

Kinetics of Ion Removal from an Iron-Rich Industrial Coproduct: II. Sulfate

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ABSTRACT

An iron-rich material (IRM) contained copious quantities of salts, including Cl and SO₄. A previous study on Cl removal hypothesized that SO₄ played a major role in the chemistry of the IRM. Therefore, this study investigated the kinetics of SO₄ removal from the IRM, which had a point of zero charge similar to those of some tropical soils. Stirred-flow (SF) and column studies showed that SO₄ removal was a time-dependent chemical reaction(s). The SF technique facilitated modeling of the chemical kinetics of SO₄ removal by providing a uniformly mixed system. The SO₄ removal mechanism from the IRM to the ambient solution, in the SF system, was a zero-order oxidation-dissolution reaction of the Fe-sulfide present as a minor constituent in the IRM. The computed value of the rate-constant was 0.043 μmol min⁻¹. In the column studies, the newly dissolved SO₄ was present in the effluent, and was adsorbed on the IRM through a ligand (OH⁻) exchange mechanism. Calcium hydroxide dissolution, together with the SO₄ adsorption, resulted in a pH increase with pore-volume.

A TiO₂-GENERATING industrial process results in a filter-cake material that is rich in Fe-oxides and contains a large amount of salts. Stirred-flow (SF) and column studies were employed to study the release of the salts from the IRM. In a previous study (Salinger et al., 1994a) it was shown that Cl decreased precipitously and that its leaching was a function only of the water volume used for the IRM washing. Chemical kinetics did not control the removal rate of Cl. Sulfur compounds were minor constituents in the waste material and SO₄ was removed from the IRM. Sulfur mineral weathering is a potential degrader of water quality, often yielding high acidity and concentrations of metals and SO₄. Such pyrite weathering is often a consequence of human activities such as processing of coal or metal ores (e.g., Moses and Herman, 1991). In this study, however, it was not clear whether the kinetics of SO₄ removal were controlled by SO₄ desorption, by dissolution of indigenous SO₄ salts, or by oxidation-dissolution processes of the Fe-sulfide present in the coke contained in the IRM.

Sulfate desorption from soil (Chao et al., 1962) and from soil kaolinite (Aylmore et al., 1967) appears to be rapid. Sulfate desorption was complete within 0.5 h from a S-deficient soil that had an appreciable capacity to adsorb SO₄ (Barrow and Shaw, 1977), from a Teakatea clay (Rajan, 1979), and from the B horizon of a Fe-podzol soil (Singh, 1984). Hodges and Johnson (1987) fitted data from SO₄ adsorption-desorption miscible-displacement and batch experiments on soils to a number of kinetic models, and concluded that diffusion of SO₄ through a reacted soil particle was the overall rate-controlling step.

Zhang and Sparks (1990) studied the kinetics of SO₄ adsorption-desorption at the goethite-water interface using pressure-jump relaxation. Based on kinetic and equilibrium modeling they concluded that the adsorption of SO₄ on goethite occurred simultaneously with the protonation of a neutral surface site, and an outer-sphere surface complex was formed involving electrostatic attraction. The calculated forward intrinsic rate constant was $2.08 \times 10^8 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$, and the backward constant was 0.144 s^{-1} . Sharpley (1990) described the kinetics of SO₄ desorption from soil using a power-form kinetic equation. Evans and Zelazny (1990) investigated the influence of naturally occurring aliphatic acids on the kinetics of Al and SO₄ release from a forested Cecil soil (clayey, kaolinitic, thermic Typic Kanhapludult). They found that both Al and SO₄ release followed pseudo-first-order kinetics. Courchesne and Hendershot (1990) fitted SO₄ desorption data from two Quebecian Spodosols to five simple kinetic equations. The Elovich equation provided the best representation of the time-dependent desorption. About one half of the SO₄ was desorbed in the first 5 min. After a 4-d reaction period, however, desorption was still proceeding slowly.

Although the mechanism of SO₄ adsorption-desorption on soil and soil constituents has been addressed in a number of papers, it is still not definitively understood. Two main mechanisms have been proposed: ligand exchange and electrostatic attraction. Ligand exchange involves the replacement of OH₂ or OH⁻ groups, from protonated (XOH₂⁺) and nonprotonated (XOH) surface adsorption sites, by SO₄²⁻. This reaction results in a decrease in adsorption with increased pH of the ambient solution (e.g., Chang and Thomas, 1963; Parfitt and Smart, 1978). Sulfate adsorption, due to electrostatic attraction to positively charged surfaces, has also been commonly reported (e.g., Hansmann and Anderson, 1985; Marsh et al., 1987).

Few reports exist on the effect of electrolyte concentration and composition on SO₄ adsorption by soils. Bolan et al. (1986) and Courchesne (1991) showed that, for the soils they tested across a pH range of 4 to 7, increasing ionic strength (*I*) always decreased SO₄ adsorption. Courchesne (1991) showed that the adsorption rate also decreased with increasing *I*, due to the presence of Cl⁻ as a competitive species for adsorption sites, and formation of NaSO₄⁻ aqueous complexes. Bolan et al. (1986) suggested that the effect of *I* on SO₄ adsorption was due to its effect on the electrostatic potential in the plane of adsorption. Sulfate was essentially adsorbed when the potential was positive.

Geochemical oxidation of pyrite at pH values above 4 is a very slow process, and the reaction products are Fe²⁺, SO₄²⁻ and H⁺. Upon hydrolysis of the Fe²⁺, more

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Abbreviations: CV, the coefficient of variation; I, ionic strength; IRM, iron-rich material; ODE, ordinary differential equations; SF, stirred-flow technique; XRD, x-ray diffraction.

acid is generated. A much faster oxidation can occur if the pyrite is oxidized by Fe^{3+} or by bacteria at pH 2 to 4 (Stumm and Morgan, 1981). The oxidation of sulfide minerals, particularly pyrite, has been extensively studied. Goldhaber (1983) suggested that the rate of pyrite oxidation from pH 6 to 9 in dissolved O_2 -saturated solutions was controlled by a surface reaction that takes place after the adsorption of an O_2 molecule. McKibben and Barnes (1986) oxidized pyrite across the pH range 1 to 4 with dissolved O_2 , H_2O_2 , and Fe^{3+} . The rate data for dissolved O_2 were fitted to the square root law (parabolic diffusion), which was independent of pH. Moses et al. (1987) showed that pyrite oxidation in O_2 -saturated solutions produced SO_4 at rates between 0.006 and 0.085 $\mu\text{M SO}_4^- \text{min}^{-1}$. The rate of pyrite oxidation at near-neutral pH was first-order with respect to the ratio of surface area to solution volume (Moses and Herman, 1991). Evangelou et al. (1985) measured rates of pyritic coal spoil oxidation–dissolution and found that the reaction rates ranged from ≈ 4.17 to $\approx 15.6 \mu\text{M SO}_4 \text{min}^{-0.5}$. According to Moses et al. (1987) and others it is almost universally acknowledged that the sulfide mineral oxidation reaction mechanism is surface reaction controlled. Other details of the nature of the mechanism, particularly the rate controlling step and the identities of the oxidizing reactant, however, are still not understood.

Sulfate leaching is more extensive in soils that are low in Fe and Al-oxides, but it has been reported also in soils that contain large amounts of Fe-oxides (Swoboda and Thomas, 1965). It is usually apparent, however, that the rate-determining step in SO_4 leaching is not SO_4 desorption or dissolution of indigenous salts, but is sulfide oxidation–dissolution reactions.

The overall conclusion from SO_4 kinetic studies is that rates of desorption are rapid. According to Zhang and Sparks (1990) chemical desorption of SO_4 may take place in a fraction of a second, or in minutes (Rajan, 1978, 1979; Barrow and Shaw, 1977; Singh, 1984; Courchesne and Hendershot, 1990; Courchesne, 1991). Dissolution of indigenous SO_4 salts are also relatively rapid (hours), whereas the rate of sulfide oxidation–dissolution is considerably slower (Evangelou et al., 1985).

The objectives of this research were to study the chemical kinetics of SO_4 removal from the IRM, and to determine which mechanism controlled the SO_4 removal rate.

MATERIALS AND METHODS

Characterization analyses of the IRM along with descriptions of the column and the SF studies are given elsewhere (Salingar et al., 1994a,b). In addition to the methods of computation described in Salingar et al. (1994a), nonobservable components (such as current mass of SO_4 in solution in the SF-chamber) were computed using the D02BBF subroutine of Numerical Algorithms Group (1988) to solve the system of ordinary differential equations (ODEs).

X-ray diffraction (XRD) analysis (random power mounts) of the IRM showed four distinct peaks characteristic of Fe-sulfide (Fe_{1-x}S), with an intense peak at 0.208 nm and weaker signals at 0.265, 0.296, and 0.173 nm. These values agreed with the d-spacing data for pyrrhotite-11C (Card no. 29-726; JCPDS, 1986).

Equilibrium Studies

Sulfate adsorption studies under controlled pH conditions were conducted at 298 K by shaking (end-to-end on a reciprocating shaker, for 24 h) 1 g IRM (air dried, <2.0 mm) in 200 mL solution. Preliminary studies indicated the reaction reached a steady state within 24 h and the solid/liquid ratio was arbitrarily chosen. These suspensions included fourteen Na_2SO_4 solutions of initial SO_4 concentrations of 10 to 300 mg L^{-1} in a background electrolyte of 0.01 M NaNO_3 . For seven solutions the pH values were adjusted to 4.19 ± 0.08 using trace quantities of 1.0 M HNO_3 and 0.2 M NaOH . For the remaining seven solutions the pH values were adjusted to 8.84 ± 0.10 . After 24 h, the pH values were determined, then the slurries were centrifuged ($30\,600 \times g$ for 30 min), filtered (0.45 μm), and SO_4 was measured using ion chromatography. The amount of adsorbed SO_4 was determined as the difference between the initial and the final SO_4 concentrations.

RESULTS

Stirred-Flow Modeling

Model predictions, which are described below, were compared with experimental data collected from SF studies to verify the assumptions of the models. The employment of this approach allows one to follow the time-dependent release of SO_4 in a very heterogeneous-complex system, for which other modeling approaches would require unobtainable knowledge of specific sites and sources of the released species.

The SF technique facilitates modeling of chemical kinetics of salt removal because uniform mixing occurs in the SF chamber (Seyfried et al., 1989). To establish SO_4 modeling, the following setup of ODEs was proposed for the SF reactor:

$$\frac{dM_{\text{SO}_4}}{dt} = k_2 - \tau_1 \quad M_{\text{SO}_4} = 0 \text{ at } t = 0 \quad [1]$$

where $\tau_1 = \xi M_{\text{SO}_4} Q$,

$$\frac{dM_{\text{ac,SO}_4}}{dt} = \tau_1 \quad M_{\text{ac,SO}_4} = 0 \text{ at } t = 0 \quad [2]$$

where t is time (min), M_{SO_4} is current mass of SO_4 in solution in the chamber (μmol), $M_{\text{ac,SO}_4}$ is accumulated SO_4 removed from the chamber (μmol), k_2 is a rate-constant of the zero-order reaction of SO_4 entering the solution ($\mu\text{mol min}^{-1}$), $\xi = V_{\text{ch}}^{-1}$ (135 L^{-1}) in which V_{ch} is volume of the chamber ($7.43 \times 10^{-3} \text{ L}$), and Q is flow-rate (L min^{-1}).

A numerical solution is preferable over an explicit solution in this study because although the flow-rate (Q) remained relatively constant throughout the study ($0.85 \pm 0.074 \text{ mL min}^{-1}$), at times there was a slight deviation in Q (Salingar et al., 1994a). The model, however, accounts

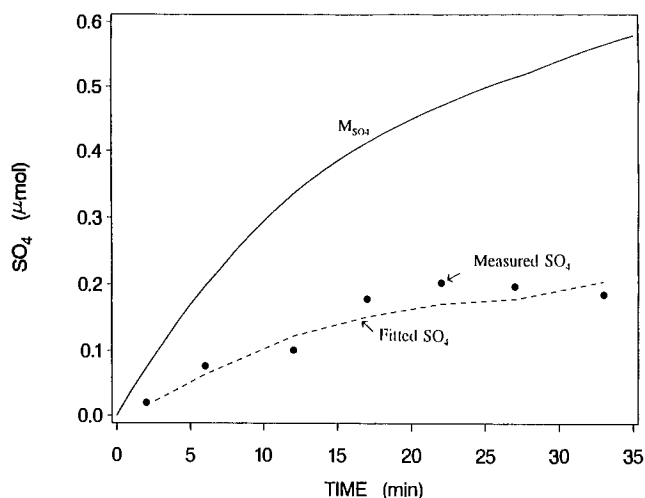


Fig. 1. Stirred-flow study: Measured, fitted and SO_4 mass in the chamber (M_{SO_4} , solid-line) vs. time. The SO_4 discharge was restricted by the flow-rate, Q . Hence, the measured SO_4 and the fitted SO_4 are below the actual SO_4 mass in the chamber.

for such alterations. For example, it depicted the fluctuations in M_{SO_4} as Q changed slightly (Fig. 1).

Equation [1] accounts for two processes in the chamber. The first expression (k_2) is a *source* term; the rate-constant ($\mu\text{mol min}^{-1}$) of the zero-order reaction at which SO_4 is coming into solution. Zero-order means that the rate of the reaction is independent of the concentration of the SO_4 substance in the IRM. The second expression (τ_1) is a *sink* term; the rate ($\mu\text{mol min}^{-1}$) at which SO_4 is removed. Under the assumption that an SF chamber is a well mixed system, a dilution process occurs in the chamber and τ_1 must be the concentration (ξM_{SO_4}) multiplied by Q . Because the rate at which SO_4 leaves the chamber (τ_1) is also the rate at which SO_4 accumulates, Eq. [2] results.

The SO_4 model components vs. t are plotted in Fig. 1. The nonobservable constituent, M_{SO_4} , was computed using the D02BBF subroutine of NAG (1988) to solve the system of ODEs (Eq. [1] and [2]). The term $dM_{\text{SO}_4}/dt \Delta t$ was fitted to the SO_4 data using nonlinear least squares where Δt is the sampling interval.

Estimated parameters for the SO_4 model, along with coefficient of variation (CV) and pseudo R^2 , are given in Table 1. The SO_4 model prediction of ξ (86 L^{-1}) was in reasonable agreement with the theoretical value of ξ (135 L^{-1}). The issue of estimation of model parameters by best fit to experimental data rather than estimation by independent measurements is discussed elsewhere (Salingar et al., 1994a). The estimated value for k_2 ($0.043 \mu\text{mol min}^{-1}$) was verified by multiplying it by t (33.7

Table 1. Theoretical and estimated values for the SO_4 model (Eq. [1] and [2]).

Parameter†	Theoretical	Estimate	Coefficient of variation	Pseudo R^2
$\xi (\text{L}^{-1})$	135	86	0.17	0.93
$k_2 (\mu\text{mol min}^{-1})$		0.043	0.41	

† ξ is the reciprocal of the volume of the stirred-flow chamber; k_2 is a rate-constant for the zero-order reaction of SO_4 coming into solution.

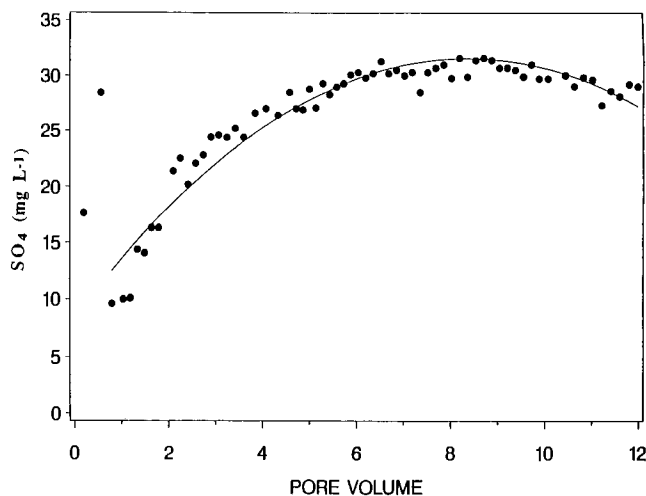


Fig. 2. Measured and predicted SO_4 concentration in column effluent vs. pore volume.

min). The resultant mass ($1.4 \mu\text{mol}$) was comparable to the measured SO_4 mass ($\approx 1 \mu\text{mol}$).

Most of the Cl mass was leached from the SF chamber by a volume-dependent process within the first 15 min (Salingar et al., 1994a). Contrary to Cl, the SO_4 mass entered the solution via a zero-order chemical reaction. Because the SF experiment took only ≈ 34 min, for practical purposes, the SO_4 source in the IRM was regarded as inexhaustible.

Column Studies

Because SF studies involve mechanical mixing and large solution to IRM ratios, column investigations were performed to better simulate field leaching conditions. Concentration of SO_4 in the column leachate vs. pore volume (ρ) is depicted in Fig. 2. At 0.2ρ , SO_4 concentration was 18 mg L^{-1} and at $\rho = 0.6$ it was 29 mg L^{-1} . These data probably reflected rapid dissolution of indigenous SO_4 salts. After 0.8ρ , however, SO_4 release showed a parabolic behavior vs. ρ . The fitted quadratic model is ($R^2 = 0.93$),

$$\text{SO}_4 = 8.39 + 5.55\rho - 0.332\rho^2 \quad [3]$$

where the CV value for the intercept was 0.083, for the linear coefficient it was 0.043, and for the quadratic coefficient it was 0.054.

The parabolic behavior of SO_4 vs. ρ , contrary to the precipitous decrease in Cl due to volume-dependent leaching (Salingar et al., 1994a), suggested that SO_4 removal entails time-dependent chemical reaction(s). Various possibilities to account for these reactions will be discussed below.

DISCUSSION

Both the SF and column studies showed that time-dependent process(es) were responsible for SO_4 removal from the IRM to solution. Yet, it was not clear which mechanism(s) controlled the removal rate: dissolution of indigenous salts, SO_4 desorption, or oxidation-dissolution processes.

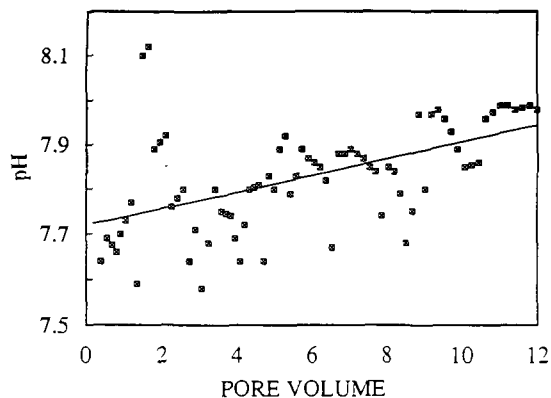
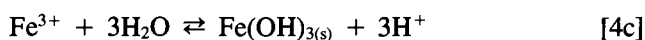
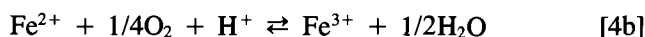


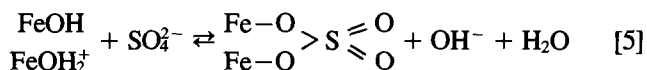
Fig. 3. Measured and trend of pH in column effluent vs. pore volume ($Y = 0.019X + 7.72$, $r^2 = 0.63$, $n = 75$).

The XRD analysis showed that Fe-sulfide (pyrrhotite) was present in the IRM. Iron-sulfide(s) oxidation-dissolution rates are lower than the dissolution rate of indigenous SO_4 salts (Evangelou et al., 1985). We assumed that indigenous salts were in solution as soon as eluent was introduced to the solid phase. Oxidation-dissolution rates are apparently also lower than SO_4 desorption from metal oxides. Zhang and Sparks (1990) found that SO_4 desorption from goethite was a first-order reaction, with a rate-constant of $k = 0.144 \text{ s}^{-1}$. A different reaction order, however, was ascertained in our SF study. A zero-order reaction with a rate-constant (k_2) of $0.043 \mu\text{mol min}^{-1}$ ($7.14 \times 10^{-4} \mu\text{mol s}^{-1}$) was determined by modeling the SO_4 removal with respect to t (Table 1). Accordingly, one may hypothesize that Fe-sulfide oxidation and subsequent mineral dissolution was the overall rate-limiting step for SO_4 removal from the IRM.

According to the geochemical oxidation of pyrite (Eq. [4a-4c]), one should expect acid production (Stumm and Morgan, 1981),



But, in this study, the pH of the effluent increased with ρ (Fig. 3). Considering the well established association between pH and SO_4 adsorption (e.g., Parfitt and Smart, 1978; Zhang and Sparks, 1990), we hypothesized that the newly dissolved SO_4 was adsorbed on the IRM and a ligand (OH^-) exchange mechanism was operational, as depicted in Eq. [5] (Parfitt and Smart, 1978),



Each mole of oxidized pyrite produces 2 mol of both SO_4^{2-} and H^+ (Eq. [4a]). One mole of H^+ is used up in the oxidation of Fe^{2+} to Fe^{3+} (Eq. [4b]). Each mole of SO_4^{2-} adsorbed on the Fe-oxide surface releases one mole of OH^- (Eq. [5]), which could have affected pH. Accordingly, Fe-sulfide oxidation did not cause a net production of acid. To check our hypothesis, we tested SO_4 adsorption under controlled low (≈ 4) and high (≈ 9) pH condi-

tions. The SO_4 adsorption at $\text{pH} \approx 9$ was lower than at $\text{pH} \approx 4$ (data not shown). These results conform with the mechanism shown in Eq. [5], in which high pH would cause a decrease in SO_4 adsorption.

Further dissolution of $\text{Ca}(\text{OH})_2$, which was added to the slurry as a neutralizing agent (Salingar et al., 1994a) may have been an additional cause of the pH rise with ρ (Fig. 3).

CONCLUSIONS

Stirred-flow and column studies indicated that the source of SO_4 supplied to the ambient solution was the result of oxidation-dissolution reactions of Fe-sulfide present in the IRM as a minor constituent. The overall kinetics of SO_4 release were determined using a SF technique, and the estimated rate-constant for this zero-order reaction was $0.043 \mu\text{mol min}^{-1}$. The newly released SO_4 in the columns underwent two processes: it was partially leached from the columns, and it was partially adsorbed on the IRM through a ligand exchange mechanism. Dissolution of $\text{Ca}(\text{OH})_2$ along with SO_4 adsorption resulted in an increased pH with ρ .

Little has appeared in the literature on salt removal from high-Fe wastes. The oxidation of sulfide minerals, particularly pyrite, has been extensively studied because it is a basic process that is central to a number of economically and environmentally important topics. This study constitutes part of a comprehensive procedure for examining the environmental soil chemistry of waste products (containing salt) with potential agricultural uses. The results can contribute to rational decisions concerning the proper utilization of the waste product.

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