**SYNTHESIS OF SULFUR-BASED WATER TREATMENT AGENT
FROM SULFUR DIOXIDE WASTE STREAMS**

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ABSTRACT

Absorption of sulfur dioxide from a simulated flue gas was investigated for the production of polymeric ferric sulfate (PFS), a highly effective coagulant useful in treatment of drinking water and wastewater. The reaction for PFS synthesis took place near atmospheric pressure and at temperatures of 30-80°C. SO₂ removal efficiencies greater than 90% were achieved, with ferrous iron concentrations in the product less than 0.1%. A factorial analysis of the effect of temperature, oxidant dosage, SO₂ concentration, and gas flow rate on SO₂ removal efficiency was carried out, and statistical analyses are conducted. The solid PFS was also characterized with different methods. Characterization results have shown that PFS possesses both crystalline and non-crystalline structure. The kinetics of reactions among FeSO₄·7H₂O, NaHSO₃ and NaClO₃ was investigated. The PFS product was used in pilot-scale tests at a municipal water treatment facility and gave good results in removal of turbidity and superior results in removal of disinfection byproduct precursors (TOC, DOC, UV-254) when compared with equal doses of ferric chloride.

Keywords: sulfur dioxide removal, air pollution, polymeric ferric sulfate, water treatment.

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INTRODUCTION

The U.S. Department of Energy's Vision 21 calls for new fossil fuel power generation facilities to be coal refineries, where industrial ecology is the framework for design. Industrial ecology describes a system for achieving sustainability in human industrial endeavors, borrowing principles from natural ecosystems to optimize flows of materials and energy between processes, industries, and communities. It is a compelling solution because it provides economic incentives to reduce the adverse environmental impacts of industrial production processes [1].

In these facilities coal will be gasified, allowing for processing of the fuel gas stream to remove sulfur and other pollutants prior to combustion, as well as production of a variety of other byproduct gas and liquid streams that can be used as chemical feedstocks in other processes. Typical desulfurization processes involve lime chemistry [2-4] where byproducts are either of relatively low value, such as gypsum, or they are waste products requiring storage and eventual landfilling. However, new technologies involving regenerable sulfur sorbents have been devised, and many are proven effective for Integrated Gasification Combined Cycle applications [5-9]. These processes remove more than 90% of the sulfur from the hot fuel gas and release it as sulfur dioxide during sorbent regeneration.

The research discussed in this paper investigates use of this sulfur dioxide as a feedstock for synthesis of polymeric ferric sulfate (PFS), a highly effective coagulant used in drinking water and wastewater treatment. PFS is described chemically as $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{(6-n)/2}]_m$ where m is a function of n , $n < 2$ [10]. The polymeric (pre-hydrolyzed) nature of PFS offers higher Fe to SO_4 ratios than ferric sulfate, and consumes less alkalinity during its use due to the hydroxyl groups included in the polymer structure. There is also evidence in the literature that PFS yields a lower rate of floc size development, suggesting a lower rate of formation of hydroxide

precipitates and therefore a faster interaction with contaminants, in comparison with ferric sulfate [11]. It is effective at removing turbidity, as well as some heavy metal contaminants such as arsenic, at lower temperatures and dosages than other agents [10]. It has also been found in this study to be at least as effective as ferric chloride in removal of disinfection byproduct precursors. PFS has been used in place of alum-based agents in some countries because of concerns with lifetime cumulative aluminum intake playing a role in the development of neurological disorders such as Alzheimer's disease [12,13]. Meanwhile, preliminary toxicity studies indicate that drinking water treated with PFS is safe for consumption [14].

Benefits of the process we propose are several. Synthesis proceeds at benign reaction conditions relative to other processes described in the literature [15], thereby reducing construction costs. In addition, it releases no hazardous byproducts into the environment, ensuring that recurring costs associated with material handling and disposal will be lower as well. Overall, we propose an economically and environmentally beneficial solution for sulfur dioxide control.

EXPERIMENTAL

Part 1. Synthesis of Polymeric Ferric Sulfate from SO₂

Methodology

A factorial test was designed to examine the effects of the following four factors on Fe(II) oxidation rate and SO₂ removal efficiency: temperature, SO₂ concentration, nitrogen flowrate, and oxidizer dosing rate. Two levels of each of these four variables were chosen, based on what conditions could be produced reliably in the laboratory. Statistical analyses were

performed on the SO₂ removal efficiency data and are presented in the discussion section. In addition, the effect of temperature alone was examined by conducting a set of trials with all variables held constant while temperature was varied between approximately 35 and 80°C.

Pilot tests of the PFS product were conducted at the Des Moines Water Works, in Des Moines, Iowa. PFS and ferric chloride, the agent currently used there, were compared in their removal of several typical pollutants.

Equipment

The synthesis system consisted in general of a simple simulated sulfur gas being sparged into a temperature-controlled reactor containing a solution of ferrous sulfate and water, from which the outlet gas was collected and analyzed. In addition, periodic liquid samples were analyzed. A schematic diagram of the system is shown in Figure 1.

The reaction vessel used was a 4 dm³ jacketed, sealed glass reaction vessel (Chemglass, Inc., Vineland, NJ). A low-temperature silicone oil (Ace Glass, Inc., Vineland, NJ) was circulated through the jacket by a heated and refrigerated Neslab RTE-111 temperature bath unit. The reactor's outlet gas stream passed through a condenser, which was maintained at approximately 3°C by a Cetac Model 2050 chiller. From there, the sample stream passed through a Permapure model MD-110-48 Nafion tube dryer (Permapure, Inc., Toms River, NJ) and then through a Cole-Parmer 0.2 micron in-line particulate filter. Finally, the sample stream entered a California Analytical Inc. model ZRF NDIR analyzer (manufactured by Fuji Electric Company, Saddle Brook, NJ) and then was discharged into the lab fume hood. The gas analyzer reads zero to 10% SO₂ to 0.01%, and has repeatability of $\pm 0.5\%$ of full scale. It also generates a low-voltage DC signal that was recorded by a desktop computer via a data acquisition board.

1. nitrogen tank	7. condenser
2. sulfur dioxide tank	8. condenser chiller unit
3. reactor heater unit	9. sample gas dryer
4. oxidizer pump	10. sulfur dioxide analyzer
5. stirrer motor	11. data acquisition computer
6. jacketed reaction vessel	

Figure 1. Schematic diagram of PFS synthesis system.

The reaction mixture was stirred at 200 ± 20 rpm for all trials by an adjustable overhead stirrer connected to a Teflon-coated steel shaft and a Teflon impeller. A Cole-Parmer Masterflex model 7553-50 peristaltic pump added sodium chlorate oxidizer solution through a neoprene drip tube in the top of the reactor at a rate controlled by a ChronTrol model XT digital timer (ChronTrol, San Diego, CA). The gas was sparged into the reactor via an 8 mm glass tube, and reaction temperature was measured with a non-mercury glass thermometer inserted into the reaction mixture. Periodic liquid samples were drawn with an additional 8 mm glass tube temporarily inserted through the top of the reactor. All surfaces in contact with the reaction mixture were either Teflon or glass.

Reagents

The ferrous sulfate used in the tests was QC Diamond Brand agricultural ferrous sulfate monohydrate (QC Corporation, Cape Girardeau, MO). The sodium chlorate used was Fisher ACS Certified sodium chlorate. The sulfur dioxide was Sulfur Dioxide, Anhydrous, 99.98% from Matheson Tri-gas Inc., Montgomeryville, PA. All other reagents used were Fisher ACS Certified unless otherwise specified.

The ferrous sulfate was analyzed in the lab for Fe(II) content, and it was found to be $96.5 \pm 1.4\%$ pure relative to stoichiometrically pure ferrous sulfate monohydrate. This number was used in the subsequent batch calculations. The oxidant as used in the reaction was a liquid solution of 33.3 mass-% sodium chlorate in distilled water.

Factorial Synthesis Runs

The calibration of the gas analyzer was verified daily using 1.00% SO₂ in nitrogen (BOC Gases, Des Moines, Iowa). The zero point was set using dried, filtered house air. Prior to each run, 630.0 g of ferrous sulfate and 874.5 ± 0.5 g water were added to the reactor, measured to 0.1 g on a Mettler model PM4000 balance. Similarly, the mass of oxidant solution was also taken before and after the reaction, allowing the amount consumed to be determined.

After adding the ferrous sulfate and water to the empty reactor, the mixture was stirred for approximately 30 minutes before the reaction began to allow the solids to dissolve and the mixture to equilibrate to the temperature of the reactor jacket. At that point, the simulated sulfur gas flow was started, consisting of a blend of SO₂ and nitrogen gases. The gas flowrates were controlled by rotameters, with each inlet concentration being verified by the gas analyzer for use in subsequent removal efficiency calculations. The interval dosing of oxidizer solution was also started with the gas flow. The dosing of oxidizer was set to be one three-second injection of solution every one, two, or three minutes, with each injection containing approximately 0.6 g of sodium chlorate. Details of the reaction conditions are given in Table 1.

Samples were taken from the reactor periodically and analyzed immediately for Fe(II) content. Samples were pulled by opening a port in the reactor lid, inserting a clean glass tube and drawing in a few milliliters of the reaction mixture. Time and temperature were recorded with each sample.

Analysis of PFS Product

Quality parameters for the liquid PFS are well established in the literature [10]. The analyses used were total iron, ferrous iron, and basicity (sometimes referred to as B-value).

Density and pH were also measured.

Table 1. Factorial test conditions and results.

Treatment	Ox. dose (g/min)	Temp (°C)	SO ₂ conc. (%)	N ₂ flow (l/min)	SO ₂ dose (ml/min)	Fe(II) conv. rate (g/hr)	SO ₂ removal eff. (% of inlet)
1	0.60	39.9	1.9	1.2	22.7	126.2	99.5
2	0.59	41.0	2.2	5.0	114.6	107.5	82.6
3	0.60	42.2	5.4	1.2	68.8	114.0	95.6
4	0.59	43.2	5.3	5.0	277.0	89.4	53.2
5	0.61	61.1	1.9	1.2	22.9	135.0	98.0
6	0.60	60.3	2.2	5.0	114.6	119.1	75.8
7	0.69	63.9	5.4	1.2	68.8	117.5	87.8
8	0.60	60.9	5.3	5.0	277.0	100.7	47.4
9	0.20	34.8	1.9	1.2	22.9	35.4	94.3
10	0.21	34.2	2.2	5.0	114.6	36.5	45.4
11	0.19	35.0	5.4	1.2	68.8	27.8	67.9
12	0.20	34.4	5.3	5.0	277.0	25.2	16.9
13	0.19	57.6	1.9	1.2	22.9	39.8	79.8
14	0.19	54.7	2.2	5.0	114.6	33.5	34.9
15	0.20	57.9	5.4	1.2	68.8	33.4	49.2
16	0.20	54.5	5.3	5.0	277.0	28.7	15.5
mid	0.30	47.6	3.7	3.1	117.3	51.2	46.9
mid	0.32	47.9	3.7	3.1	117.3	50.6	50.8
mid	0.31	47.0	3.7	3.1	117.3	49.9	50.0
mid	0.31	47.8	3.7	3.1	117.3	52.3	50.2
mid	0.31	47.6	3.7	3.1	117.3	48.2	51.3
r3	0.61	39.0	5.4	1.2	68.0	123.8	93.0
r8	0.62	59.0	5.3	5.0	277.0	107.1	47.5
r12	0.20	34.2	5.3	5.0	277.0	28.2	24.2
r16	0.22	56.4	5.3	5.0	277.0	31.7	18.0

The total iron content of the PFS was measured by taking a 1.5 g sample of the liquid PFS product and acidifying it with hydrochloric acid. The sample was then heated to boiling, and all iron was reduced to Fe^{2+} by addition of stannous chloride and titanium trichloride. A titration was then performed using a standardized potassium dichromate titrant, with diphenylamine sodium sulfonate indicator. The titration reaction is given here in Equation (1), and the subsequent calculation of total iron in Equation (2).

$$X_1 = \frac{(V)(C)(0.05585)(6)}{M} \times 100\% \quad (2)$$

X_1 =total iron concentration (mass-%) in the PFS liquid, V =volume (mL) of potassium dichromate titrant consumed, C =molar concentration of the titrant, M =mass (g) of liquid PFS sample, and 0.05585 is the mass in grams of 0.001 mole of iron.

The concentration of ferrous iron was determined with a similar titration. A sample of approximately 2.0 g of liquid PFS product was acidified with sulfuric and phosphoric acids, and then titrated with a standardized potassium permanganate solution. The net reaction occurring in this analysis is shown in Equation (3), and the calculation is given in Equation (4).

$$X_2 = \frac{(V - V_0)(C)(0.05585)(5)}{M} \times 100\% \quad (4)$$

X_2 =ferrous iron concentration (mass-%) in the PFS liquid, V =volume (mL) of potassium permanganate titrant consumed, V_0 =volume of the titrant consumed by a distilled water blank, C =molar concentration of the titrant, M =mass (g) of liquid PFS sample, and 0.05585 is the mass in grams of 0.001 mole of iron.

The basicity is the mass ratio of OH^- to Fe^{3+} in the polymer, which gives an indication of the degree to which the iron has been hydrolyzed [10,16-18]. Furthermore, it can be used as a measurement of the extent of polymerization according to the chemical formula for PFS. Basicity was measured by taking a 1.5 g sample of the liquid PFS product and adding to it a known quantity of dilute hydrochloric acid. After allowing the mixture to stabilize for 10 minutes, a small amount of potassium fluoride was introduced to shield the iron, and phenolphthalein was added as an indicator. The solution was then titrated with dilute sodium hydroxide to find the quantity of acid neutralized by the polymer. The basicity is calculated as shown in Equation (5).

$$B = \frac{(V - V_0)(C)(0.0170)}{\frac{(M)(X_1 - X_2)}{18.62}} \times 100\% \quad (5)$$

B=ratio of OH^- to Fe^{3+} (mass-%), V=volume (mL) of sodium hydroxide titrant consumed, V_0 =volume of the titrant consumed by a distilled water blank, M=mass (g) of liquid PFS sample, C=molar concentration of the titrant, 17.0= mass (g) of one mole of OH^- , 0.017= mass (g) of 0.001 mole of OH^- , and 18.62= mass (g) of 1/3 mole iron.

Density of the liquid PFS product was measured using a 10 mL Gay-Lussac adjusted density bottle (supplied by Cole Parmer). A direct correlation was found between total iron content and density of the liquid PFS product, allowing a measurement of one of these parameters to be used to estimate the other. pH was measured from a 1 mass-% solution of the liquid PFS product in water, using a Corning pH Meter 320 calibrated with Fisher certified buffers at $\text{pH } 1.00 \pm 0.02$ and $\text{pH } 4.00 \pm 0.02$. All titrant solutions and calibrations were made using Fisher ACS Certified chemicals and deionized water.

Table 2 shows the acceptable range of the PFS quality parameters used in this study.

Table 2. PFS quality parameters and optimal value ranges.

pH (1 mass-% solution)	Total iron (mass-%)	Iron(II) (mass-%)	Density (g/cm ³)	Basicity (mass-%)
2.0-3.0	≥ 9.0	≤ 0.1	≥ 1.3	8.0-12.0

Basicity and pH ranges given are based on acceptable behavior of liquid PFS in storage and treatment. Too high of either value decreases the stability of the product, with a tendency to form precipitates [10]. Meanwhile, a low basicity value indicates a lower degree of polymerization. A very low Fe(II) content is desirable since this species has a tendency to stain fixtures and surfaces and is difficult to precipitate.

Part 2. Pilot Study on the Application of Produced Polymeric Ferric Sulfate at Des Moines Water Works

Apparatus

The pilot system was designed as an operating model of the Des Moines Water Works production facilities, and is broken into three stages. A schematic diagram is shown in Figure 2. The first stage is a presedimentation block where an initial dose of coagulant is added to raw river water, which makes up approximately half of the total output of the plant. After flocculation and settling sections, the water continues into the treatment stage, where it is supplemented by approximately the same volume of water taken from a series of shallow wells a short distance inland from the riverbank. This water is much less turbid, and therefore doesn't require the presedimentation step. At this point, an additional dose of coagulant, equal to twice

the first, is added to the flow. Lime slurry is also dosed to achieve a pH of 10.6 in the final settling basin. Just before leaving the treatment stage, a small amount of CO₂ is added to the water to reduce the pH to the final production level. A small dose of polyphosphate is also added to prevent lime caking in the filters. Final filtration is effected with two parallel sand filtration columns.

Figure 2. Schematic diagram of Des Moines Water Works pilot plant.

PFS and ferric chloride coagulants were compared by dosing premixed stock solutions at 2 ppm, 3 ppm, and 4 ppm (as Fe) on alternate days. Each agent-dose combination was started in the afternoon, and system was allowed to stabilize overnight. The next day six hourly turbidity samples were taken before the next agent-dose combination was started. Measurements of turbidity were made at three points: raw water, end of presedimentation stage, and end of treatment stage (pre-filter), using a Hach 2100AN turbidimeter calibrated daily with Gelex Secondary Standards. The following measurements were also made of the raw and pre-filter waters at the time of the last turbidity sample (with the exception of those at 4 ppm, taken with the first turbidity sample): TOC and DOC by a Shimadzu TOC-5000, UV-254 by a Shimadzu

1201 UV-VIS, and total alkalinity by titration. Analyses were made according to standard methods on file in the DMWW laboratory.

Part 3. Study on the Kinetics of Oxidation of Fe^{2+} and HSO_3^{2-} with ClO_3^-

Methods

The reaction between NaClO_3 , FeSO_4 and NaHSO_3 can be expressed as follows

Assuming that $c_{\text{NaClO}_3,0}$, $c_{\text{FeSO}_4,0}$ and $c_{\text{NaHSO}_3,0}$ represent the initial mole concentrations of reactants

NaClO_3 , FeSO_4 and NaHSO_3 , respectively, initial concentration of NaCl is 0, and c_{Cl^-} is the

concentration of NaCl or Cl^- generated during the reaction or the quantity of NaClO_3 or ClO_3^-

consumed, then the concentrations of all the reactants at any time, t , should be $c_{\text{NaClO}_3,0} - c_{\text{Cl}^-}$,

$c_{\text{FeSO}_4,0} - 2c_{\text{Cl}^-}$, $c_{\text{NaHSO}_3,0} - 2c_{\text{Cl}^-}$, respectively, and the increasing rate of c_{Cl^-} can be expressed as

follows

$$\frac{dc_{\text{Cl}^-}}{dt} = k(c_{\text{NaClO}_3,0} - c_{\text{Cl}^-})^{n_1} (c_{\text{FeSO}_4,0} - 2c_{\text{Cl}^-})^{n_2} (c_{\text{NaHSO}_3,0} - 2c_{\text{Cl}^-})^{n_3} \quad (7)$$

where k represents the global rate coefficient and exponents n_1 , n_2 , and n_3 are the orders with

respect to reactants NaClO_3 , FeSO_4 and NaHSO_3 . Reaction orders n_1 , n_2 and n_3 are not

necessarily integers because reaction 6 is not an elementary reaction.

Special initial reactant concentrations need to be designed in order to derive reaction orders n_1 , n_2 and n_3 . For example, when $c_{\text{NaClO}_3,0}$ and $c_{\text{FeSO}_4,0}$ are much larger than $c_{\text{NaHSO}_3,0}$,

c_{NaClO_3} and c_{FeSO_4} at any time t of the reaction 6 can be considered as constants, or

$$c_{\text{NaClO}_3} = c_{\text{NaClO}_3,0} - c_{\text{Cl}^-}$$

$$\approx c_{NaClO_3,0} \quad (8)$$

$$c_{FeSO_4} = c_{FeSO_4,0} - 2c_{Cl^-}$$

$$\approx c_{FeSO_4,0} \quad (9)$$

and then Equation 7 can be simplified as

$$\frac{dc_{Cl^-}}{dt} = k_3 (c_{NaHSO_3,0} - 2c_{Cl^-})^{n_3} \quad (10)$$

$$\text{where } k_3 = kc_{NaClO_3,0}^{n_1} \cdot c_{FeSO_4,0}^{n_2} \quad (11)$$

Taking the logarithm of Equation 10 yields

$$\log \frac{dc_{Cl^-}}{dt} = n_3 \log(c_{NaHSO_3,0} - 2c_{Cl^-}) + \log k_3 \quad (12)$$

The c_{Cl^-} at any time, t , of the reaction was measured with a Dionex Series 4000i ion

chromatograph, which leads to the establishment of the relationship of c_{Cl^-} vs. time.

Consequently, the reaction order with respect to $NaHSO_3$, n_3 , can be derived by curve fitting

$\log \frac{dc_{Cl^-}}{dt} \sim \log(c_{NaHSO_3,0} - 2c_{Cl^-})$. It is noted that the value of $\frac{dc_{Cl^-}}{dt}$ at time t was obtained from

$c_{Cl^-} - t$ curve by using a tangential approach [19]. Similarly, when $c_{NaClO_3,0}$ and $c_{NaHSO_3,0}$ are

much larger than $c_{FeSO_4,0}$, n_2 , can be obtained by curve fitting $\log \frac{dc_{Cl^-}}{dt} \sim \log(c_{FeSO_4,0} - 2c_{Cl^-})$,

which is based on the relationship of $c_{Cl^-} \sim t$ attained through experimental data. In addition,

when the initial concentrations of the reactants $FeSO_4$ and $NaHSO_3$, $c_{FeSO_4,0}$ and $c_{NaHSO_3,0}$, are

much larger than $c_{NaClO_3,0}$, the reaction order with respect to $NaClO_3$, n_1 , can be inferred by

curve fitting the experimental $c_{Cl^-} \sim t$ relationship and its corresponding $\log \frac{dc_{Cl^-}}{dt} \sim$

$\log(c_{NaClO_3,0} - c_{Cl^-})$ plot.

Furthermore, the initial reactant concentrations with the relationship of $2c_{NaClO_3,0} = c_{FeSO_4,0} = c_{NaHSO_3,0}$ were designed to derive global rate coefficient k at a known temperature.

Given initial concentrations of three reactants, Equation 7 can be reorganized as

$$\begin{aligned} \frac{dc_{Cl^-}}{dt} &= k(c_{NaClO_3,0} - c_{Cl^-})^{n_1} \cdot 2^{n_2} (c_{NaClO_3,0} - c_{Cl^-})^{n_2} \cdot 2^{n_3} (c_{NaClO_3,0} - c_{Cl^-})^{n_3} \\ &= 2^{n_2+n_3} \cdot k \cdot (c_{NaClO_3,0} - c_{Cl^-})^{n_1+n_2+n_3} \end{aligned} \quad (13).$$

Integration of Equation 8 with the boundary condition ($c_{Cl^-,0} = 0$)

$$\int_0^Z \frac{dZ}{(c_{NaClO_3,0} - c_{Cl^-})^{n_1+n_2+n_3}} = \int_0^t 2^{n_2+n_3} \cdot k dt \quad (14)$$

results in

$$(c_{NaClO_3,0} - c_{Cl^-})^{1-(n_1+n_2+n_3)} - c_{NaClO_3,0}^{1-(n_1+n_2+n_3)} = 2^{n_2+n_3} \cdot k \cdot (n_1 + n_2 + n_3 - 1)t \quad (15)$$

or

$$k = \frac{(c_{NaClO_3,0} - c_{Cl^-})^{1-n_1-n_2-n_3} - c_{NaClO_3,0}^{1-(n_1+n_2+n_3)}}{2^{n_2+n_3} (n_1 + n_2 + n_3 - 1)t}. \quad (16)$$

Therefore, the global rate coefficient k at a specified temperature can be determined using

Equation 16 given that n_1 , n_2 and n_3 have been obtained, and c_{Cl^-} at time t is measured.

The temperature range, 40-80 °C, important for the FeSO₄-based sulfur removal approach, is reasonably narrow, consequently variations of the pre-exponential factor and the activation energy of reaction 6 with temperature can be ignored [19-20]. Therefore, the relationship

between the global rate constant (k) and reaction temperature (T) can be expressed in the empirical Arrhenius form below

$$k = A \exp\left(-\frac{E}{RT}\right), \quad (17)$$

where A is the pre-exponential factor, E is the activation energy of reaction 6 and R is the ideal gas constant. The plot of $\log k$ versus $1/T$ can be used to extract values for A and E in Arrhenius form (Equation 17), since the slope and interception of such a plot are $-E/2.303R$ and $\log A$, respectively.

Apparatus

The reactions between NaClO_3 , FeSO_4 and NaHSO_3 were conducted in a 1.0 L double-wall glass reactor with three inlets on the top. A stir set through the central inlet of the reactor was used to mix the reactants during the reaction. A thermometer passed through another inlet to measure the temperature in the reactor. The prepared reactant solutions were added through the additional inlet. A DL-501 thermostat was used to control the temperature in the reactor by circulating water around the reactor. Water and solutions of reactants NaClO_3 , FeSO_4 and NaHSO_3 were prepared in advance and stored in separate vessels. All the chemicals used for the reactions and analysis of this study were analytical grade.

Measurement of Cl^- Concentration

The concentrations of Cl^- during the reaction at different times were measured for monitoring the extent of reaction. To this end, the reactions in the reactor need to be stopped immediately after a desired period of reaction time. Sodium hydroxide solution (0.1 M) was prepared and used for that purpose, since the reaction between NaClO_3 , FeSO_4 and NaHSO_3

stops when the pH of reaction 1 is higher than 7 [21]. The pH was monitored using a Fisher Scientific model 310 pH meter. Change of c_{Cl^-} was monitored for 240 seconds in each test. Rates for most non-zero and positive order reactions are higher at early times than later period; accordingly, a shorter sampling interval, 5 seconds, was chosen for the first 30 seconds of c_{Cl^-} monitoring time. This increased the density of the data points in the initial period of $c_{Cl^-} \sim t$ plots, where the $c_{Cl^-} \sim t$ curves typically appear steep, and thus improved the accuracy of curve fitted $c_{Cl^-} \sim t$ relationship. Ten seconds was used as the time interval for the remaining sampling period. Samples were taken using pipettes. The value of c_{Cl^-} was determined using a Dionex Series 4000i ion chromatograph. The instrument was calibrated with a set of NaCl standard solutions at concentrations of 0, 50, 100, 150 and 200 ppm.

Preparation of the Solution for the Determination of Reaction Orders

All the tests designed for the determination of reaction orders were conducted at 60 °C. As previously mentioned, the initial concentration of the reactant for which the reaction order is to be determined should be much smaller than other reactants. Accordingly, 0.4425 mM NaClO₃, 88.5 mM FeSO₄ and 88.5 mM NaHSO₃ solutions ($c_{FeSO_4,0} = c_{NaHSO_3,0} \gg c_{NaClO_3,0}$) were prepared and used for the determination of the reaction order of NaClO₃, 44.25 mM NaClO₃, 0.885 mM FeSO₄ and 88.5 mM NaHSO₃ ($2 c_{NaClO_3,0} = c_{NaHSO_3,0} \gg c_{FeSO_4,0}$) solutions for the determination of reaction order of FeSO₄, and 44.25 mM NaClO₃, 88.5 mM FeSO₄ and 0.885 mM NaHSO₃ solutions ($2 c_{NaClO_3,0} = c_{FeSO_4,0} \gg c_{NaHSO_3,0}$) for the determination of reaction order of NaHSO₃.

Preparation of Solutions for the Determination of Arrhenius Form

Rate constants were calculated at different temperatures in order to determine the Arrhenius equation for reaction 6. To obtain the data needed for these purposes, 44.25 mM NaClO₃, 88.5 mM FeSO₄ and 88.5 mM NaHSO₃ solutions ($2c_{NaClO_3,0} = c_{FeSO_4,0} = c_{NaHSO_3,0}$) were prepared and used for reactions at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C. The concentrations of Cl⁻ generated, c_{Cl^-} , were measured 180 s after the reactions started. Rate constants at different temperatures were calculated using Equation 17.

RESULTS AND DISCUSSIONS

Part 1. Synthesis of Polymeric Ferric Sulfate from SO₂

Stoichiometric Model

The SO₂ absorption and Fe(II) conversion are believed to occur via the pair of reactions given in Equations (18) and (19),

where sodium chlorate is used to oxidize the S(IV) to S(VI) and Fe(II) to Fe(III). The iron oxidation is dependent to some extent upon the acid produced in Equation 18. Water is produced in Equation 19 and eventually incorporated into the polymer through subsequent hydrolysis.

Examination of the reactions gives some insight into behavior of the basicity quality parameter. In the semi-batch system used in this investigation, basicity was found to decrease steadily if the reaction was continued after the Fe(II) concentration approached zero. At that

point the iron reaction rate becomes very slow, and the acid produced by the absorption of the SO_2 is able to accumulate in solution. This increased availability of acid steadily reduces the basicity of the PFS. Therefore the amount of time that the SO_2 absorption was continued after the Fe(II) was consumed allowed control of this parameter.

Batch calculations were made based on the reaction stoichiometry as given above. Production of a 2 kg batch of liquid PFS with 10% iron was assumed, and stoichiometric quantities of ferrous sulfate, sodium chlorate, and SO_2 were calculated. Finally, the remaining water required was found by difference, taking into account the waters of hydration in the ferrous sulfate. The iron measurements made during the course of the reactions reveal that the initial Fe(II) concentration, equal at that point to the total iron, is greater than 10%. This is due to the fact that as the reaction progresses, sodium chlorate solution and SO_2 are added to the mixture, decreasing the total iron concentration toward an endpoint target of 10%. It was found that the conversion of Fe(II) to Fe(III) was completed before the stoichiometric quantity of SO_2 was added, with some variation depending on the rate of SO_2 absorption and oxidant dosing, due to the fact that some of the protons required for this reaction were provided by the water in solution. Thus, the synthesis required less SO_2 than originally calculated.

A mole balance of the reactants is given in Table 3, showing that the quantity of SO_2

Table 3. Reactant mole balances showing net oxidant accumulation and stoichiometric ratios.

Treatment	SO_2 abs. rate (mmol/min)	Ox. input rate (mmol/min)	Fe(II) conv. rate (mmol/min)	Net ox. accum. (mmol/min)	SO_2 :Fe(II) (% stoichiometric)
1	0.797	5.634	37.681	-0.912	4.2
2	3.342	5.540	32.122	-0.928	20.8
3	2.321	5.634	34.036	-0.813	13.6
4	5.205	5.540	26.714	-0.647	39.0
5	0.791	5.728	40.327	-1.257	3.9
6	3.067	5.634	35.560	-1.315	17.2
7	2.132	6.479	35.096	-0.081	12.2
8	4.637	5.634	30.088	-0.927	30.8
9	0.761	1.878	10.576	-0.139	14.4

10	1.837	1.972	10.913	-0.459	33.7
11	1.649	1.784	8.302	-0.149	39.7
12	1.653	1.878	7.513	0.075	44.0
13	0.644	1.784	11.876	-0.410	10.9
14	1.412	1.784	10.013	-0.355	28.2
15	1.195	1.878	9.969	-0.182	24.0
16	1.516	1.878	8.566	-0.055	35.4

absorbed is between 3.9% and 44.0% of the amount predicted from the reaction stoichiometry given in Eq. (6) and (7). A net accumulation of oxidant was also calculated by taking the oxidant input rate and subtracting the SO₂ absorption and Fe(II) conversion rates divided by their stoichiometric coefficients from Equations. 18 and 19. It is a small negative quantity in all cases but one, supporting the proposed stoichiometric model if consideration is given to the net storage of SO₂ by the solution saturated with the gas. These calculations assume 10% total iron in the reaction solution, atmospheric pressure in the reactor, and gas flowrates measured at 20°C.

Factorial Analysis

The factors used were temperature, oxidant addition rate, SO₂ concentration, and nitrogen flowrate. Sulfur dioxide removal efficiency and Fe(II) oxidation rate data from a typical run in the factorial analysis are shown in Figure 3. To obtain trends and statistical results, average SO₂ removal efficiencies were calculated for each run by taking a mean of all the data points starting 30 minutes after the reaction began and running until the last Fe(II) data point was collected and the reaction was stopped. The initial 30-minute period was omitted from the average to allow the outlet gas concentration to stabilize. Similarly, a linear regression was performed on the five Fe(II) data points measured during the reaction, as well as one initial point calculated from the raw materials added to the reactor, to find a rate of Fe(II) conversion for each run. The Fe conversion data expressed in the plot was based on a total iron concentration of 10%. The R²

Figure 3. Typical factorial run data (treatment 6).

values for the linear fit were above 0.90 in all cases except one, and greater than 0.95 in most.

These two values, average SO₂ removal efficiency and Fe(II) conversion rate, were taken as the quantitative results of each run to be used in the analysis. These values are shown in Table 1.

Due to limitations of the experimental apparatus, the data collected in this study does not allow clear separation of the effects of nitrogen flowrate and SO₂ concentration. Therefore it may be more illustrative to consider total SO₂ dose, which is calculated from the nitrogen flowrate and SO₂ concentration, and gives a volumetric flow of SO₂ into the reactor as mL per minute pure SO₂.

Some trends are evident in the data. Foremost it can be seen that the oxidant dosing rate has the most profound effect on both the Fe(II) and SO₂ conversion. In addition, for a given

temperature and oxidant dose, SO₂ removal efficiency is inversely proportional to the inlet SO₂ dose due to the oxidant being a limiting reagent. Next, it can be seen that for a given SO₂ and oxidant dose, the rate of Fe(II) conversion increases with temperature. Conversely, SO₂ removal efficiency decreases markedly with temperature under the same conditions, due to the faster Fe(II) reaction consuming more of the available oxidant. The effect is especially strong in runs 9-16 where the amount of available oxidant is relatively low. This result suggests that the iron reaction is more sensitive to temperature than the SO₂ reaction.

The statistical analysis for this study was based on 16 factorial runs, and five duplicates of one additional set of conditions near the midpoint of the factorial set. The SAS software package (The SAS Institute, Cary, NC) was used for all analyses. The 16 factorial runs were done in a randomized order, while the midpoints were made as a separate block following. In addition, a repetition of the first four runs was done after the midpoints to examine blocking effects in runs performed after the reactor was replaced due to failure of the drain valve following the final run of the 16 factorial runs. It was determined that blocking effects were not significant between the original and replacement reactors at the 5 % level. Analysis of covariance was used to look for evidence of interaction of the reactor with the factors and treatments, and none was found at the 10% level.

Regression models were analyzed to investigate the effects involved between the factors. The assumed model was as shown in Equation 20, where the factors oxidant, temperature, nitrogen, and sulfur dioxide are abbreviated by O, T, N, and S, respectively. The terms ρ_1 and ρ_2 are intercepts for each reactor, and β_1 - β_4 , β_5 - β_8 , and β_9 - β_{14} are coefficients for the linear, quadratic, and two-way cross-product effects, respectively.

$$\begin{aligned}
y = & \rho_1 \cdot 1_{[\text{reactor}=1]} + \rho_2 \cdot 1_{[\text{reactor}=2]} + \beta_1 O + \beta_2 T + \beta_3 S + \\
& \beta_4 N + \beta_5 O^2 + \beta_6 T^2 + \beta_7 S^2 + \beta_8 N^2 + \beta_9 OT + \\
& \beta_{10} OS + \beta_{11} ON + \beta_{12} TS + \beta_{13} TN + \beta_{14} SN
\end{aligned} \tag{20}$$

This model was compared to a reduced model containing only the blocking and linear effects. It was found using type-1 sum of squares that the reduced model was not significantly worse at describing the outcome. This was verified using a lack-of-fit test. In addition, the model in Equation 20 was compared to a full ANOVA model by treating each of the 17 treatment combinations as qualitative variables and performing a lack-of-fit test between the two resulting models. The result was that there was a significant amount of variance that was not explained by the model in Equation 20, which is likely to lie in three- or four-way interactions between the factors.

Both the ANOVA analysis and the linear effects model indicate that maximum SO₂ removal occurs when oxidant concentration is high and the other three factors are low. Presented in Table 4 is a comparison of all treatments to the estimated best, shown at the top, in terms of SO₂ removal efficiency. The p-values shown reflect application of the Dunnett-Hsu adjustment to control the probability of a type-1 error at 5% when taking all comparisons simultaneously. LS Mean values are the removal efficiencies calculated for each treatment combination by a least squares method, accounting for the error adjustment. It is seen that the top five treatments are not significantly different from each other, and that all but one have a high oxidant level and low levels of one or more of the other three factors. The only treatment in the group that has a low oxidant level also has low levels of all three other factors. Thus, the statistical analysis confirms that the oxidant dose is the most influential factor among the four on the SO₂ removal efficiency in this study.

Table 4. Statistical comparison of SO₂ removal efficiency in factorial treatments.

Treatment	Ox. dose (g/min)	Temperature (°C)	SO ₂ conc. (vol-%)	N ₂ flow (l/min)	LS Mean	P-value
1	0.60	39.9	1.87	1.2	100.41	-
5	0.61	61.1	1.87	1.2	98.91	0.9999
9	0.20	34.8	1.87	1.2	95.21	0.6594
3	0.60	42.2	5.42	1.2	94.30	0.4057
7	0.69	63.9	5.42	1.2	88.71	0.0657
2	0.59	41.0	2.24	5.0	83.51	0.0107
13	0.19	57.6	1.87	1.2	80.71	0.0045
6	0.60	60.3	2.24	5.0	76.71	0.0015
11	0.19	35.0	5.42	1.2	68.81	0.0002
4	0.59	43.2	5.25	5.0	54.11	0.0000
15	0.20	57.9	5.42	1.2	50.11	0.0000
17	0.30	47.6	3.65	3.1	48.92	0.0000
8	0.60	60.9	5.25	5.0	47.45	0.0000
10	0.21	34.2	2.24	5.0	46.61	0.0000
14	0.19	54.7	2.24	5.0	35.81	0.0000
12	0.20	34.4	5.25	5.0	20.55	0.0000
16	0.20	54.5	5.25	5.0	16.75	0.0000

Temperature Effects

A series of four data runs was performed at different temperatures, with oxidant and gas conditions held constant. SO₂ concentration was set at the 5% level, while nitrogen flowrate was at 1 l/min, and oxidizer was dosed at 1-minute intervals. Results are shown in Figure 4. The rate of Fe(II) conversion increased with temperature, while SO₂ absorption decreased. This supports the observation from the factorial data that the iron reaction is more sensitive to temperature than the SO₂ reaction. As the rate of the iron conversion increases it sequesters more of the oxidant, a limiting reagent for both reactions, which makes less available for the oxidation of SO₂ and, in turn, reduces its absorption from the gas phase.

Figure 4. Effect of temperature on absorption rate of SO₂ and conversion rate of Fe(II) (SO₂ concentration was 2.2%, nitrogen flowrate was 5.0 l/min, and oxidant was dosed at 0.60 g/min for all runs shown)

Part 2. Pilot Study on the Application of Produced Polymeric Ferric Sulfate in Des Moines

Water Works

The pilot study looked primarily at turbidity and disinfection byproduct precursor removal. Other water quality parameters such as alkalinity, temperature, and pH were also measured. Due to the fact that this study was done in a pilot plant situation, raw water quality varied significantly between runs and during the course of each run. Therefore trends will be highlighted rather than repeatable quantitative results.

Over the course of the study period, the temperature of the raw water was 28-30°C and its pH varied between 7.6 and 7.9. Turbidities at the three stages of treatment as well as overall removal efficiencies for the six agent-dose combinations are shown in Table 5. The turbidity

Table 5. Pilot study turbidity and alkalinity removal results.

	2 ppm		3 ppm		4 ppm	
	PFS	FeCl ₃	PFS	FeCl ₃	PFS	FeCl ₃
Raw water NTU	17.5	15.1	14.5	14.1	14.1	14.0
Presed. NTU	5.0	4.3	5.2	3.3	3.8	4.3
Pre-filter NTU	2.0	3.0	2.9	1.5	2.4	1.7
NTU reduction	88.6%	80.1%	80.0%	89.4%	83.0%	87.9%
Raw water Alk.	167	163	166	171	169	169
Pre-filter Alk.	68	63	70	53	55	57
Alk. Consumption	59%	61%	58%	69%	67%	66%

figures given are an average of six hourly measurements. The turbidity removal capabilities of PFS and ferric chloride are not shown to differ greatly in this study, although PFS does show promise at the lower dose; more studies are being carried out to explore this. It was noted by the

Table 6. Disinfection byproduct precursor removal in pilot study.

	2 ppm		3 ppm		4 ppm	
	PFS	FeCl ₃	PFS	FeCl ₃	PFS	FeCl ₃
Raw water TOC	4.96	5.71	5.95	5.80	6.23	5.44
Pre-filter TOC	2.39	1.95	2.16	2.07	2.01	2.01
TOC reduction	51.8%	65.9%	63.7%	64.3%	67.7%	63.0%
Raw water DOC	3.04	3.08	3.41	2.75	3.33	3.60
Pre-filter DOC	1.80	2.17	2.12	2.11	2.01	2.01
DOC reduction	40.8%	29.6%	37.8%	23.3%	39.6%	44.2%
Raw water UV-254	0.104	0.077	0.130	0.072	0.178	0.127
Pre-filter UV-254	0.036	0.072	0.049	0.046	0.046	0.041
UC-254 reduction	65.4%	6.5%	62.3%	36.1%	74.2%	67.7%

plant operators that in comparison to ferric chloride, PFS produced a larger and less dense floc that was slower to settle. Initial and final alkalinities are also given in Table 5, in mg/l as CaCO₃, with corresponding removal efficiencies. Raw water alkalinities were fairly consistent throughout the trials, and the data confirms that in general PFS did consume less alkalinity than ferric chloride during the treatment process. Table 6 shows removal data for TOC, DOC, and

UV-254 disinfection byproduct precursors, given in mg/l, for the same agent-dose combinations. TOC removal was higher with PFS at 3 ppm and 4 ppm, while removal of DOC was greater with PFS at 2 ppm and 3 ppm. UV-254 removal was higher with PFS at all three dosages. These trends show that PFS is highly effective at removal of organic matter, which is consistent with other studies done on polymeric inorganic coagulants [17,18].

Part 3. Study on the Kinetics of Oxidation of Fe^{2+} and HSO_3^{2-} with ClO_3^-

$c_{\text{Cl}^-} \sim t$ Relationships

The results of the tests on the change of c_{Cl^-} with time under different combinations of initial reactant concentrations are shown in Figures 5, 6 and 7. The trends of the curves in Figures 5, 6 and 7 indicate that none of the reaction orders for NaClO_3 , FeSO_4 and NaHSO_3 were zero, since none of those plots is linear. All three of the curves, shown in Figures 5, 6 and 7 rise steeply at the beginning of the reaction and become flat after about 100 seconds, however, each has a different initial rate (within the first 5 seconds). From this, one can determine that the reaction rates of NaClO_3 , FeSO_4 and NaHSO_3 are closely correlated with initial reactant concentrations.

Figure 5. Change of Cl^- concentration with time ($c_{NaClO_3,0} = 0.04425$ mM, $c_{FeSO_4,0} = 88.5$ mM and $c_{NaHSO_3,0} = 88.5$ mM, $T = 60$ °C)

Figure 6. Change of Cl^- concentration with time ($c_{NaClO_3,0} = 44.25$ mM, $c_{FeSO_4,0} = 0.0885$ mM and $c_{NaHSO_3,0} = 88.5$ mM, $T = 60$ °C)

Figure 7. Change of Cl^- concentration with time ($c_{NaClO_3,0} = 44.25$ mM, $c_{FeSO_4,0} = 88.5$ mM and $c_{NaHSO_3,0} = 0.0885$ mM, $T = 60$ °C)

Derivation of Reaction Orders

The data points in Figures 8, 9 and 10 were derived numerically from Figures 5, 6 and 7 using a tangential method [19]. The resulting linear plots, Figures 8, 9 and 10, each have a regression coefficient higher than 0.95. The slopes of the lines are the reaction orders of reactants $NaClO_3$, $FeSO_4$ and $NaHSO_3$, and are approximately 1.1, 1.1 and 1.4, respectively. Therefore, Equation 7 can be expressed as follows:

$$\frac{dc_{Cl^-}}{dt} = k(c_{NaClO_3,0} - c_{Cl^-})^{1.1}(c_{FeSO_4,0} - 2c_{Cl^-})^{1.1}(c_{NaHSO_3,0} - 2c_{Cl^-})^{1.4} \quad (21)$$

Figure 8. Determination of reaction order of NaClO_3 ($c_{\text{NaClO}_3,0} = 0.04425 \text{ mM}$, $c_{\text{FeSO}_4,0} = 88.5 \text{ mM}$ and $c_{\text{NaHSO}_3,0} = 0.0885 \text{ mM}$, $T = 60^\circ\text{C}$)

Figure 9 Determination of reaction order of FeSO_4 ($c_{\text{NaClO}_3,0} = 44.25 \text{ mM}$, $c_{\text{FeSO}_4,0} = 0.0885 \text{ mM}$ and $c_{\text{NaHSO}_3,0} = 88.5 \text{ mM}$, $T = 60^\circ\text{C}$)

Figure 10. Determination of reaction order of NaHSO_3 ($c_{\text{NaClO}_3,0} = 44.25 \text{ mM}$, $c_{\text{FeSO}_4,0} = 88.5 \text{ mM}$ and $c_{\text{NaHSO}_3,0} = 0.0885 \text{ mM}$, $T = 60 \text{ }^\circ\text{C}$)

Establishment of Arrhenius Form

The average concentrations of Cl^- in the reaction system at 150 seconds under temperature $40 \text{ }^\circ\text{C}$, $50 \text{ }^\circ\text{C}$, $60 \text{ }^\circ\text{C}$, $70 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ are shown in Table 7. Global rate coefficient k

Table 7. Cl^- concentrations (c_{Cl^-}) at 150 s and global rate coefficients calculated for reaction 1 under the different temperature ($c_{\text{NaClO}_3,0} = 44.25 \text{ mM}$, $c_{\text{FeSO}_4,0} = 88.5 \text{ mM}$ and $c_{\text{NaHSO}_3,0} = 88.5 \text{ mM}$)

Temperature ($^\circ\text{C}$)	40	50	60	70	80
c_{Cl^-} (mM)	4.73	7.04	9.02	10.5	11.6
k ($\text{mol}^{-2.6} \cdot \text{dm}^{2.6} \cdot \text{s}^{-1}$)	17.3	43.3	102.3	230.0	494.0

at $40 \text{ }^\circ\text{C}$, $50 \text{ }^\circ\text{C}$, $60 \text{ }^\circ\text{C}$, $70 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$, calculated with the c_{Cl^-} values in Table 1 and Equation

11, are also listed in Table 7. From these global rate coefficients, it is evident that rate increases

with temperature. The global rate coefficient increases by approximately 100% when temperature increases 10 °C in the temperature range tested, which is consistent with van't Hoff rule [22].

Based on the results in Table 7, the relationship between $\log k$ and $1/T$ was determined as demonstrated in Figure 11. A regression coefficient of 0.98 in Figure 11 indicates that a good

Figure 11. Determinations of activation energy and the pre-exponential factor in Arrhenius form ($c_{\text{NaClO}_3,0} = 44.25 \text{ mM}$, $c_{\text{FeSO}_4,0} = 88.5 \text{ mM}$, $c_{\text{NaHSO}_3,0} = 88.5 \text{ mM}$ and $t = 150 \text{ s}$)

linear relationship between $\log k$ and $1/T$ exists. Therefore, the Arrhenius form of reaction 1 can be expressed as

$$k = 7.2 \times 10^{12} \cdot e^{-\frac{8291}{T}} (\text{mol}^{-2.6} \cdot \text{dm}^{2.6} \cdot \text{s}^{-1}) \quad (14)$$

In conclusion, the reaction between NaClO_3 , FeSO_4 and NaHSO_3 , potentially used for sulfur removal from flue gas, was characterized. A kinetic model, including reaction orders and activation energy, has been established by tracking the change of the concentration of the

chlorine ion with time during the reactions with different initial reactant concentrations. This study is essential in understanding the underlying chemical mechanism of the new sulfur removal technique, which can provide the basis for the design and optimization of the process.

CONCLUSIONS

Sulfur dioxide in a simulated flue gas has been successfully used to produce a high efficient water and wastewater treatment agent, polymeric ferric sulfate. The sulfur removal efficiencies of the proposed technique have been proved to be higher than 90%. Factors affecting sulfur removal efficiencies include reaction temperature and dosages of oxidizing agent and absorbing agent. Pilot study results obtained from Des Moines Water Treatment have shown that PFS is an effective coagulant. It can be used to remove both turbidity and organic pollutants in water. Even though the kinetics of reactions used for the removal of sulfur in this research cannot be conducted, study on the kinetics of a similar reaction has shown the initial concentration of each reactant has effect on the oxidation of HSO_3^{2-} and Fe^{2+} . Both of them are the very important raw material in the proposed sulfur removal approach.

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APPENDIX

STANDARD OPERATING PROCEDURES FOR POLYMERIC FERRIC SULFATE SYNTHESIS SYSTEM

Preparation for the Reaction

Ensure that the hood fan is operating before starting the reaction. The **green light only**, indicating “normal” operation, must be illuminated.

Personal protective equipment (PPE) that must be worn during the operation of the reactor: Goggles, neoprene gloves, and lab coat.

Note: The chiller and RTE bath circulator are operated with a controller that is always on. The chiller is set to 2°C and the RTE to 60°C. No adjustment is necessary unless the bath temperature needs to be raised or lowered for the reaction. For additional information on the operation of the controller, refer to the controller operations manual.

1. Turn on the SO₂ analyzer with the switch on the left front of the unit. The analyzer requires at least 30 minutes to warm up.
2. Adjust temperature of the bath circulator by manipulating the directional arrows after pressing enter. After reaching the desired temperature, press enter twice on the front of the RTE. If further instructions are needed, refer to the RTE operations manual.
3. Put the oxidant solution, if required, into the flask in front of the peristaltic pump and insert the tubing for the pump into the flask. Insert the other end of the tubing, with

adaptor, into the closest neck of the reactor lid. Clip on the adaptor with a 24/40 keck clip.

4. Ensure that the drain tube at the bottom of the vessel is closed.
5. Place the lid on top of the reactor and secure with the metal fastener.
6. Put FeSO_4 or fly ash solutions into the vessel through a 24/40 neck opening.
7. Insert the stirrer into the large neck opening in the lid of the reactor and use a 45/50 keck clip to firmly attach the neck adaptor and stirrer to the lid. Plug in the stirrer to the wall socket in the hood. To adjust the speed of the stirrer, turn the knob on the top of the motor right or left as applicable, not to exceed 200rpm.
8. Insert a sparge tube into the left neck of the reactor lid and attach the tubing from the gas lines to the end of the sparge tube. Turn the screw of the metal fastener so it is firmly attached and does not leak. Fasten the neck adaptor containing the spurge tube to the lid of the reactor with a 24/40 keck clip.
9. Insert the condenser to the back neck opening of the reactor lid and fasten with a 24/40 keck clip.
10. Insert a glass plug into the front neck opening of the reactor lid and fasten with a 24/40 keck clip.
11. Turn the hand wheel on the breathing air gas cylinder to turn on the flow and adjust so the hissing through the Nafion drying tube is approximately 1-2 LPM.
12. Turn on the PC and enter the MS-DOS commands to collect data from the SO_2 analyzer as outlined in the instruction sheet attached to the computer. At the prompt, type in SO_2 . The program will then ask for a filename and a reaction temperature ($^{\circ}\text{C}$). Enter appropriate responses.

Conduct the Reaction

During all the operations of the reactor, the pressure gauge on the inlet gas line must be monitored. Back-pressure buildup of **less than 10 psig** will ensure the successful and safe operation of the system. Pressure regulators on the cylinders should be adjusted to the output of no more than 10 psig.

SO₂ Operations

13. Turn the hand wheel on the N₂ gas on. Adjust the associated flow meter to deliver 5 SCFH N₂.
14. Turn on the peri-pump and adjust knob or program on the control box to deliver required amount of oxidant. For further information of the programming of the peri-pump, or other attached equipment, refer to the controller operation manual.
15. Turn the hand wheel of the SO₂ gas on. Adjust the associated flow meter to deliver the desired volume. The concentration can be verified by passing the inlet gas through the analyzer and is set by individual experimental design. The switch on the outlet gas line must be in the perpendicular position relative to the tubing.
16. Turn on outlet gas flow meter to enable the flow of outlet gas to the analyzer. To determine the percent concentration of SO₂ in the outlet gas, the switch on the outlet gas line must be in the parallel position relative to the tubing.
17. For calibration instructions of the SO₂ analyzer, refer to the manual.

Shutdown the Reactor

18. Turn off all of the gas cylinders. To attempt to remove the sulfur dioxide out of the system, turn off the cylinders in the following order: SO₂, N₂, breathing air.
19. Turn off the peristaltic-pump by stopping the program on the controller or turning off the knob on the pump.
20. Stop the data collection program on the PC by pressing any button. Copy to a disk, if necessary. Turn off PC and monitor.
21. Turn off the SO₂ analyzer with the switch on the front of the unit.
22. Unplug the stirrer from the wall outlet.
23. Obtain a Nalgene container of appropriate size for the volume of product in the reaction vessel.
24. Insert drain tube at the bottom of the reactor into the top of the Nalgene container and turn the knob at the bottom of the reactor to open the drain. Let the product drain into the container.