Heat Stable Salt Accumulation and Solvent Degradation in a Pilot-Scale CO₂ Capture Process Using Coal Combustion Flue Gas

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ABSTRACT

Solvent degradation is a major factor in the cost associated with carbon capture using aqueous amine solutions. Heat stable salts (HSS) from oxidative amine degradation and acidic flue gas components, including SO₂, NOₓ and HCl can accumulate in amine solvents and lead to corrosion, extra energy requirements and reduced capture efficiency. Accurate and reliable quantitation of HSS concentration is essential to monitor solvent degradation and corrosion potential inside the system. Two separate amine solvents were tested in a 0.1 MWth carbon capture pilot plant. 30% Monoethanolamine (MEA) was used as a baseline solvent and compared to a developed amine solvent, CAER-B2. Six HSS were identified in each solvent and the accumulation rates were determined. The observed HSS build-up was similar in magnitude to other published amine based CO₂ capture plant data. The 30% MEA solvent accumulates HSS at a higher rate (48 ppm/hr vs. 22 ppm/hr) as the CAER-B2 which can be attributed to higher input SO₂ levels during the solvent test campaign. Corrosion benchmark levels of HSS were exceeded for CAER-B2 and 30% MEA within a few days of normal operation.

Keywords: Heat stable salts; Carbon capture; Corrosion; Amine degradation; Flue gas contaminants.

INTRODUCTION

Solvent degradation is a major factor in the cost associated with carbon capture using amine solvents. Amine solvents can degrade through oxidation, thermal degradation and through reactions with flue gas components to form heat stable salts (HSS) (Salizar et al., 2003). HSS accumulation can lead to extra energy requirements for reclaiming because the bound amine portion of the HSS cannot be regenerated under stripper conditions (Gao et al., 2011; Sexton and Rochelle, 2011; Supap et al., 2011).

Some HSS are formed from soluble acidic flue gases, including SO₂, NOₓ and HCl which are important flue gas pollutants from coal power plants (Zhou et al., 2012). Amine oxidative degradation can yield other anion HSS species including acetate, formate, glycolate and oxalate. Oxidative degradation products can contribute to amine losses, impact system economics, create environmental impacts and contribute to further amine solvent degradation (Sexton and Rochelle, 2011; Supap et al., 2011). HSS accumulation can also have a significant impact on process operations such as causing foaming in the absorber and frequent filter exchange (Verma and Verma, 2009). Finally, HSS buildup can increase the corrosion behavior of amine solvents in carbon capture operations due to the active oxidant function groups present (Nainar and Veawab, 2009).

Corrosion is a specific area of focus due to the additional operational and maintenance costs resulting from replacement of process components, operational downtime and decreased performance (Tanthapanichakoon and Veawab, 2006). Corrosion is a problem at all amine carbon capture operations at locations including the absorber, stripper, reboiler and at pump and valve locations where temperature are high and acidic gases are present (Soosaipakaram and Veawab, 2008). Several HSS anion species have been directly related to increased corrosion in carbon steel in amine solvent systems. Specifically, soluble SO₂, as sulfite (SO₃⁻), sulfate (SO₄²⁻) and thiosulfate (S₂O₃²⁻) from flue gas, have been shown to increase corrosion (Kladkaew et al., 2009; Nainar and Veawab, 2009; Gao et al., 2012). Other HSS from oxidative degradation of amines including oxalate, formate, glycolate and acetate also contribute to higher carbon steel corrosion rates (Tanthapanichakoon and Veawab, 2006). The corrosion rates increase with higher concentrations of all of the HSS species.

Accurate and reliable quantitation of HSS concentration is essential to monitor solvent degradation and corrosion potential in carbon capture operations and when developing and evaluating new amine solvents. In this work, the deployment of an accurate and reproducible ion...
chromatography (IC) analysis method to quantify 10 potential HSS that may be present in amine carbon capture solvents is reported. This method was evaluated during lab-scale solvent development then used to analyze two separate amine solvents during test campaigns in a 0.1 MWth carbon capture pilot plant with coal-derived flue gas generator. 30% MEA was used as a baseline solvent and compared to a proprietary amine solvent, CAER-B2, developed at University of Kentucky. Six HSS were identified in each solvent during pilot operation and the accumulation rates were determined and compared to previously published reports.

EXPERIMENTAL METHODS

CAER Pilot Plant and Operating Conditions

CAER operates a 0.1 MWth pilot-scale CO₂ capture facility with a coal-fired flue gas generator. The CO₂ capture facility consists of a 7.3 m (24 ft) tall by 10 cm (4") ID scrubber with a 25.4 cm (10") ID solvent recovery column downstream, a 4.3 m (14-ft) tall stainless steel stripper, and a condenser for solvent recovery in the stripper exhaust. The flue gas generator (FGG) is a coal combustion system designed to deliver flue gas to the CO₂ capture pilot plant with a thermal design capacity of 200,000 Btu/hr. Flue gas exiting the combustor enters a high-temperature cyclone to remove particulate matter. After the cyclone, the SO₂ concentration is lowered in the flue gas with a wet flue gas desulfurization (WFGD) unit. The average pilot plant operating conditions are outlined in Table 1 and in Frimpong et al. (2012). Two different solvent campaigns were conducted with 30% (wt) MEA and CAER-B2 solvent. Both solvents did not contain any oxidation or corrosion inhibitors and were not reclaimed during the test campaigns.

Anion Chromatography

Ion chromatography was performed using a Dionex ICS-3000 system (Dionex-ThermoScientific, Sunnyvale, CA) with an AS autosampler. The IC system has separate pumps, suppressors and conductivity detectors for simultaneous anion and cation analysis. The anion system consisted of an ASRS 300 suppressor, EGC III KOH (potassium hydroxide) eluent generator, IonPac AS15 analytical column and an AG15 guard column operated at 30°C. A CRD-200 Carbonate Removal Device ( Dionex) was installed on the anion system to reduce the amount of dissolved carbon dioxide in the samples. The anions were separated with an eluent gradient with an initial KOH concentration of 2 mM and increased to 5 mM at 4 minutes. This was followed by an increase to 30 mM at 24 minutes and then increased to 45 mM at 32 minutes and held for 4 minutes. The conductivity detector was maintained at 35°C. A 25 µL injection loop was installed with a sample injection volume of 10 µL.

Calibration Standards

Certified anion standards of chloride, bromide, fluoride, nitrite, nitrate, sulfate, acetate, oxalate and formate were obtained at a stock concentration level of 100 mg/L (ppm) from Environmental Express (Charleston, SC). Glycolate (Alltech, Deerfield IL) and thiosulfate (Inorganic Ventures, Christiansburg VA) were obtained at a stock concentration level of 1000 ppm. Individual calibration standards for each anion were prepared by diluting the stock solutions with 18.2 MΩ water. Sulfite standards were prepared from sodium sulfite (+98%, Sigma-Aldrich, St. Louis MO) and stabilized from oxidation with a dilute (0.5%) formaldehyde solution prepared from a 10% solution (Red Bird Services, Batesville IN).

Pilot Solvent Sample Preparation

Lean and rich carbon loaded solvent samples were collected from the pilot plant and prepared for IC analysis with 18.2 MΩ water to a 500 times dilution factor for anion analysis. Separate solvent samples were prepared for sulfite analysis by immediately diluting 500 times in a 0.5% formaldehyde solution and analyzed within 3 days. All samples were stored at 4°C prior to analysis.

RESULTS

An IC-anion method was developed to separate and quantify the anionic species identified as potential HSS from coal combustion and degradation of amine scrubbing solvents. This method was examined for its reproducibility and reliability. Authentic anion standards were prepared at six different concentration levels from 0.05–25 mg/L (ppm) for the anions, with the exception of sulfite. Calibration curves, limit of detection (LOD) and limit of quantitation (LOQ) for 10 potential HSS anions were calculated and displayed in Table 2. The correlation coefficients from each anion show excellent linearity with near-unity between conductivity (signal) and concentration in the ranges analyzed. The precision was analyzed by completing all measurements in triplicate with relative standard deviation (RSD) of less than 10% for all calibration standards. The LOD’s were calculated with a signal-to-noise ratio (S/N) of 3. The LOQ’s were calculated from the LOD and the sample dilution factor (500X). Sample dilution was necessary to avoid overloading the column capacity and to bring the anion analyte concentration within the linear calibration range while reducing the background conductivity from the high amine concentration present in the amine solvent samples. The retention times and LOD’s of two additional

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Run-time (hr)</th>
<th>CO₂ (vol%)</th>
<th>O₂ (vol%)</th>
<th>SO₂ (ppm)</th>
<th>NO₃ (ppm)</th>
<th>Flue gas residence time (sec)</th>
<th>L/G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% MEA</td>
<td>100</td>
<td>14</td>
<td>6</td>
<td>250</td>
<td>90</td>
<td>3.9</td>
<td>40–50</td>
</tr>
<tr>
<td>CAER–B2</td>
<td>185</td>
<td>14</td>
<td>6</td>
<td>170</td>
<td>80</td>
<td>3.9</td>
<td>40–50</td>
</tr>
</tbody>
</table>

* Liquid to gas ratio (L/G) reported in gallons per minute (GPM) over 1000 actual cubic feet per minute (ACFM).
Table 2. Anion calibration curve, limit of detection and limit of quantitation summary for heat stable salts (HSS) by ion chromatography.

<table>
<thead>
<tr>
<th>HSS</th>
<th>Source</th>
<th>Response Factor</th>
<th>$R^2$</th>
<th>Concentration Range</th>
<th>LOD*</th>
<th>LOQ**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolate</td>
<td>Solvent Degradation</td>
<td>0.0755</td>
<td>0.9971</td>
<td>0.05–25</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Acetate</td>
<td>Solvent Degradation</td>
<td>0.0569</td>
<td>0.9920</td>
<td>0.05–25</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Formate</td>
<td>Solvent Degradation</td>
<td>0.1244</td>
<td>0.9563</td>
<td>0.05–25</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Chloride</td>
<td>Flue gas/water</td>
<td>0.2109</td>
<td>0.9997</td>
<td>0.05–25</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Flue gas</td>
<td>0.1506</td>
<td>0.9974</td>
<td>0.05–25</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Sulfite</td>
<td>Flue gas</td>
<td>0.0924</td>
<td>0.9946</td>
<td>1–25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Flue gas</td>
<td>0.1187</td>
<td>0.9993</td>
<td>0.05–25</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Flue gas</td>
<td>0.1530</td>
<td>0.996</td>
<td>0.05–25</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Oxalate</td>
<td>Solvent Degradation</td>
<td>0.1361</td>
<td>0.9872</td>
<td>0.05–25</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>Flue gas</td>
<td>0.1367</td>
<td>0.9997</td>
<td>0.05–25</td>
<td>30</td>
<td>16</td>
</tr>
</tbody>
</table>

* LOD calculated with S/N = 3. ** LOQ calculated with 500x sample dilution. † Sulfite standards were stabilized with 0.5% formaldehyde solution to inhibit oxidation.

Anions, fluoride and bromide, were determined (7.6 and 20.4 min respectively) but these anions were not identified in any of the pilot solvent samples and therefore calibration curves for these anions were not constructed.

Sulfite Oxidation Stability

Sulfite can potentially be oxidized within the solvent to sulfate by oxidants such as dissolved oxygen in the aqueous sample solution (Iammarino et al., 2010). To ensure consistent sulfite numbers a method was developed to inhibit this oxidation and to also establish the acceptable window for when sulfite could be measured accurately. Several inhibitors were considered as to inhibit the oxidation reaction, with formaldehyde ultimately selected due to its minimal impact on other analysis and common availability (Michigami and Ueda, 1994). Several different formaldehyde concentration levels from 0.1%–5.0% were examined with standard sulfite (100 mg/L) in a 30% MEA solution as a representative amine. The sulfite and oxidation induced sulfate levels were monitored over time by IC. Fig. 1 shows the oxidation of sulfite after only four hours (bottom black line) and after 24 hours (top gray line) in a 30% MEA aqueous solution prepared with a 500 times dilution factor. Formaldehyde solutions from 0.5% to 5.0% were effective at stabilizing the sulfite ion for at least 14 days. The 0.5% formaldehyde solution performed the best at inhibiting sulfite oxidation while being compatible with the anion IC analysis. It has been found that higher concentrations of formaldehyde caused a significant increase in the background conductivity. Over a 14 day period, the sulfite anion was stable at 4 different concentration levels (1–25 ppm) and had a linear correlation ($R^2 > 0.99$) in the concentration range examined (see Table 2). The absolute sulfate level in each standard also remained stable over the 14 day period with less than 5% oxidation loss of sulfite. Given this result, sulfite calibration standards were stabilized in a solution of 0.5% formaldehyde and used to construct the calibration curve.

Carbonate Suppression in Lean and Rich Samples

The carbonate removal device (CRD) was installed prior to the guard column to suppress the amount of dissolved carbon dioxide in rich and lean carbon-loaded samples to improve the anion chromatography. The carbon dioxide, as carbonate, co-elutes as a large broad peak with several of the anion analytes including bromide, nitrate, sulfate and oxalate. The background conductivity is also significantly higher and unstable due to the presence of dissolved carbon dioxide in the sample when analyzed without the CRD causing poor peak resolution. The gas permeable membrane inside the CRD allows CO$_2$ to diffuse out of the eluent thereby lowering the amount of carbonate, which allows for good peak resolution and lower background conductivity as illustrated in Fig. 2. Without the CRD the peaks for nitrate and sulfate, two of the primary HSS analytes of interest, are not well resolved which can lead to inaccurate and variable quantitation. With the CRD, both peaks are resolved with less variability (usually < 5%) between multiple injections. Bromide is completely obscured by the carbonate peak in a carbon-loaded sample but is resolved when using the CRD. The CRD was used during all subsequent anion analysis of calibration standards and carbon-loaded pilot samples.

Pilot Test Campaigns

During the 30% MEA test campaign, six out of the 10 potential anion HSS were identified in the pilot samples.
Fig. 3 shows a representative ion chromatogram from a 30% MEA pilot sample, with the HSS accumulation rates during the test campaign shown in Fig. 4. Sulfate (3400 ppm), formate (799 ppm) and nitrate (720 ppm) were identified as the primary anion species after 100 hours of run time. The concentration levels for nitrite and chloride and thiosulfate were much lower at 2, 40 and 67 ppm respectively. The nitrite and chloride levels remained constant during the 100 hour test campaign. Nitrite is believed to undergo further chemistry either by oxidizing other species or being oxidized to nitrate and this may explain its steady concentration. The chloride level is stable presumably due to being present in the process water, as opposed to building up as a flue gas contaminant. Sulfate, formate and thiosulfate accumulated in the solvent at a predominantly linear rate during this test campaign. The nitrate accumulation rate was initially slow and linear but jumped during the last 20 hours of run time. The total HSS accumulation during the 30% MEA campaign is equivalent to 0.47 wt% of the solvent after 100 hours at an average rate of 48 ppm per hour.
Fig. 4. Heat stable salt accumulation in 30% MEA solvent test campaign in CAER pilot plant.

Fig. 5 illustrates the HSS accumulation with the CAER-B2 solvent during 185 hours of run time. Again, only six HSS were identified and accumulated in the solvent. The primary HSS were sulfate (2920 ppm) and formate (1694 ppm). The nitrate and nitrite levels initially increased to 160 and 124 ppm respectively at 34 hours, then decrease during the rest of the campaign to 80 and 64 ppm at the end of the test campaign. Chloride remained constant in the 25–30 ppm range, while thiosulfate slowly increased to 75 ppm by the end of the campaign. The total HSS accumulation during the CAER-B2 campaign accounted for approximately 0.41% (w/w) of the solvent after 185 hours of run time, at an accumulation rate of 22 ppm per hour. The small decrease in the HSS concentration values at the 100 and 150 hour marks in this campaign can be attributed to the addition of make-up solvent to the pilot to maintain the system volume.

DISCUSSION

Method Evaluation and Sulfite Oxidation Inhibition

Ion chromatography is ideal for identifying and quantifying anion heat stable salt species from amine carbon capture solvents. Each IC system may be somewhat different in terms of the components including column size, injection loop and detector response. Finding the appropriate method parameters for each system is necessary to insure accurate, reliable and reproducible quantitation.

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The sensitivity of the conductivity detector and the concentration levels in the solvent samples makes sample dilution necessary. The anion levels in the pilot solvent samples analyzed required a 500 times dilution, with this dilution factor, the concentration levels were firmly within the linear calibration range while still providing good limits of detection (see Table 2) and minimizing background conductivity that can results from high residual amine concentration in the samples. Higher HSS concentration levels from continued accumulation may require higher dilution factors. The carbonate removal device added to the IC system allowed anion analysis without requiring another preparation step to remove the dissolved carbon dioxide from the solvent sample. Lean and rich carbon loaded samples could be analyzed with no difference in the quantitation results. The calibration curves constructed with the presented method were valid (< 10% deviation) up to 6 months later when evaluated with check standards.

Formaldehyde showed the most promise for short-term sulfite stability in amine solvent samples, but using formaldehyde to inhibit sulfite oxidation is not without some potential drawbacks. Formaldehyde can act as a reducing agent in the presence of a metal catalyst, converting nitrate to nitrite and eventually to nitrogen gas (Numata et al., 2006). Formaldehyde can also cause interference with several analytes due to co-elution and increased background conductivity as observed in this study with formaldehyde concentration levels above 0.5% (Gobbi et al., 1998). Nitrate and nitrite standards in a 0.5% formaldehyde solution did not show the reductive losses, however when a representative 30% MEA pilot solvent sample was added to the formaldehyde solution, the nitrate level decreased from 850 ppm to 500 ppm while the nitrite level increased from < 5 ppm to 25 ppm. The pilot solvent sample may contain a catalytic amount of metal or another reducing species to cause the nitrate reduction (Fanning, 2000). The amount of formate in this sample also increased, likely the result of co-elution from the formaldehyde causing an artificially inflated formate concentration level.

The possibility exists for the sulfite anions present in the solvent sample to be oxidized to sulfate in the absorber or during sample preparation due to the presence of oxygen and water, yielding artificially low sulfite values (Zhou et al., 2012). In the pilot samples collected, the presence of sulfite could not be confirmed suggesting that any sulfite initially present in the solvent was quickly oxidized to sulfate in the absorber or in the time between collection, sample preparation and analysis. Several attempts were made to stabilize sulfite by collecting the solvent sample and immediately preparing it in 0.5% formaldehyde and analyzing it within an hour, but again sulfite was not observed in these samples. However, given the potential impact sulfite can have on corrosion, it is important to continually monitor the solvent for sulfite accumulation.

Ideally a separate sample preparation procedures for sulfite and the remaining HSS analytes is practiced. This is
Based on the fact that formaldehyde elution can interfere with some other peaks of interest, specifically glycolate, acetate and formate. Briefly, a small portion of each solvent sample should be split with one portion stabilized immediately in a 0.5% formaldehyde solution and stored at 4°C and analyzed for sulfite within 2 weeks of sample collection. The other portion should be prepared as outlined previously to a 500 times dilution factor and used to analyze for the remaining HS species. This sample should also be stored at 4°C prior to analysis.

**Pilot HSS Analysis**

The largest portions of the HSS in both solvent campaigns are from the sulfur based sulfate, and to a lesser extent thiosulfate as illustrated by the final HSS levels in Table 3. This was expected due to the high input SO$_2$ level in the flue gas. However, the removal efficiency of SO$_2$ during the 30% MEA and CAER-B2 solvent campaigns were lower than the near 100% removal reported by Gao et al. (2012) using simulated flue gas containing between 214 and 317 ppm SO$_2$ with a tertiary amine blend and from Knudsen et al. (2007) using coal derived flue gas scrubbed below 6 ppm SO$_2$ with a SCR and wet limestone desulphurization.

The sulfate levels differed from 3400 ppm in the 30% MEA to 1600 ppm in the CAER-B2 after approximately 100 hours of run time in each campaign as seen in Fig. 6. One potential reason for this behavior is the higher SO$_2$ concentration in the flue gas during the 30% MEA campaign. While the SO$_2$ level will fluctuate during the course of a campaign run over several weeks, the levels were higher during the MEA campaign and could be contributing to the higher sulfate levels and corresponding total HSS level in the solvent, but more investigation is needed to completely understand the differences in HSS accumulation between these two solvents. Overall, the 30% MEA solvent accumulates HSS at nearly twice the rate (48 ppm/hr vs. 22 ppm/hr) as the CAER-B2 as observed in Fig. 7.

Several threshold HSS concentration levels have been presented ranging from 1–10% wt (amine) and up to 5% total wt of the solvent (Kadner and Reider, 1995; Knudsen et al., 2007; Verma and Verma, 2009; Vitse et al., 2011). The HSS threshold values are benchmarks used to determine when the amine solvent should be purified to remove the HSS and other degradation products. Given the observed accumulation and assuming a continued linear rate, the total HSS concentration levels in 30% MEA and CAER-B2 will reach 1.0% wt after approximately 200 and 450 hours of operation respectively. However, it must also be observed that the acid gas components of the flue gas are comparable to what might be observed directly from a WFGD and are thus higher than what would be expected in a post-combustion CO$_2$ capture scenario utilizing a pretreatment tower to reduce HSS accumulation. It should be noted that the accumulation rate observed here is similar in magnitude to other published amine based CO$_2$ capture data. Gao et al. (2011) reported HSS accumulation rates of 0.2% wt at 100 hours and approximately 0.4% wt at 200 hours in pilot scale experiments and Wilson et al. (2004) reported a rate of 0.4% wt at the Saskpower Boundary Dam CO$_2$ capture pilot plant. The accumulation rate with 30% MEA at the Esbjerg pilot plant was approximately 0.75% wt at 200 hours (Knudsen et al., 2007), which is comparable to the observed accumulation rates for the CAER-B2 and 30% MEA campaigns in the CAER pilot plant.

**Corrosion Implication**

Several factors can directly influence the corrosion rates in amine based carbon capture systems. Amine, O$_2$, SO$_2$ and CO$_2$ loading levels can all lead to higher corrosion rates by increasing either the amount dissolved oxygen or H$^+$ present in solution (Kladkaew et al., 2009; Gao et al., 2012). Heat stable salts have been identified as a major

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Run-time (hr)</th>
<th>Formate</th>
<th>Chloride</th>
<th>Nitrite</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Thiosulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% MEA</td>
<td>100</td>
<td>799</td>
<td>40</td>
<td>&lt; 3</td>
<td>720</td>
<td>3400</td>
<td>67</td>
</tr>
<tr>
<td>CAER-B2</td>
<td>185</td>
<td>1694</td>
<td>29</td>
<td>80</td>
<td>64</td>
<td>2929</td>
<td>75</td>
</tr>
</tbody>
</table>

Fig. 5. Heat stable salt accumulation in CAER-B2 solvent test campaign in CAER pilot plant.
cause of amine carbon capture systems problems including amine losses, foaming and corrosion (Verma and Verma, 2009). HSS can induce corrosion in amine solvents by acting as a chelating agent, lowering the solution pH and increasing the solution conductivity. Verma and Verma (2009) published benchmark maximum anion levels in the solvent needed to keep corrosion rates at less than 10 mils/year to minimize the negative impacts on operational performance. The levels range from 250 ppm for chloride and oxalate, to 500 ppm for formate and sulfate to over 10,000 ppm for thiosulfate.

During the 30% MEA test campaign, the sulfate level reached the maximum corrosion benchmark after less than 30 hours. Formate levels passed the maximum benchmark at around 80 hours while chloride and thiosulfate levels remained below the benchmarks during the entire campaign. During the CAER-B2 test campaign, the sulfate and formate levels passed the corrosion maximum benchmarks after 25 and 75 hours respectively, with the remaining HSS species staying below the benchmark levels during the entire campaign. These results suggest that within a few days of normal operation, corrosion inside the system will start as HSS levels quickly build up in the solvent. Furthermore, it indicates that the reclaimer duty may be higher than expected based on total HSS accumulation evaluation. Beyond this, since some of the HSS that meet the corrosion thresholds for the current system are from amine derived degradation products and not exclusively from flue gas components, the need for a pretreatment tower in a commercial process may be unwarranted unless the solvent degradation can be minimized.

HSS accumulation can be controlled by eliminating flue gas contaminants directly, reducing oxidative degradation or removing HSS from the solvent. Several different options exist to remove HSS and other contaminants including ion-exchange membranes, electrodialysis and reclaiming (Meng et al., 2008; Verma and Verma, 2009; Vitse et al., 2011). These technologies can be energy intensive adding to the overall operating costs. Solvent loss and degradation can also occur during HSS removal further adding to the operating costs.

CONCLUSIONS

This study described the evaluation of HSS accumulation in two separate amine solvents during testing in a 0.1 MWth coal combustion carbon capture pilot plant. 30% MEA was used as a baseline solvent and compared to a proprietary amine solvent, CAER-B2. Six HSS were identified in each
solvent during pilot operation including sulfate, thiosulfate, formate, nitrate, nitrite and chloride. The 30% MEA solvent accumulated HSS at nearly twice the rate (48 ppm/hr vs. 22 ppm/hr) as the CAER B2, primarily due to the higher input SO₂ levels in the flue gas during this solvent test campaign. The accumulation rates of both solvents were similar in magnitude to other published amine based CO₂ capture plant data.

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DISCLAIMER

Reference to any companies or specific commercial products does not constitute its endorsement or recommendation by the University of Kentucky Center for Applied Energy Research.

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