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

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The corrosion behavior of two coagulants used in water treatment, ferric chloride (FC) and polymeric ferric sulfate (PFS) prepared from SO₂ was investigated. Corrosion tests were performed to compare the corrosivity of these two coagulants on aluminum 6061 and steel 4140 specimens. Results showed that both temperature and concentration of the coagulants substantially impact corrosion rates. The corrosion rates increased with the increase of temperature and concentration. The results from a scanning electron microscope (SEM) showed that chloride caused more serious pitting than sulfate anion on both aluminum and steel specimens. Although SEM confirmed the existence of pitting corrosion, the results of weight loss indicated that the uniform corrosion predominate the corrosion mechanism, and pitting corrosion played a less important role. The test proved that PFS was less corrosive than FC, which may lead to the large-scale application of PFS in waste treatment in the near future.

**Keywords:** Corrosivity; Polymeric sulfate ferric; Ferric chloride; Coagulants; Water treatment
Executive Summary

From 9/2000 to 12/2002, the major focus of this research is to investigate the absorption of sulfur dioxide from a simulated flue gas for the production of polymeric ferric sulfate (PFS), a highly effective coagulant useful in treatment of drinking water and wastewater. 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. Characterization of solid PFS 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 organic matters.

In 2003, the corrosion behavior of two coagulants, ferric chloride (FC) and PFS was investigated. Corrosion tests were performed to compare the corrosivity of these two coagulants on aluminum 6061 and steel 4140 specimens. Results showed that both temperature and concentration of the coagulants substantially impact corrosion rates. The corrosion rates increased with the increase of temperature and concentration. The results from a scanning electron microscope (SEM) showed that chloride caused more serious pitting than sulfate anion on both aluminum and steel specimens. Although SEM confirmed the existence of pitting corrosion, the results of weight loss indicated that the uniform corrosion predominate the corrosion mechanism, and pitting corrosion played a less important role. The test proved that PFS was less corrosive than FC, which may lead to the large-scale application of PFS in waste treatment in the near future.
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INTRODUCTION

Ferric chloride (FC) has been widely used in water treatment due to its good performance on turbidity removal. It is more effective than aluminum-based coagulants at removing total organic carbon (TOC) [1], achieving the same removal effect with a lower dosage [2]. Iron (III) coagulants were also found to be effective in wide ranges of pH and temperature at removing humic substances from water, a main Trihalomethanes (THMs) precursor when coagulated water was chlorinated [3]. As a conventional coagulant, aluminum has long been suspected of being both carcinogenic and mutagenic [4]. Given the possible health risks, it is necessary to monitor aluminum residue in treated water and take appropriate measures to keep it below a certain level. Iron-based coagulants do not pose the health risks of their aluminum counterparts. Therefore, the advantage of using FC in place of aluminum-based coagulants is apparent.

There are special challenges to using FC coagulants, however. Users complain about its high corrosivity [5]. It causes corrosion problems that shorten the lifespan of equipment and pipelines in water treatment plants. The presence of chloride from FC may cause pitting corrosion, the most destructive and insidious form of corrosion [6].

A newly developed prepolymerized iron-based salt, polymeric ferric sulfate (PFS), has received recent attention for its superior capability in removing turbidity and reducing algae, color and natural organic matter (NOM) while causing less corrosion and leaving less iron residue than ferric chloride [7, 8]. Research also suggests that sulfate is more effective at humic substance removal than chloride [3]. Unlike FC, which undergoes fast hydrolyzation after its addition to water [9], the ferric anion in PFS is partially hydrolyzed before it’s added to water, thus producing Fe(III) hydrolysis species,
and polynuclear complexes of Fe(III), \([Fe_m(OH)_n]^{(3m-n)}\) [7]. By controlling the preparation conditions, such as the method of base addition, aging temperature and time, the composition of these PFS’s hydrolysis products, and PFS’s coagulation effect, can be effectively optimized [8].

Given the aforementioned advantages, PFS is considered to be a promising alternative to FC. However, few systemic tests have been made to compare the corrosivity of these two coagulants. This paper discusses tests that were conducted to evaluate the corrosive performance of PFS synthesized in the laboratory. When compared to FC test results, the findings of the PFS tests indicate that it has strong potential as a coagulant for water treatment.

**EXPERIMENTAL**

Experiments were designed to compare the degree of corrosion caused by FC and PFS. The parameters selected were temperature, concentration of coagulant, and types of specimen material. The test was designed according to the relative standards of American Society for Testing and Materials (ASTM). The standards involved were G1-90 (Reapproved 1999) Practice for preparing, cleaning, and evaluating corrosion test specimens; G3-89 (Reapproved 1999) Practice for conventions applicable to electrochemical measurements in corrosion testing; G16-95 (Reapproved 1999) Guide for applying statistics to analysis of corrosion data; G31-72 (Reapproved 1999) Practice for laboratory immersion corrosion testing of metals.

**FC Solution.** Reagent grade FeCl₃·6H₂O (Assay 97.3%, Fisher) was dissolved in deionized water to make the FC solution. Two different concentrations of solution were prepared, one containing 1 wt % and the other, 10 wt % Fe(III),
**PFS Solution.** A PFS solution was made in the laboratory of the Center for Sustainable Environmental Technologies (CSET) at Iowa State University (ISU), Ames, USA. It contained 10.5 wt% iron and its characteristics were: basicity = 12%; [Fe(III)] > 10 wt% and [Fe(II)] < 0.2 wt% [10-14].

PFS was synthesized using a method developed by Fan [10]. Each round of the synthesis process was controlled to produce 5000 g PFS, which should contain 10 wt% Fe(III). The first step of the synthesis was the addition of 2222.2 g FeSO₄·7H₂O [22.5 wt% Fe(II)] into a 4000 mL reactor (ChemGlass) containing 2351 g H₂O accompanied with continuous mixing at the speed of 60 rpm for a period of 30 minutes. After mixing, 266.9 g H₂SO₄ (Fisher Scientific, 96.5 wt%, density = 1.84 g/cm³) and 160 g sodium chlorate (Fisher Scientific, 99.6 wt%) were added to the reactor at an appropriate speed to avoid extra heat accumulation. The synthesized PFS solution was determined the total iron, Fe(II) concentration and basicity [10]. The relative parameters of the produced PFS were: 0.03 wt% of Fe(II), 10.44% of total iron and 11.4% of basicity. All these parameters reached the PFS quality standard of China [15], making it eligible for water treatment usage.

The synthesized PFS was diluted to 1 wt% Fe(III) and 10 wt% Fe(III) for the corrosion test.

**Specimen Treating Solutions.** Two kinds of solutions, phosphoric acid and hydrochloric acid, were made up to treat the corroded specimens and remove the corrosion product. The phosphoric acid solution was made up by mixing 50 mL phosphoric acid (Fisher Scientific, H₃PO₄, specific gravity = 1.69) and 20 g chromium trioxide (Fisher, 99.9%) followed by addition of deionized water to make 1000 mL
solution. The hydrochloric acid solution was made up of 1000 mL hydrochloric acid (Fisher Scientific, HCl, specific gravity = 1.19), 20 g antimony trioxide (Sb₂O₃, Aldrich), and 50 g stannous chloride (SnCl₂).

**Corrosion Specimens.** Two materials, aluminum 6061 and steel 4140, were used in the corrosion test. The metals were processed at ISU's Chemistry Machine Shop into circular specimens with a diameter of 38 mm and thickness of 3 mm. An 8-mm diameter hole was drilled in the middle for convenient mounting. The average weight of the aluminum and steel specimens were 9.5 g and 27.7 g respectively.

The sample disks were immersed in FC and PFS solutions that both contained 1 and 10 wt% Fe(III) at five different temperature settings, i.e. 5 °C, 20 °C, 35 °C, 50 °C and 65 °C for 10 hours.

**Characterization of Corroded Specimens.** To compare the corrosion effects of PFS and FC, the specimens were examined with a Hitachi S-2460N Scanning Electron Microscope (SEM) set at high vacuum mode with 20 kV beam. Micrographs from the SEM were used to investigate the surface morphology of the corroded specimens.

**Apparatus and Operational Procedures.** Before testing, the specimens were polished with No. 100 abrasive paper (aluminum oxide, made in Poland) to remove the surface oxidation layer of metal and eliminate variations on the metallic surface. Final surface treatment was accomplished with No. 180 abrasive paper (silicon carbide, made in Poland) and acetone (Fisher Scientific, 99.0%, density = 0.7847 g/mL). All specimens were weighed with Mettler AE100 Analytical Balance and these initial weights were recorded.
The corrosion test started with the addition of 1000 mL PFS or FC solution into the 1000 mL reactor (ChemGlass). The setup of the experimental apparatus is illustrated in Figure 1. Controlled with a temperature bath unit, the temperature of the reaction solution was stabilized at the set point. After the temperature of solution reached the set point, five specimens were immersed into the solution and timing was started. The specimens were tied to the mounting rack with nylon string and suspended in the solutions to avoid contact with each other.

Every two hours, one specimen was taken out of the reactor, treated with a chemical solution to remove corrosion products, and weight losses were measured. The aluminum specimens were treated with a phosphoric acid solution for 10 minutes at 95 °C followed by washing with water and acetone. The steel specimens were treated with a hydrochloric acid solution for 25 minutes at 25 °C followed by washing with water and acetone. In all cases, the dried specimens were weighed on a balance. The weight of the corroded specimen was subtracted from its initial weight, thus giving the weight after two hours of corrosion. By using the same way, weight losses of specimens at the immersion time of four, six, eight and ten hours were obtained. After the corrosion test, the corroded specimens were examined with SEM surface morphology to determine the effects of types and concentrations of the coagulant solutions on them. Three different magnitudes-50, 200 and 500-were used to acquire the surface morphology.

RESULTS AND DISCUSSION

Electrochemical explanation. When the metal specimens were immersed into the coagulant solutions, an electrochemical reaction took place with the metal acting as an anode and the impurities within metal as a cathode. This reaction then resulted in the loss
of metal in the anode reaction, and hydrogen gas generation in the cathode reaction. The electrochemical reactions involved in the corrosion are as shown with (1) and (2) [16],

\[
\begin{align*}
\text{Fe} + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2 & E_0 = 0.44V \\
2\text{Al} + 6\text{H}^+ & \rightarrow 2\text{Al}^{3+} + 3\text{H}_2 & E_0 = 1.68V
\end{align*}
\]

Apart from these two electrochemical reactions, redox reaction also played an important role in the corrosion behavior. The FC solution containing 10 wt% Fe(III) boiled within 10 minutes of immersing the aluminum specimens. The temperature increased rapidly from 20 °C to higher than 100 °C. After the reaction was finished, solution samples were analyzed for Fe(II) and Fe(III). The solution contained 10 wt% Fe(II) and 0 wt% Fe(III); obviously, all of the Fe(III) was converted into Fe(II) through the reaction.

According to $\Delta G$ values of the redox reaction that may take place, the reaction can proceed during all the test periods. For the aluminum case, the concentration of Al(III) and Fe(II) at the beginning of the reaction was negligible compared to the Fe(III) concentration, which made $\Delta G$ negative (3) [16,17]. For the reaction to stop proceeding to the right, the concentration of Fe(III) will almost be negligible. That means Fe(III) can be virtually completely reacted if enough aluminum is provided. For the steel case, Fe(II) was negligible at the beginning of reaction. Fe(III) should be much lower than Fe(II) to make the reaction stop, which means all Fe(III) is almost completely consumed if enough steel is provided (4) [16,17]. In both cases, redox reaction will happen as long as the metals and coagulants exist in the solution.

\[
\text{Al} + 3\text{Fe}^{3+} \rightarrow \text{Al}^{3+} + 3\text{Fe}^{2+} \quad E^0 = 2.45V
\]
\[ \Delta G = \Delta G^0 + RT\ln Q = -169.1 + 1.99 \times 10^{-3} T \ln \frac{[\text{Al}^{3+}] [\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \]  \hspace{1cm} (3) 

\[ \text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+} \quad \text{E}^0 = 1.21 \text{V} \]

\[ \Delta G = \Delta G^0 + RT\ln Q = -58.8 + 1.99 \times 10^{-3} T \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \]  \hspace{1cm} (4) 

**Effects of Temperature.** Test results showed that temperature had a substantial influence on corrosion: the higher the temperature, the higher the weight loss in the metal specimens. For the case of a steel specimen immersed in a PFS solution containing 10 wt% Fe(III) for 10 hours, the specimen’s weight loss at the temperature of 65 °C was 6.8686 g, about twenty-two times higher than that at 5 °C, which was only 0.3032 g.

Figure 2 illustrates the relationship between corrosion weight change and temperature. When the temperature was increased, the corrosion rates increased dramatically in all reaction system. The reaction rates at 65 °C in some systems, such as steel immersed in PFS solution containing 1 wt% and 10 wt% Fe(III), however, were not as high as those expected from the trend obtained from the previous four corrosion rates at lower temperatures. That may be explained by the tendency of PFS to more easily subject to hydrolyzation at higher temperatures than FC solutions containing the same concentration of Fe(III) [10], which was shown as (5):

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \]  \hspace{1cm} (5) 

The hydrolyzation resulted in a decrease of Fe(III) concentration in solution. Consequently, the reaction rate between iron and Fe(III), a major reaction that caused the corrosion of the steel specimen, was also inhibited caused by \( \Delta G \) approaching to zero, which means the termination of reaction.
For steel immersed in an FC solution containing 10 wt% Fe(III), the reaction proceeded smoothly when the temperature was below 65 °C. However, the reaction became rather furious accompanied with lots of bubbles produced and temperature increase caused by heat accumulation through reaction.

**Effect of concentration.** The corrosion rates increased with the increase of solution concentration. At temperature of 5 °C, the corrosion rate of the steel specimens in the FC solution containing 10 wt% Fe(III) was 140 g/cm².hr, while the corrosion rate in the FC solution containing 1 wt% Fe(III) was only 17 g/cm².hr. When the temperature increased to 65 °C, the corrosion rates of the steel specimens in these two solutions were 576 g/cm².hr and 155 g/cm².hr, respectively. For the aluminum specimens, the corrosion rates were 23 g/cm².hr and 9 g/cm².hr in the PFS solutions containing 10 wt% and 1 wt % Fe(III) at the temperature of 5 °C. When the temperature was increased to 65 °C, the corrosion rates changed to 1150 g/cm².hr and 28 g/cm².hr. The reaction rates in the PFS solution containing 10 wt% Fe(III) were 4000% higher than reaction rates in solutions containing 1 wt% Fe(III). When the aluminum was immersed in an FC solution containing 1 wt% Fe(III), the weight loss was 0.7773 g. The corrosion rate of aluminum in the FC solution containing 10 wt% Fe(III) was much higher. However, the rate was unable to be determined since the aluminum specimens were completely corroded in 15 minutes. Obviously, higher concentration solutions are more corrosive than lower concentrations (Figures 4 and 5).

**Effect of solution and metal.** Generally speaking, test results showed that PFS is less corrosive than the FC solution, especially when both contain 10 wt% of Fe(III). For aluminum, all of the weight loss data obtained from the corrosion test justified the trend
that PFS will cause less weight loss than an FC solution containing the same concentration of Fe(III). With steel, however, PFS containing 1 wt% Fe(III) caused more weight loss than an FC solution containing 1 wt% Fe(III) at temperatures of 20 °C and 35 °C. When the PFS concentration was 1 wt% Fe(III), its corrosion effect on aluminum was less than steel (Figure 6). With an FC solution containing 1 wt% Fe(III), the weight loss was higher in aluminum in the first several hours. The rate of weight loss of steel, however, surpassed that of aluminum in the latter period of the experiment (Figure 7).

Steel was more resistant than aluminum to both PFS and FC solutions containing 10 wt% Fe(III). Its resistance to the corrosion of PFS solution containing 1 wt% Fe(III), however, was less than aluminum. At the end of the 10-hour experiment, steel also lost more weight than aluminum in the FC solution containing 1 wt% Fe(III). At the immersion time of 10 hours and 20 °C, the weight loss caused by the PFS solution containing 1 wt% Fe(III) was 0.8241 g, or 34% higher than that caused by the FC solution containing 1 wt% Fe(III), which was only 0.6150 g. The weight loss caused by the PFS solution containing 1 wt% Fe(III) at 35 °C was 1.0399 g, or 19% higher than that caused by the FC solution containing 1 wt% Fe(III), which was only 0.8714 g.

Both PFS and FC are acid salts, which means solutions containing them will have a low pH value when dissolved in water. An increase in the concentration of acid salts leads to acidification of the solution, and their action or corrosion will be determined to a large extent by the corrosion behavior change of the given metal with the change in pH of the medium. The electrochemical reaction will produce hydrogen gas, which is shown as (1) and (2). Steel was more resistant to aluminum in acid solution in that the electrochemical potential of iron system lower than aluminum one.
PFS can be expressed with the formula \([\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{(6-n)/2}]_m\), where \(m\) is a function of \(n\) (\(n<2\)) [10]. Since PFS has a higher basicity, it produces \(\text{H}^+\) ion when added to water compared to FC, which contains the same amount of iron. Accordingly, the pH value of PFS was higher than that of FC containing the same concentration of Fe(III), which resulted in a lower electrochemical potential and corrosion rate [18], as shown by Equation (6) [16]. Thus, the PFS solution was less corrosive to the facilities than FC when used as a coagulant substitute. This trend was also confirmed by the fact that more hydrogen gas bubbles were produced in PFS solutions compared to those in FC solutions containing the same concentration of Fe(III) when the same metal specimens were used.

\[
E = E_0 - \frac{RT}{nF} \ln Q = E_0 - \frac{RT}{nF} \ln \left( \frac{[\text{Fe}^{2+}]}{[\text{H}^+]}) \right)
\]  

(6)

The anion in these two coagulants may also contribute to the difference in corrosive behavior. The FC solution contained chloride anion, which is able to attack most metals in an aqueous environment [19]. This anion, when present in a solution, will cause pitting corrosion on the surface of metals. It may act as an anodic accelerator that destroys the protective film on the anodic areas, thereby accelerating the rate of the anodic process. Pits were observed using SEM on all specimens corroded by ferric chloride, no matter aluminum or steel. Moreover, when the specimens immersed in PFS containing \(\text{SO}_4^{2-}\), an anion that was not considered an agent as aggressive as \(\text{Cl}^-\) [20], the surface of the metals were also attacked by pitting, although less severe than the pitting created by \(\text{Cl}^-\).

Apparently, chloride anion generated substantial pitting corrosion on the surface of steel. For the \(\text{SO}_4^{2-}\) anion, it corroded the steel with a different mechanism. The steel specimens were less severely corroded by pitting. Rather, they were more likely to be attacked by intergranular corrosion.
From the SEM results, the pitting number generally increased with the increase of temperature. However, the increase of pit number and diameter with temperature can not account for the variation of the weight loss caused by temperature change, which may indicate that the pitting corrosion was not the main mechanism that caused the corrosion differences between FC and PFS on both aluminum and steel specimens. The main corrosion behavior, therefore, may contribute to uniform corrosion. Test results showed that the uniform corrosion caused by FC corrosion was much more severe than PFS when both solutions contained 10 wt% Fe(III).

**CONCLUSIONS**

Test results showed that PFS was less corrosive than FC, especially when both of solutions contained 10 wt% Fe(III). For aluminum, all of the weight loss data from the corrosion test justified the trend that PFS will cause less weight loss than the same concentration of FC. With steel, however, the PFS solution containing 1 wt% Fe(III) caused more weight loss than the FC solution containing 1 wt% Fe(III) at 20 °C and 35 °C. When the PFS solution contained 1 wt% Fe(III), its corrosion effect on aluminum was less than steel. Higher concentration solutions were more corrosive than lower concentration ones. Temperature has a substantial influence on corrosion: the higher the temperature, the higher the weight loss from the sample disks.

Steel was more resistant than aluminum to both PFS and FeCl3 solutions containing 10 wt% Fe(III). Its resistance to the corrosion of the PFS solution containing 1 wt% Fe(III), however, was less than aluminum. At the end of the 10-hour experiment, steel also lost more weight than aluminum in the FC solution containing 1 wt% Fe(III).

According to the SEM results, the number and diameter of pits generally increased with an increase in temperature. However, pitting was not the main mechanism that
caused the corrosivity differences between FC and PFS solutions on aluminum and steel specimens. Test results showed that the uniform corrosion caused by FC solution was much more severe than PFS solution when both contained 10 wt% Fe(III). The chloride anion in FC caused the major pitting in steel, while sulfate anion does not have this aggressive action.
REFERENCES


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APPENDIX
Figure 1. Experimental setup of the corrosion test

(1) Reaction vessel, (2) Corrosion specimens, (3) Coagulant solution, (4) Reactor temperature bath unit, (5) Specimen mounting rack.
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specimen immersed in FC solution containing 10 wt% Fe(III), (6) Steel specimen immersed PFS solution containing in 10 wt% Fe(III).