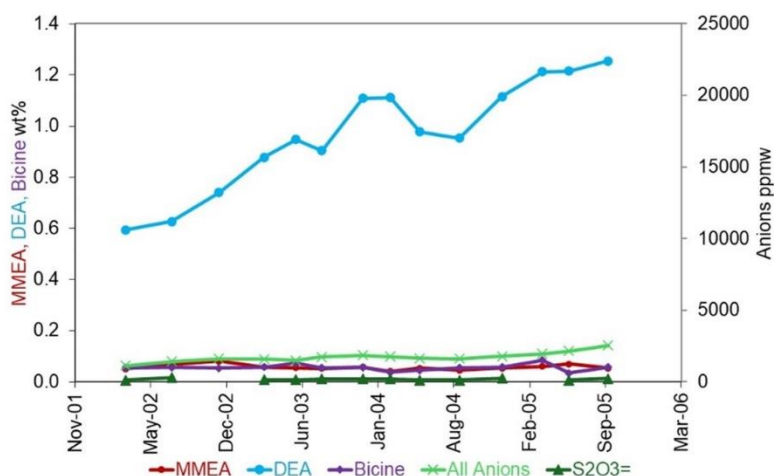
Table A1: Constants used in the calculation of rates at 298°K

	10 <sup>4</sup>	10 <sup>6</sup>	10 <sup>4</sup>	10 <sup>4</sup>	10 <sup>4</sup>	10 <sup>4</sup>
k <sub>2</sub>	k <sub>2,MMEA</sub>	k <sub>H2O</sub>	k <sub>DEA</sub>	k <sub>MDEA</sub>	k <sub>MMEA</sub>	k <sub>2,MDEA</sub>
3.13	7.04	1.68	7.23	3.54	21.6	43

## Appendix B. Degradation with Minor, Chronic SO<sub>2</sub> Ingress

Another Shell-operated SCOT unit (“SCOT Unit #12”) experienced chronic, but minor, ingress of SO<sub>2</sub>. Some degradation of solvent was observed over a long period of operation, without significant solvent replacement. After 3.5 years of operating with minor SO<sub>2</sub> ingress, in which about 100-300 ppmw thiosulfate was observed, the solvent accumulated about +0.6%wt DEA and +1500 ppmw of organic acids. Constant, low concentrations of bicine and MMEA were observed (less than 1000 ppmw) – neither accumulated.

Figure B1. Recycle at Turndown: 2 Compositions



This history is an example of something often seen in SCOT MDEA: DEA may slowly build up over long periods of time, without accompanying accumulation of MMEA. Presumably, with only low rates of formation, MMEA would ‘weather’ over time due to its volatility, and accumulation would not be observed.



## Appendix C. Early-Generation Amines Considered for SCOT Application

### DEA

A successful solvent for CO<sub>2</sub> *removal* applications, DEA is a 2' amine and reacts much slower with CO<sub>2</sub> than MEA does. DEA was investigated in the 1960's research pilot plant and it showed CO<sub>2</sub> slip in the range of 30-50%. That level of slip was considered to be inadequate for SCOT application due to the amount of recycle it would produce.

### DIPA

DIPA, a 2' amine, reacts quickly with CO<sub>2</sub>, but more slowly than DEA does. DIPA was investigated in the pilot plant, and was found to provide slip on the order of 70-80%. That level of slip was considered to be adequate for SCOT application, and DIPA was the original amine applied in commercial SCOT service.

**Table C1. Waterton Primary Treating (DIPA) Data**

Component	Sour Gas	Sales Gas	Acid Gas
CO <sub>2</sub>	4.45	----	17.89
H <sub>2</sub> S	15.93	----	76.94
Apparent CO <sub>2</sub> Slip, %		nil	

In fact, DIPA is also applied to *remove* (not slip) CO<sub>2</sub> in applications such as LNG processing, SMR H<sub>2</sub> synthesis, Gasification and Refinery product treating. DIPA's ability to react with CO<sub>2</sub> is critical in these other applications.

In SCOT application, DIPA's ability to react with CO<sub>2</sub> is limited by design of the process and by operating conditions, making DIPA a successful CO<sub>2</sub> slip solvent, even though the amine is capable of removing CO<sub>2</sub> at other conditions.

**Table C2. Waterton SCOT (DIPA) Test Run Data**

Date	11/29/1989	11/29/1989	11/29/1989
Time	11:44	11:12	10:49
ID	Contactor Inlet	Contactor Outlet	SCOT Acid Gas
H <sub>2</sub>	1.821	1.706	0.000
Ar	0.980	1.020	0.000
N <sub>2</sub>	81.962	85.261	4.850
CO	0.018	0.031	0.000
CO <sub>2</sub>	14.000	11.905	63.504
H <sub>2</sub> S	1.219	0.063	31.646
COS	0.000	0.001	0.000
Apparent CO <sub>2</sub> Slip, %		85.0	
H <sub>2</sub> S Leak, ppmv		630	

At the site of the first world-scale application of SCOT in the Waterton Gas Plant, a separate solvent inventory of DIPA *removed* CO<sub>2</sub> in the primary treating system to ppm-level in the treated gas. Table C1 shows data from that primary

treater, ca. 1973.<sup>25</sup> Yet in the SCOT unit at Waterton, DIPA *slipped* CO<sub>2</sub> effectively. Table C2 shows example plant test data from Waterton's SCOT absorber, where CO<sub>2</sub> slip was approximately 85%.<sup>26</sup>

This apparent contradiction demonstrates an important fact about selective removal of H<sub>2</sub>S in the presence of CO<sub>2</sub>: the *potential* of the amine to react with CO<sub>2</sub> *is not everything*... CO<sub>2</sub> slip can be enhanced by *limiting the opportunity* of the amine to react. In SCOT, contactor design and operating conditions exploit this fact, such that even a some-what CO<sub>2</sub>-reactive amine like DIPA can be made to successfully slip a large majority of the CO<sub>2</sub> in the process.

## MDEA

MDEA became widely available commercially in the early 1980's, and it began to be applied in SCOT service. MDEA is a 3' amine: it is incapable of direct reaction with CO<sub>2</sub>. As with all alkaline amines, MDEA enhances the rate of the very slow CO<sub>2</sub> reaction with water. That enhanced rate is still much slower than the reaction rates seen with CO<sub>2</sub>-reactive 2' amines like DEA.

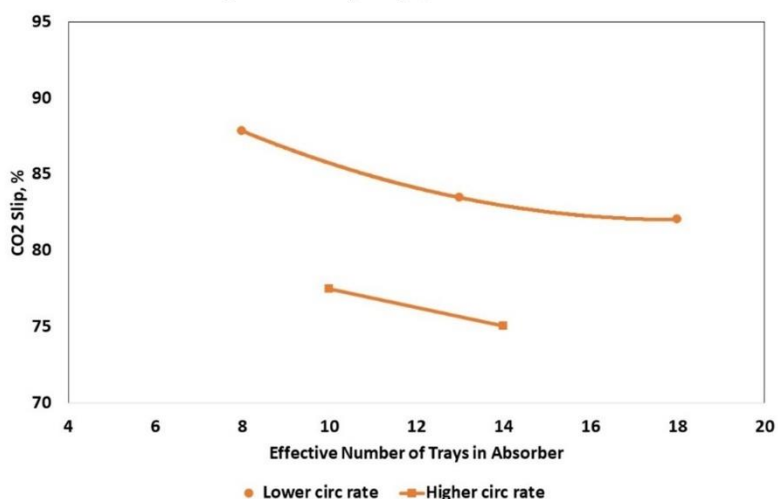
MDEA has been extremely successful in SCOT application, with hundreds of deployments globally, including conversions of DIPA-based units to MDEA service. Early pilot plant testing of MDEA as an improvement over DIPA demonstrated that MDEA, despite being a less-alkaline amine, could achieve deep treating of H<sub>2</sub>S while slipping somewhat more CO<sub>2</sub>.

Figure C1 shows example data from early pilot plant campaigns conducted by Shell, where important lessons were learned for SCOT units employing MDEA.<sup>27</sup> In a pilot plant with high-efficiency trays, fewer trays improved CO<sub>2</sub> slip as did lower circulation rates, and a short absorber approached 90% slip.

It was learned that conditions matter: the number of trays applied in the contactor, the depth of regeneration in the stripper, and the solvent circulation rate all were important variables.

A multi-variable design optimization methodology for MDEA-based SCOT units evolved, originally based on calculation tools such as nomographs, and later, spreadsheets. In the early 1980's,

Figure C1. Pilot Plant Data, CO<sub>2</sub> Slip with MDEA  
High Efficiency Trays, Constant Gas Rate



<sup>25</sup> Hocking, Drake "Air Quality Management for Natural Gas Production in Alberta: Background to the Problem and an Application to the Paretian Decision Model, Canadian Forestry Service, Information Report NOR-X-69, March 1973

<sup>26</sup> Shell internal performance testing

<sup>27</sup> Internal Shell Research Report ca 1988

computer-based design programs were created internal to Shell that combined vapor-liquid and ionic equilibria, mass transfer models, equipment features, and reaction kinetics. Those tools allowed the process designer to exploit the slow reaction kinetics of MDEA in designs that easily achieved the 250-ppm SO<sub>2</sub> emission limit typical of USA applications yet still provided high values of CO<sub>2</sub> slip. External to Shell, the development of commercial simulation tools such as TSWEET, and later ProMax, provided the industry with tools to troubleshoot and optimize Claus+SCOT train performance.

## Appendix D. Past Publication, Conceptual Scheme for MDEA Degradation, and Academic Information on Purity/Blends

### 2' Amines and Organic Acids

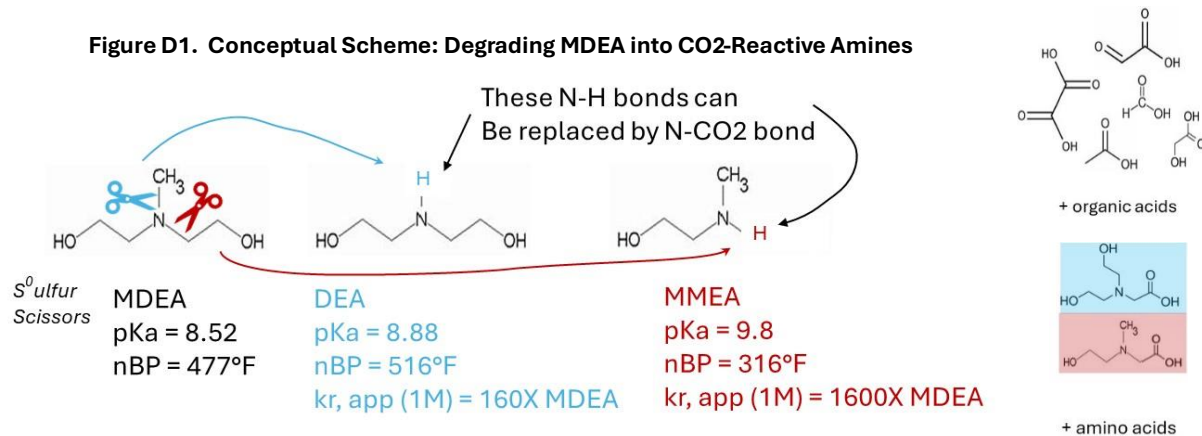
An article published in 1999 disclosed results of solvent analysis from commercial applications of MDEA-based tail gas treating solvents.<sup>28</sup> By monitoring the composition of solvent over time, the authors demonstrated that following a large intrusion of SO<sub>2</sub> into the solvent, ‘fragments’ of MDEA accumulate. Those fragments included organic acids, amino acids, and CO<sub>2</sub>-reactive 2' amines. The mechanism of degradation was not disclosed in the article, but the evidence of accumulation of degradation products was clear. After SO<sub>2</sub> intruded into SCOT solvent, operating with that contaminated solvent for a period of time resulted the buildup of degradation products.

### Comments from Vail Sulfur Symposium 2020

The fact that MDEA can partially degrade in SCOT service into CO<sub>2</sub>-reactive amines is now well-recognized. In the 2020 Vail Sulfur Symposium, one industry expert stated that the presence of CO<sub>2</sub>-reactive amines in the MDEA solvent harms CO<sub>2</sub> slip to the point of near-inoperability. Specific harmful effects were cited as: inadequate H<sub>2</sub>S treating, overwhelmed reboiler capacity, and excessive buildup of CO<sub>2</sub> in the recycle. Considering that partial MDEA degradation has been reported as common in operating tail gas unit solvents, some question exists as to how impactful that partial degradation typically is in practice.

### Conceptual Scheme of MDEA Degrading into CO<sub>2</sub>-Reactive 2' Amines

Figure D1 shows conceptually how severing the N-C bonds in MDEA – with hypothetical “Sulfur Scissors” chopping off an alkyl arm of MDEA – resulting in the two CO<sub>2</sub>-reactive amines, DEA and MMEA. The intention is not to describe the actual chemical mechanisms involved; but instead to bring familiarity to the degradation products which accumulate.



<sup>28</sup> Critchfield, J., and J. Jenkins, “Evidence of MDEA degradation in tail gas treating plants”, Petroleum Technology Quarterly, 2Q 1999

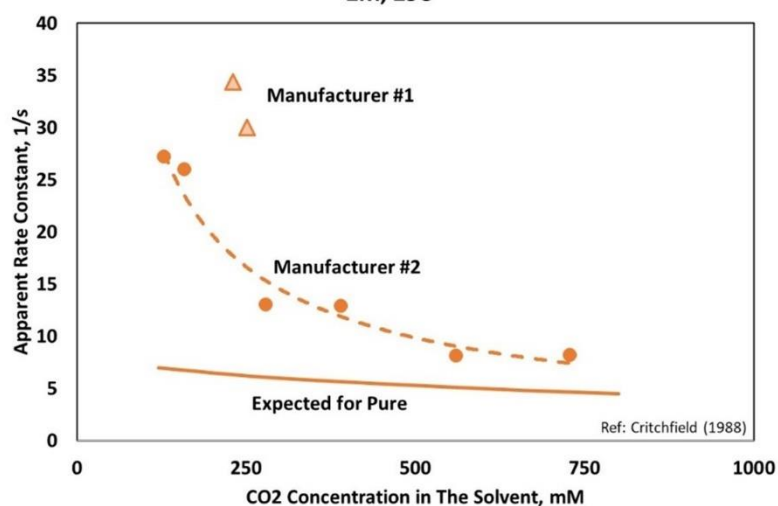
DEA and MMEA are stronger bases than MDEA. DEA is less volatile, and MMEA is much more volatile than MDEA. Both amines are very fast-reacting towards CO<sub>2</sub>, with MMEA being about 10X faster than DEA.

In addition to the 2' amines, organic acids result from the lost “arms” of MDEA. Aminoacids are also produced, analogous to adding an oxidized ethanol group to the DEA and MMEA structures. These aminoacids are not discussed further in this paper as their effect on reaction rates with CO<sub>2</sub> is not significant.

Academic research in the 1980's documented that blends of MDEA and CO<sub>2</sub>-reactive amines such as DEA or MEA accelerated CO<sub>2</sub> reaction rates in the blends. In 1986, it was disclosed that research-purity MDEA contained small amounts of CO<sub>2</sub>-reactive amines, and that the presence of differing amounts of reactive amines could explain some variability between researchers in measured MDEA kinetic constants.<sup>29</sup> In 1988, commercial-purity MDEA from different sources

was demonstrated to display different rates of reaction with CO<sub>2</sub>.<sup>30</sup> Those rates were much higher than expected for pure MDEA; further it was demonstrated loading of the solvent decreased the effect of CO<sub>2</sub>-reactive impurities on reaction rate (Figure D2).

**Figure D2. Rate Constants of Commercial Purity MDEA  
2M, 25C**



### CO<sub>2</sub> Reaction Rates with 2' Amines

Buildup of 2' amines in SCOT solvent increases CO<sub>2</sub> reaction rate constants. Littell (1991)<sup>31</sup> measured reaction kinetics of single amines and of a number of amine blends, including DEA/MDEA blends. Figure D3 shows pseudo-first order kinetic constants for various amines from that work.<sup>32</sup>

<sup>29</sup> G. F. Versteeg “Mass Transfer and Chemical Reaction Kinetics in Acid Gas Treating Processes”, Table 1, p 135

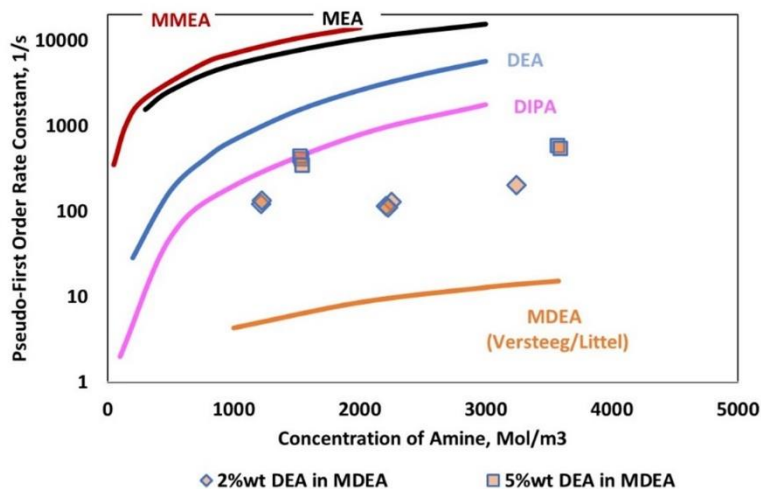
<sup>30</sup> Critchfield, J. E., “CO<sub>2</sub> Absorption/Desorption in Methyl-diethanolamine Solutions Promoted with Monoethanolamine and Diethanolamine: Mass Transfer and Reaction Kinetics, PhD Dissertation University of Texas at Austin, 1988

<sup>31</sup> Littell, R. J., Selective Carbonyl Sulfide Removal in Acid Gas Treating Processes, Dissertation University of Twente, 1991

<sup>32</sup> The MDEA rate constants are Littell’s reanalysis of Versteeg’s results

DEA/MDEA blends containing 2 and 5%wt DEA react an order of magnitude faster than MDEA itself reacts. At typical operating strength of 3000-4000 Mol/m<sup>3</sup> (roughly, 35-50%wt, as MDEA), these accelerated blends still react much slower than DIPA reacts. That comparison provides perspective: even degraded MDEA solutions might still perform better (slip more CO<sub>2</sub>) than DIPA – the original solvent in SCOT application.

Figure D3. Pseudo-First Order Rate Constants, 25°C



MMEA is a much faster-reacting 2' amine than DEA is, and so MMEA has greater potential to accelerate blends with MDEA. A recent simulation case study employed an assumed composition of MMEA and DEA to demonstrate that small amounts of 2' amines could affect CO<sub>2</sub> slip in a tail gas treating unit, and that MMEA was more powerful than DEA in that regard.<sup>33</sup>

The 1999 PTQ publication demonstrated a qualitative difference in the behavior of DEA and MMEA as MDEA degrades: It was noted that big SO<sub>2</sub> events, with fast degradation, MMEA accumulates.<sup>34</sup> But slow degradation rates resulted in primarily DEA, with little or no MMEA accumulating.<sup>35</sup>

<sup>33</sup> The Contactor™, by Optimized Gas Treating, Inc, Volume 18, Issue 5, May 2024

<sup>34</sup> Critchfield, J., and J. Jenkins, "Evidence of MDEA degradation in tail gas treating plants", Petroleum Technology Quarterly, 2Q 1999.

<sup>35</sup> An example of this slow degradation is shown in Appendix B

## Appendix E. Additional Figures showing Norco S-3 SCOT Historical Operating Data

Figure E1. SO<sub>2</sub> in Stack

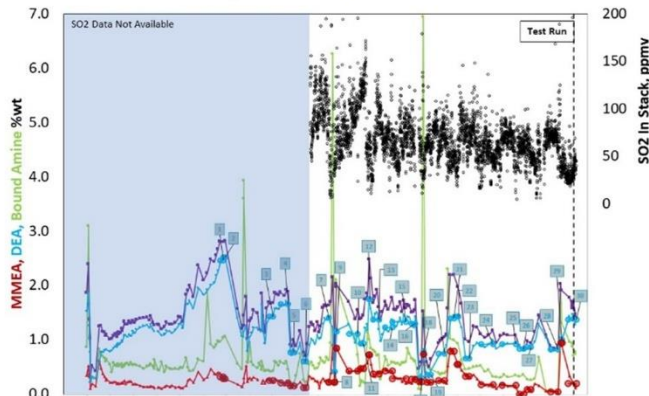


Figure E2. Steam Ratio

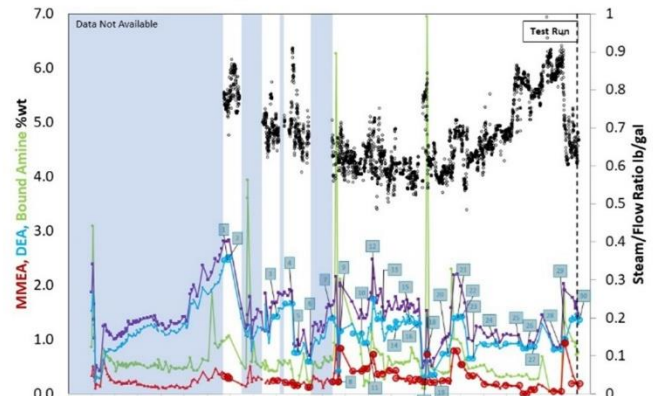


Figure E3. Lean Sulfide

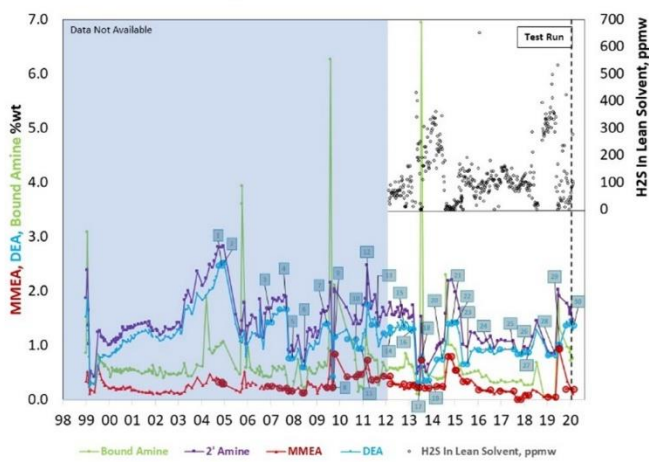
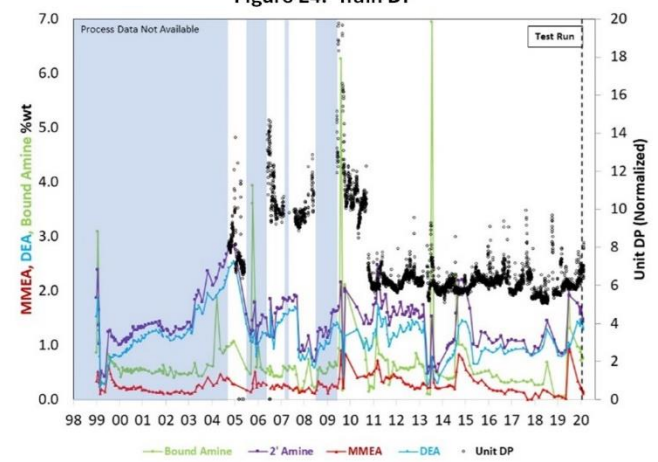


Figure E4. Train DP



## Appendix F. S-3 SCOT Process Data – 2' Amine Effect – Other Variables

There is no obvious effect of building up the concentration of MMEA or DEA on the following variables:

*SO<sub>2</sub> in the Incinerator Stack (Figure F1)*

Buildup of MMEA or DEA in the solvent does not show an effect on SO<sub>2</sub> performance.

*Claus+SCOT Train Differential Pressure (Figure F2)*

Train differential pressure does not correlate with buildup of MMEA or DEA.

*Steam (Figure F3)*

There is no obvious change in steam rate based on 2' amine concentration in the solvent.

*Lean solvent CO<sub>2</sub> concentration (Figure F4)*

There is no obvious connection between the amount of 2' amines in the solvent and the measured concentration of CO<sub>2</sub> in the lean solvent. However, the reported values are very low, and near detection-limit for the method used. What can be said: building 2' amines did not increase the amount of CO<sub>2</sub> in the lean solvent significantly.



Figure F1. SO<sub>2</sub> In Incinerator Stack

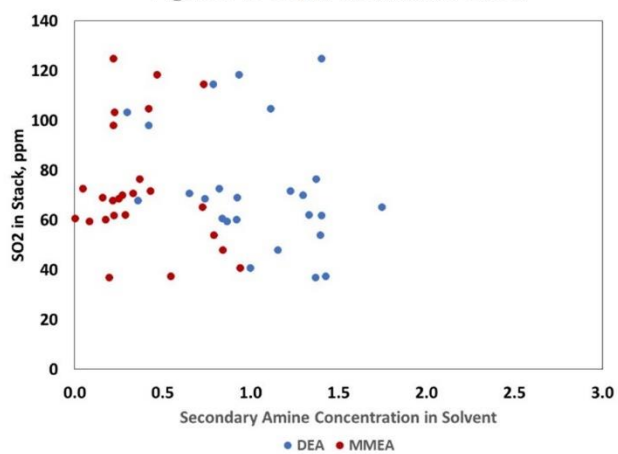


Figure F2. Differential Pressure, Claus+SCOT

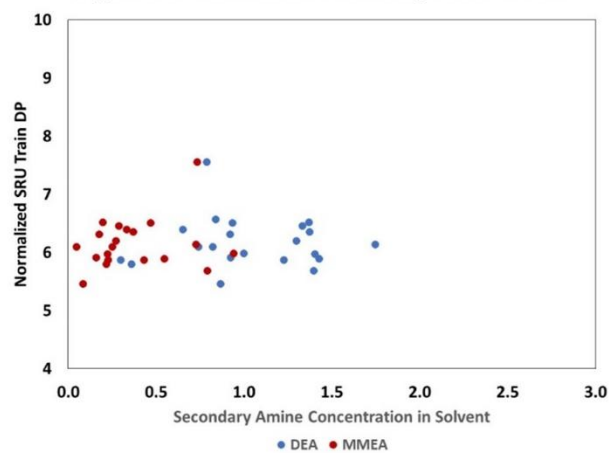


Figure F3. Steam Ratio

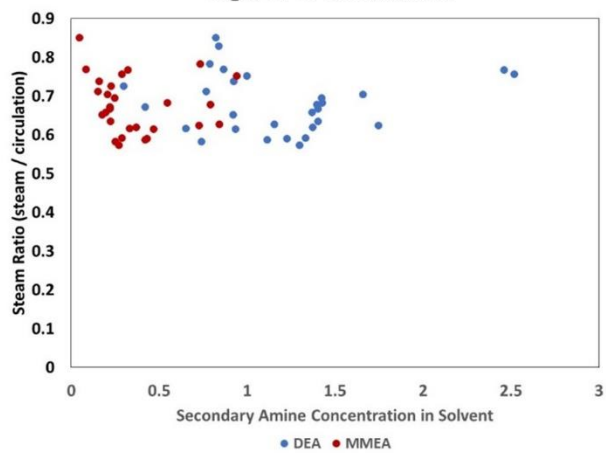
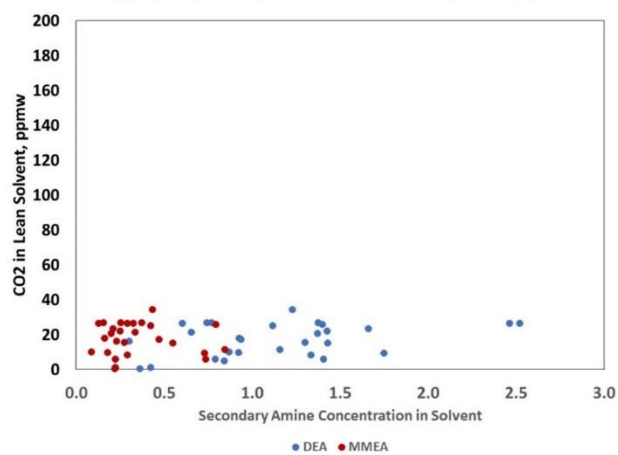


Figure F4. Lean Solvent CO<sub>2</sub> Concentration



## Appendix G. Cautionary Statement

The companies in which Shell plc directly and indirectly owns investments are separate legal entities. In this content “Shell”, “Shell Group” and “Group” are sometimes used for convenience where references are made to Shell plc and its subsidiaries in general.

Likewise, the words “we”, “us” and “our” are also used to refer to Shell plc and its subsidiaries in general or to those who work for them.

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