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# 1 Introduction

This LAUNCH deliverable has results of the nitrogen sparging to reduce amine oxidation performed by the University of Texas.

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# Role of carbon treating in piperazine oxidation

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#### Abstract

Bench-scale experiments were performed to test the effects of carbon treating on piperazine (PZ) with ongoing oxidation. The combined mitigation of carbon treating and  $N_2$  sparging was also tested. When carbon treating is applied, the UV-Vis absorbance at 320 nm, the NH<sub>3</sub> rate, and the accumulation rate of dissolved Fe and total formate decrease. Carbon treating can remove Cr and Mn from the solvent and stop the solvent from foaming. The effects of carbon treating lasts when the carbon is bypassed, which is possibly due to the removal of catalytic degradation products. Therefore, it is better to apply carbon treating in the early stage of oxidation. Combining carbon treating and nitrogen sparging is more effective in oxidation mitigation than applying the methods separately. The amount of Fe removed by the carbon bed is greater than the result calculated from the solvent inventory and concentration difference of Fe in solvent, indicating that the Fe colloids or other "soluble" Fe can dissolve into the solvent when the Fe in solvent is adsorbed and removed. The carbon can remove the degradation products that can complex with Fe<sup>3+</sup>, even if they are not complexed. Since the source of Fe includes fly ash and corrosion, removing the ligands instead of all the available Fe is a more feasible target.

Keywords: CO2; piperazine; oxidation; carbon treating; Fe

## 1. Introduction

5 m piperazine (PZ) is a promising second-generation solvent for amine scrubbing in post-combustion carbon capture due to its good thermal stability, high capacity, and high rate of  $CO_2$  absorption<sup>[1]</sup>. During long-term operation, PZ can degrade into NH<sub>3</sub>, piperazinone (PZ-one), ethylenediamine (EDA), and heat stable salts including formate<sup>[2]</sup>.

In a pilot plant test performed at the National Carbon Capture Center (NCCC), carbon treating showed potential to mitigate oxidation by reducing the NH<sub>3</sub> production. Activated carbon adsorbed Fe and Cr from the solvent, but the dissolved Fe concentration did not decrease due to replenishment with the available soluble Fe<sup>[3]</sup>. In this work, more work was done to understand the species being removed with Fe. Two bench-scale experiments were performed to understand the role of carbon treating better. These experiments started with the end solvent collected from the NCCC 2019 campaign, which contained 30 mmol/kg total formate, 0.13 mmol/kg Fe, 9.6 mmol/kg EDA, and 13.9 mmol/kg PZ-one. The 1.6 mmol/kg Li<sup>+</sup> in the solvent was used as a tracer to account for the water balance.

#### 2. Experimental Devices

#### 2.1. High Temperature Oxidation Reactor (HTOR)

Bench-scale experiments were performed in the high temperature oxidation reactor (HTOR), which cycles amine between a low-temperature reactor and a high-temperature oil bath up to 150 °C. This apparatus simulates solvent oxidation in the amine scrubbing process, with the reactor simulating the absorber, and the oil bath simulating the stripper. The total inventory is 1.6 L, and the solvent has a flow rate of 0.2 L/min. The inventory at low temperature is 1.0 L, and the inventory at hot rich condition is 0.6 L. The gas rate is 7.5 L/min prepared by mixing compressed air with CO<sub>2</sub>. The concentration of the CO<sub>2</sub> is set to provide the desired loading of the solvent, which cannot exceed 0.3 to prevent flashing occurring at the high temperature. Nitrogen sparging can be applied to the bubble removal vessel to remove dissolved oxygen. Previous HTOR tests were performed to understand the effects of N<sub>2</sub> sparging, catalyst, and inhibitors<sup>[2]</sup>. A glass column that is 15 cm in inner diameter and 300 mm tall was added between the peristaltic pump and the bubble removal vessel to serve as a carbon bed. The carbon bed is 15.9 mm in diameter and 1 ft tall and can hold a maximum of 17 g carbon. The HTOR configuration is shown in Fig. 1.



Fig. 1. HTOR apparatus

2.2. Carbon Adsorption Column (CAC)

A 25-mL burette was used to perform the carbon adsorption experiment. As shown in Fig. 2, the column was filled with carbon, and the bottom was plugged with glass wool. The solvent flowing out from the column is fed through a peristaltic pump, which transfers the solvent back to the top of the column at a rate of 0.5 mL/s. The mass of the carbon in the column and the total solvent amount are measured to calculate the carbon-to-solvent ratio, and the solvent is collected from the top for further analysis<sup>[4]</sup>.



Fig. 2. Carbon adsorption column

# 3. Analytical Methods

## 3.1. Anion IC

The concentration of heat stable salts including formate, acetate, glycolate, and oxalate generated from PZ degradation was measured with anion chromatography. A Dionex ICS-6000 Ion Chromatography System was used with an IonPac AG15 guard column and an IonPac AS15 analytical column<sup>[5,6]</sup>. Standards between 0.01 mmol/kg and 0.5 mmol/kg were used to obtain the elution time of the species and a calibration curve. The total heat stable salts are analyzed after breaking the bond between the salts and the amine by treating with 10 N NaOH 1:1 volumetrically for 24 hours. The treated samples are then diluted 50 times in a 1.5 mL plastic vial. The same scripts are used to analyze for heat stable salts and total heat stable salts. Table 1 includes the species in most degraded samples and their elution time.

Species	Elution Time (minutes)
glycolate	19.3
acetate	19.9
formate	20.7
propionate	22.2
chloride	24.5
nitrite	26.0
sulfate	29.9
oxalate	30.0
nitrate	32.7

Table 1	. Species	quantified b	v Anion IC
			/

#### 3.2. Cation IC

PZ and other cation degradation products were measured with cation chromatography. A Dionex<sup>TM</sup> ICS-6000 Capillary HPIC<sup>TM</sup> system was used with an IonPac CG 17 guard column and an IonPac CS 17 analytical column<sup>[7,8]</sup>. Standards between 0.01 mmol/kg and 0.5 mmol/kg were used to obtain the elution time of the species and a calibration curve. The samples are diluted 10000 times gravimetrically in a 1.5 mL plastic vial, and 25  $\mu$ L is required for each injection. Table 2 includes the species in most degraded samples and their elution time.

Table 2. Species quantified by Cation re-				
Species	Full Name	CAS #	Time (minutes)	
$\mathrm{NH_4^+}$			5.0	
PZ-one	2-oxopiperazine	5625-67-2	6.8	
FPZ	1-formylpiperazine	7752-92-2	7.4	
EDA	ethylenediamine	107-15-3	17.9	
PZ	piperazine	110-85-0	20.2	
HEP	1-(2-hydroxyethyl)piperazine	103-76-4	21.7	
MPZ	1-methylpiperazine	109-01-3	22.4	
EPZ	1-ethylpiperazine	5308-25-8	23.7	
DMPZ	1,4-dimethylpiperazine	106-58-1	25.2	
AEP	aminoethylpiperazine	140-31-8	29.3	

Table 2. Species quantified by Cation IC

#### 3.3. ICP-OES

A Varian 10-ES Axial ICP-OES was used to analyze metals by the specific wavelength of UV light emitted in argon plasma flame at 7000K <sup>[2]</sup>. 0.32 mL samples were diluted by 7.68 mL with 2 wt % nitric acid to allow for multiple analyses, and standards between 0.5 ppm and 25 ppm were prepared for each run. For samples with low metal concentrations, a small dilution factor was used to allow a reasonable signal to noise ratio. Since PZ can interfere with the absorbance of light in the measurement, the standards were prepared with the same concentration of PZ added to eliminate the interference. For each element, two to three high intensity wavelengths that are not interfered with by other metals were used, and three measurements were performed at each wavelength. The average results from the measurements of the three wavelength were reported, and the standard deviation is usually within 2% to 3%. The same metal species with different oxidation states are not differentiated, and the results represent the total amount of certain metal species in the samples. The characteristic wavelengths of the commonly analyzed metals are listed in Table 3.

Table 3. Characteristic wavelengths for ICP-OES metal quantification

Elements	Measure Wavelengths (nm)			
Lithium (Li)	670.783	610.365		
Potassium (K)	766.491	769.897		
Iron (Fe)	234.350	238.204	259.940	
Chromium (Cr)	205.560	206.158	267.716	
Nickel (Ni)	216.555	221.648	231.604	
Manganese (Mn)	257.610	259.372	260.568	
Copper (Cu)	213.598	224.700	324.754	

#### 3.4. UV-Vis

The UV-Vis measurements were performed with two instruments: a NanoDrop<sup>TM</sup> One Microvolume UV-Vis Spectrophotometer, and a Varian Cary 5000 UV-Vis-NIR Spectrophotometer. The NanoDrop worked well with samples that have high absorbance, while the Varian Cary can only measure in a range between 0 and 2.5 A. 1.5  $\mu$ L of sample was analyzed with the NanoDrop first to get an estimation of absorbance range. The sample was then diluted to close to 1 A with water for a second measurement with the Varian Cary. 3.5 mL of the diluted sample was injected in a disposable cuvette with a light path of 10 nm. A dilution-corrected absorbance was reported by multiplying the measured absorbance and the dilution factor. The instrument was calibrated with zero transmittance and water blank each time before the analysis.<sup>[4]</sup>

#### 4. Discussions and Results

#### 4.1. Identification of the UV-Vis Absorbance Peak at 320 nm

Different metal ions were added into clean and degraded samples. While the addition of  $(NH_4)_2Fe(SO_4)_2$  did not produce any peak at 320 nm or 538 nm, the addition of  $NH_4Fe(SO_4)_2 \cdot 12H_2O$  replicated the peak at 320 nm, shown as the purple curve in Figure 3  $NH_4Fe(SO_4)_2 \cdot 12H_2O$  in 5 m PZ absorbs at 293 nm instead of 320 nm, indicating that the 320 nm peak was caused by a complex of  $Fe^{3+}$  and the degradation products.



Fig. 3. Absorbance of Fe<sup>3+</sup> in clean PZ and degraded sample

There is a linear relationship between the increase in absorbance and the added  $Fe^{3+}$  concentration shown in Fig. 4, indicating that there is excess of degradation product ready to complex with the  $Fe^{3+}$ .  $Fe^{3+}$  is not the only species contributing to the 320 nm peak as the  $Fe^{3+}$  concentration calculated by UV-Vis was much higher than the Fe concentration given by ICP. Ni<sup>2+</sup>, Cr<sup>3+</sup>, and Mn<sup>2+</sup> also absorb close to 320 nm, and can add to the peak intensity at 320 nm. It is probable that the 320 nm peak represents some overall metal level in the solvent<sup>[4]</sup>.



Fig. 4. Calibration curve of Fe<sup>3+</sup>complex at 320 nm

#### 4.2. HTOR 28: Moderately Degraded PZ from 55 °C to 150 °C with Carbon Treating and Nitrogen Sparging

In HTOR 28, the effect of carbon treating on oxidation was tested. Nitrogen sparging was applied in the middle of the experiment, testing the combined mitigation effect of carbon treating and nitrogen sparging. A 7.5 L/min synthetic flue gas was created by mixing air with 0.5% CO<sub>2</sub> to maintain a loading of 0.25, which is close to the lean loading in real plant operations. The solvent was cycled between 55 °C and 150 °C at 0.2 L/min. The system experienced a severe water balance issue in the first 140 hrs, so only the data after 140 hrs are reported. The process changes in HTOR 28 are recorded in Table 4. Foaming was observed at the baseline condition and disappeared within 24 hrs after carbon treating was applied. Table 5 shows a summary of the species accumulation rates measured in the HTOR 28.

Table 4. Process changes during HTOR 28		
Process Change		
Baseline (No carbon or N <sub>2</sub> )		
Carbon treating		
N <sub>2</sub> sparging + carbon treating		
N <sub>2</sub> sparging + depleted Carbon		
End of experiment		

Table 5. Summary of degradation and corrosion products, and PZ oxidation rate in HTOR 28

Species	Baseline	Carbon Bed	Carbon Bed + N <sub>2</sub> Sparging	Depleted Carbon + N <sub>2</sub> Sparging
Gas-phase NH <sub>3</sub> rate (µmol/kg-hr <sup>2</sup> )	$2.42\pm0.01$	$0.27\pm0.01$	$-0.23\pm0.01$	$1.40\pm0.00$
PZ (mmol/kg-hr)	$-4.0 \pm 1.3$	$-2.8 \pm 0.6$	$-1.4 \pm 0.5$	$-2.0 \pm 0.2$
320 nm absorbance (A/hr)	$1.00\pm0.10$	$0.17 \pm 0.09$	Constant at 200 A	$0.69\pm0.11$
Total formate (mmol/kg-hr)	$0.14\pm0.3$	$0.08\pm0.01$	$0.05\pm0.02$	$0.06 \pm 0.4$
Fe (µmol/kg-hr)	$2.9 \pm 0.2$	Constant at 0.57 mmol/kg	$-0.5 \pm 0.3$	$2.4\pm0.8$
PZ-one (mmol/kg-hr)	$0.52\pm0.12$	Constant at 160 mmol/kg	$\textbf{-0.29} \pm 0.10$	Constant at 115 mmol/kg

The PZ concentration normalized by Li is plotted in Fig. 5. The overall PZ loss rate was 2.1 ± 0.2 mmol/kg-hr.

This is 5 times the  $NH_3$  production rate, and since little PZ was observed in the gas outlet, only 1 mol of  $NH_3$  was produced when 5 mols of PZ was oxidized. The slope of the best-fitted curve in each time period is included in Table 5. A model consisting of four connecting linear regression curves that maximize  $R^2$  for the whole data set was created, and the slopes are shown in Figure 8. However, since the concentration of PZ is high, the loss rate is not accurate enough in regions with only 4 or 5 data points, but it shows that qualitatively both carbon treating and  $N_2$  sparging reduced the PZ loss rate, and the combined treating mitigated oxidation more significantly.



Fig. 5. Normalized PZ in HTOR 28 (0.5% CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

A strong correlation between  $NH_3$ , Fe, and the dilution-corrected absorbance was observed, and is plotted with cumulative  $NH_3$  in Fig. 6. The strong correlation shows that applying the carbon bed or the nitrogen sparging are both useful in mitigating oxidation and combining these two mitigation methods worked better than using either one of the methods alone.

At the baseline condition, the absorbance increased at  $1.00 \pm 0.10$  A/hr. When the carbon bed was turned on, the accumulation rate decreased to  $0.17 \pm 0.09$  A/hr, perhaps because the carbon bed was removing the absorbing species. After nitrogen sparging was turned on, the absorbance remained constant at 200 A, indicating that nitrogen sparging reduces the production rate of the complexing products. When the carbon bed was depleted, the absorbance increased again at a rate of  $0.69 \pm 0.11$  A/hr.

Compared to the initial Fe of 0.13 mmol/kg, the Fe throughout the experiment was considerably higher, indicating that the solubility limit in the HTOR is higher than the solubility limit at NCCC. Fe increased at the baseline condition at a rate of  $2.9 \pm 0.2 \mu mol/kg$ -hr. When the carbon bed was turned on, Fe stayed relatively constant, and decreased at a rate of  $0.5 \pm 0.3 \mu mol/kg$ -hr when N<sub>2</sub> sparging was turned on. When the carbon bed was depleted, the Fe started increasing again at  $2.4 \pm 0.8 \mu mol/kg$ -hr. These data show that carbon treating reduces Fe accumulation by 2.9  $\mu mol/kg$ -hr, and N<sub>2</sub> sparging reduces Fe accumulation by 0.5  $\mu mol/kg$ -hr. The Mn decreased when there was a working carbon bed, which matched the previous observance that the carbon bed can remove dissolved Mn at a low rate. The Cr decreased when the carbon bed was turned on but reached steady state at 0.32 mmol/kg<sup>[4]</sup>.

The NH<sub>3</sub> production rate represented the oxidation rate of the PZ solvent. At the baseline condition, the NH<sub>3</sub> rate started low at 0.25 mmol/kg-hr and increased linearly at a rate of  $2.42 \pm 0.01 \mu mol/kg-hr^2$ . The trend of increase stopped when carbon treating was applied, but there was no step change in the NH<sub>3</sub> rate. Between 320 hrs and 357 hrs, the cooler was not working properly and the solvent after the cross exchanger was maintained at 75 °C instead of the desired 62 °C, which caused a higher temperature in the reactor. The NH<sub>3</sub> rate decreased immediately after the cooler was reset, indicating that oxidation occurs even at the relatively low temperature of 75 °C. After nitrogen sparging was applied, there was a step decrease in the NH<sub>3</sub> rate, after which the NH<sub>3</sub> rate continued to decrease. In previous HTOR experiments with no carbon bed, the NH<sub>3</sub> rate decreased when nitrogen sparging was applied, but the NH<sub>3</sub> rate still increased as the experiment continued<sup>[2]</sup>. At 483 hrs, the NH<sub>3</sub> rate started increasing at 1.4 µmol/kg-hr<sup>2</sup>

even though no operating changes were applied to the system. This is believed to be due to depleted carbon. From 483 hrs to the end of the experiment, the results represented the mitigation effects of nitrogen sparging only. The slope of the  $NH_3$  rate was 50% smaller with  $N_2$  sparging compared to the baseline condition. The cumulative  $NH_3$  produced throughout the experiment was 183.5 mmol/kg, which corresponded to an oxidation rate of 0.34 mmol PZ/kg-hr.

To conclude, the nitrogen sparging reduces the NH<sub>3</sub> production rate and its rate of increase. Carbon treating does not reduce NH<sub>3</sub> production rate but reduces its rate of increase. Combining nitrogen sparging and carbon treating is more effective than applying nitrogen sparging or carbon treating separately.



Fig. 6. Correlation of cumulative NH<sub>3</sub>, NH<sub>3</sub> rate, Fe, and dilution-corrected absorbance at 320 nm in HTOR 28 (0.5% CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

The PZ-one, EDA, and total N products are plotted in Fig. 7. The total N products represents the total amount of N in the degradation products are cumulative NH<sub>3</sub>, PZ-one, EDA, MPZ, AEP, and FPZ. At the baseline condition, the PZ-one increased linearly at  $0.52 \pm 0.12$  mmol/kg-hr, and the PZ-one stopped increasing and leveled out at 160 mmol/kg with the carbon bed. After N<sub>2</sub> sparging was applied, the PZ-one started to decrease at  $0.29 \pm 0.10$  mmol/kg-hr until the effects of the carbon bed diminished. EDA decreased steadily, and no significant difference in decomposition rate was observed, so the degradation of EDA is independent of the application of the carbon bed or N<sub>2</sub> sparging. A model consisting of four connecting linear regression curves that maximize R<sup>2</sup> of the whole data set was created for the total N products, and the slopes are shown in Fig. 7.



Fig. 7. Normalized PZ-one, EDA, and total nitrogen products in HTOR 28 (0.5% CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

The concentrations of total formate, total acids, and total oxidized carbons are plotted in Fig. 8. The total acids include total formate, total acetate, and total oxalate, and the total oxidized carbon is equal to the sum of the total acids and PZ-one. The slopes of the best-fitting curve for total formate in different periods are included in Table 5. Models consisting of four connecting linear regression curves that maximize  $R^2$  of the whole data set was created for total acids and total oxidized carbon, respectively. Carbon treating and N<sub>2</sub> sparging result in a decrease in the accumulation rate of the degradation products. A lag in the rate change was observed because the production of acids and oxidation of carbon are results of oxidation from the intermediates.



Fig. 8. Normalized total formate, total acids, and total oxidized carbon in HTOR 28 (0.5% CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

Excess  $0.2 \text{ N H}_2\text{SO}_4$  was added to 1.25 g of HTOR 28 end carbon to quantify the Fe removed more accurately. 8 batches of  $\text{H}_2\text{SO}_4$  were added, and each batch was drained completely before the new batch was added. The Fe

concentration in the rinse became negligible after 256 g of 0.2 N H<sub>2</sub>SO<sub>4</sub> was used to rinse the carbon, and almost all the Fe was removed from the carbon. From the Fe concentration and the mass of 0.2 N H<sub>2</sub>SO<sub>4</sub>, it is calculated that there was 67.37 mmol Fe/kg of carbon on the HTOR 28 used carbon. Since there was 36.3 mmol Fe/kg of carbon on the clean carbon, a total of 0.48 mmol Fe was adsorbed by the carbon in the HTOR 28, which corresponds to 0.30 mmol Fe/kg solvent with an inventory of 1.6 L. Similar to results in the NCCC 2010 pilot test [3], this concentration is much larger than the difference of Fe before and after carbon treating, confirming that soluble solid  $Fe^{+2/+3}$  dissolved to continuously replenish the Fe in solution.

# 4.3. HTOR 29: Moderately Degraded PZ from 55 °C to 150 °C with Carbon Treating and Nitrogen Sparging

HTOR 29 was designed to be a parallel experiment to HTOR 28. The experiment started with the NCCC 2019 end solvent, which was the same initial solvent as in HTOR 28. 15.5 g of carbon was applied at the beginning of the experiment and was bypassed at 142 hrs. The system ran a baseline condition from 142 to 414 hrs, and then nitrogen sparging was applied till the end of the experiment. 7.5 L/min of synthetic flue gas was created by mixing air with 0.5% CO<sub>2</sub> to maintain a loading of 0.25, which is close to the lean loading in real plant operations. The solvent was cycled between 55 °C and 150 °C at 0.2 L/min. The process changes in HTOR 29 are recorded in Table 6. Table 7 shows a summary of the rates of species measured in the HTOR 29.

Time (hrs)	Process Change
0	Carbon treating
142	Bypassed carbon treating
414	N <sub>2</sub> sparging
600	N <sub>2</sub> sparging at double liquid depth
664	End of experiment

Table 6. Process changes during HTOR 29

Table 7. Summary of degradation and corrosion products, and PZ oxidation rate in HTOR 29			
Species	Carbon Bed	Baseline	N <sub>2</sub> Sparging
Gas-phase NH <sub>3</sub> rate (µmol/kg-hr <sup>2</sup> )	$0.30\pm0.01$	$1.51\pm0.01$	$0.81 \pm 0.02$
PZ (mmol/kg-hr)	$-1.4 \pm 0.2$	$-2.6 \pm 0.4$	$-1.5 \pm 0.5$
320 nm absorbance (A/hr)	$0.18\pm0.01$	$0.52\pm0.03$	$0.23\pm0.02$
Total formate (mmol/kg- hr)	$0.07\pm0.02$	$0.12\pm0.01$	$0.05\pm0.04$
FPZ (mmol/kg-hr)	$0.06\pm0.01$	$0.11\pm0.01$	$0.05\pm0.02$
Total oxalate mmol/kg-hr	$0.008 \pm 0.005$	$0.045\pm0.004$	$0.026\pm0.004$
Fe (µmol/kg-hr)	$-1.4 \pm 0.2$	$2.7\pm0.2$	$2.3 \pm 0.4$
PZ-one (mmol/kg-hr)	$-0.08 \pm 0.05$	$0.16\pm0.04$	Constant (150 mmol/kg)

The Fe, UV-Vis absorbance at 320 nm, and  $NH_3$  rate followed a similar relationship to results in HTOR 28, and are plotted with cumulative NH<sub>3</sub> in Fig. 9. While being carbon treated, the absorbance increased at  $0.18 \pm 0.01$  A/hr, which was the same rate in the carbon treated region in HTOR 28. When the carbon bed was bypassed, the absorbance increased at  $0.52 \pm 0.03$  A/hr. Compared to the 1 A/hr at the baseline condition in HTOR 28, we see that although the carbon bed was bypassed, the removal slows down the accumulation of UV-absorbing components, indicating that applying carbon treating in the early stages of oxidation can have a better effect. When N<sub>2</sub> sparging was applied, absorbance increased steadily at 0.23  $\pm$  0.02 A/hr. Combining the results from HTOR 28, N<sub>2</sub> sparging reduces the

accumulation rate by 0.3 A/hr, and this rate is not related to the initial rate of accumulation before  $N_2$  sparging. No change is observed when greater liquid depth was used for  $N_2$  sparging.

Fe decreases at  $-1.4 \pm 0.3 \,\mu$ mol/kg-hr initially after reaching 0.05 mmol/kg when the carbon bed was applied at the start of the experiment. After that, the low concentration of dissolved Fe resulted in a low removal rate, so no further decrease was observed in the Fe. When the carbon bed was bypassed, the Fe accumulation rate increased significantly to  $2.7 \pm 0.2 \,\mu$ mol/kg-hr, which is the same rate observed in the baseline region in HTOR 28. This suggests that the accumulation of Fe is not dependent on whether the solvent has been treated. Even after treatment, Fe continues to increase at the same rate once the carbon bed is bypassed. Therefore, to maintain low Fe in operation, the carbon bed needs to be kept on consistently. When N<sub>2</sub> sparging was initiated, Fe increased at  $2.3 \pm 0.4 \,\mu$ mol/kg-hr, which is the same rate observed between 480 and 580 hrs in HTOR 28. This confirms that N<sub>2</sub> sparging can reduce the Fe accumulation rate seems to decrease furthermore, but due to the short experimental time, this conclusion needs further validation. All the metal ion concentrations increased when there was no carbon bed applied due to corrosion of the stainless steel. The Cr decreased when the carbon bed was turned on and reached 0.11 mmol/kg. Both the removal rate and accumulation rate were the same as in the HTOR 28<sup>[4]</sup>.

In the first 30 hrs, NH<sub>3</sub> production dropped from 0.4 mmol/kg-hr to 0.06 mmol/kg-hr due to the stripping of NH<sub>3</sub> dissolved in the stock solvent. With carbon treating, the NH<sub>3</sub> rate increased linearly at  $0.30 \pm 0.01 \mu$ mol/kg-hr<sup>2</sup>, which is equal to the rate observed in the carbon treated region in HTOR 28. After the carbon bed is bypassed, the NH<sub>3</sub> rate increased at a higher rate of  $1.51 \pm 0.01 \mu$ mol/kg-hr<sup>2</sup>, lower than the  $2.42 \pm 0.01 \mu$ mol/kg-hr<sup>2</sup> observed in the baseline region in HTOR 28. This indicates that the effect of carbon lasted, possibly due to the removal of catalytical degradation products or NH<sub>3</sub> precursors. When the N<sub>2</sub> sparging was turned on, the NH<sub>3</sub> rate decreased by 0.12 mmol/kg-hr, and the acceleration rate was halved to  $0.81 \pm 0.2 \mu$ mol/kg-hr<sup>2</sup>. The cumulative NH<sub>3</sub> production was 200.5 mmol/kg in HTOR 29, which corresponds to a PZ oxidation rate of 0.3 mmol/kg-hr with at stoichiometry of 1.0.



Fig. 9. NH<sub>3</sub> rate in HTOR 29 (0.5 % CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

The PZ concentration normalized by Li is plotted in Fig. 10. The slope of the best-fitting curve for each region is shown in Table 7. A model consisting of three connecting linear regression curves that maximize  $R^2$  of the whole data set was created and the slope is shown in Fig. 11. The rate in the baseline condition was lower than in HTOR 28, indicating that the effects of carbon treating in the first 140 hrs lasted after the carbon was bypassed due to the removal of possible catalytic products. Therefore, it is better to apply carbon treating in the early stages of oxidation.



Fig. 10. PZ normalized by Li in HTOR 29 (0.5 % CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

PZ-one, EDA, and total N products are normalized by Li and plotted in Fig. 11. The degradation products included total N products: cumulative NH<sub>3</sub>, PZ-one, EDA, MPZ, AEP, and FPZ. At the baseline condition, PZ-one decreased at  $0.08 \pm 0.05$  mmol/kg-hr with carbon treating and increased linearly at  $0.16 \pm 0.04$  mmol/kg-hr in the baseline. PZ-one stopped increasing and levelled out at 150 mmol/kg with N<sub>2</sub> sparging. This result matched the results in the HTOR, and the accumulation rate in HTOR 29 at baseline condition is lower than that in HTOR 28, suggesting the benefits of applying carbon treating early. EDA accumulated steadily until it reached 50 mmol/kg. The concentration decreased after that, and no significant difference in decomposition rate was observed, which is the same result observed in HTOR 28.



Fig. 11. Normalized PZ-one, EDA, and total N products in HTOR 29 (0.5 % CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

The normalized total formate, total acid, and total oxidized carbon are plotted in Fig. 12. Most of the formate existed as FPZ. The formate increased at a low rate and was independent of the operating conditions. The total acids includes total formate, total acetate, and total oxalate, and the total oxidized carbon is equal to the sum of the total acids and PZ-one. The slopes of the best-fitting curve for total formate in different periods are included in Table 5. A model consisting of four connecting linear regression curves that maximize  $R^2$  of the whole data set was created for total acids and total oxidized carbon, respectively. The highest rate was observed in the baseline region. Compared to

HTOR 28, the formate accumulation rate in baseline is lower, suggesting that carbon treating removed precursors of formate, therefore the effects on formate existed even when the carbon was bypassed. As a result, applying carbon treating in the early stage of oxidation may be more effective. Mitigation effects were observed for both carbon treating and  $N_2$  sparging.



Fig. 12. Normalized total formate, total acids, and total oxidized carbon in HTOR 29 (0.5 % CO<sub>2</sub>, 55 °C to 150 °C, NCCC 2019 end solvent, carbon bed, and N<sub>2</sub> sparging)

Excess 0.2 N  $H_2SO_4$  was added to 2.96 g of HTOR 29 end carbon to quantify the Fe removed more accurately. 8 batches of  $H_2SO_4$  were added, and each batch was drained completely before the new batch was added. The time and amount of  $H_2SO_4$  added is shown in Table 9. The Fe concentration became negligible after 334 g of 0.2 N  $H_2SO_4$  was used to rinse the carbon, and almost all the Fe was removed from the carbon. From the Fe concentration and the mass of 0.2 N  $H_2SO_4$ , it is calculated that there was 48.4 mmol Fe/kg of carbon on the HTOR end carbon. Since there was 36.3 mmol Fe/kg of carbon on the clean carbon, a total of 0.19 mmol Fe was adsorbed by the carbon in HTOR 29, which corresponds to 0.12 mmol Fe/kg solvent with a total inventory of 1.6 L. Similar to results from HTOR 28, this concentration is much higher than the difference of Fe before and after carbon treating, confirming that the dissolved Fe is replaced by the dissolution of soluble Fe.

#### 4.4. Removal of the Ligands

Both experiments showed that Fe can be removed by the activated carbon, but more soluble Fe can redissolve if the ligands remained in the solvent. This explains why the dissolved Fe remained low after Fe additions in clean solvent at both bench and pilot scale, and shows that adding sulfide to precipitate Fe had no effect on dissolved Fe concentration<sup>[2]</sup>, since the concentration of the ligands were minimal in clean solvent. Therefore, instead of removing all the Fe available, removing all the ligands from degradation can be a more viable method.

An experiment in the Carbon Adsorption Column was performed to understand the effect of removing the ligand. Figure 14 and Figure 15 show the UV-Vis absorbance when different amounts of  $Fe^{3+}$  were added to a degraded solvent and carbon-treated degraded solvent. The degraded solvent was collected after 2100 hrs of operation in the NCCC 2018 campaign<sup>[9]</sup>. In Fig. 14, the peak at 320 nm increased when  $Fe^{3+}$  was added, which matched the conclusion that there were excessive amounts of ligand not complexed with  $Fe^{3+}$  in the solvent, and the complexed  $Fe^{3+}$  has an absorbance of 320 nm. In Fig. 15, the peak at 293 nm increased when  $Fe^{3+}$  was added, and 293 nm is the absorbance wavelength of ionic  $Fe^{3+}$  in clean PZ. This indicates that the ligands were all removed by the carbon, resulting in the  $Fe^{3+}$  not becoming complexed and a measured absorbance at 293 nm instead of 320 nm. The apparent solubility limit of  $Fe^{3+}$  in the solvent decreased from 12.8 mmol/kg to 4.2 mmol/kg. Therefore, carbon treating may

be useful in preventing Fe from further dissolving into the degraded solvent if no further ligand is produced in the solvent.







Fig. 15. UV-Vis absorbance profile of carbon-treated degraded solvent with variable Fe<sup>3+</sup> addition

### 5. Conclusions

- Fe<sup>3+</sup> can complex with degradation products in PZ solvent and absorbs at 320 nm. Ni<sup>2+</sup>, Cr<sup>3+</sup>, and Mn<sup>2+</sup>, complexed or not, contribute to the absorbance at 320 nm.
- Carbon treating is effective in removing degradation and corrosion products and mitigating oxidation in the HTOR. When carbon treating is applied, the increase in NH<sub>3</sub> rate slows down, the UV-Vis absorbance at 320 nm decreases, and the accumulation rate of Fe and total formate decreases. Carbon treating can remove Cr and Mn from the solvent and stop the solvent from foaming. 15.5 g of carbon with 1.6 L of NCCC degraded solvent reduces PZ oxidation rate by 0.4 mmol/kg-hr.
- The Fe removed by the carbon bed is larger than the result calculated from the solvent inventory and concentration difference of Fe in solvent. This is because other "soluble" Fe can dissolve into the solvent when the Fe in solvent is adsorbed by the carbon.
- Combining carbon treating and nitrogen sparging is more effective in oxidation mitigation than applying the methods separately. Observations included a decrease in NH<sub>3</sub> production rate, UV-Vis absorbance at 320 nm, accumulation rate of Fe, and total formate.
- The effects of carbon treating last when the carbon is bypassed, possibly due to the removal of catalytic degradation products. Therefore, it is better to apply carbon treating in the early stages of oxidation.
- Carbon treating removes all the degradation products that can complex with Fe<sup>3+</sup>, even if they are not complexed.

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