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Journal Article

1988  
WWRC-88-15

In

Environmental Geological Water Science

Volume 11, No. 3

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# Solubility Relationships of Aluminum and Iron Minerals Associated with Acid Mine Drainage

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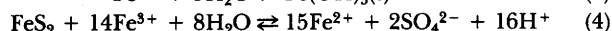
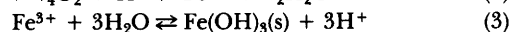
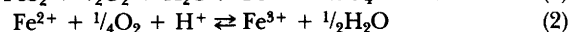
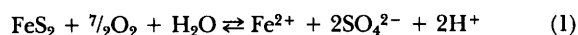
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**ABSTRACT** / The ability to properly manage the oxidation of pyritic minerals and associated acid mine drainage is dependent upon understanding the chemistry of the disposal environment. One accepted disposal method is placing pyritic-containing materials in the groundwater environment. The objective of this study was to examine solubility relationships of Al and Fe minerals associated with pyritic waste disposed in a low leaching aerobic saturated environment. Two eastern oil shales were used in this oxidizing equilibration study, a New Albany Shale (unweathered, 4.6 percent pyrite), and a Chattanooga Shale (weathered, 1.5 percent pyrite). Oil shale samples were equilibrated with distilled-deionized water from

1 to 180 d with a 1:1 solid-to-solution ratio. The suspensions were filtered and the clear filtrates were analyzed for total cations and anions. Ion activities were calculated from total concentrations. Below pH 6.0, depending upon  $\text{SO}_4^{2-}$  activity,  $\text{Al}^{3+}$  solubility was controlled by  $\text{AlOHSO}_4$  (solid phase) for both shales. Initially,  $\text{Al}^{3+}$  solubility for the New Albany Shale showed equilibrium with amorphous  $\text{Al}(\text{OH})_3$ . The pH decreased with time, and  $\text{Al}^{3+}$  solubility approached equilibrium with  $\text{AlOHSO}_{4(s)}$ . Below pH 6.0,  $\text{Fe}^{3+}$  solubility appeared to be regulated by a basic iron sulfate solid phase with the stoichiometric composition of  $\text{FeOHSO}_{4(s)}$ . The results of this study indicate that below pH 6.0,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  solubilities, are limited by basic Al and Fe sulfate solid phases ( $\text{AlOHSO}_{4(s)}$  and  $\text{FeHSO}_{4(s)}$ ). The results from this study further indicate that the acidity in oil shale waters is produced from the hydrolysis of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  activities in solution. These results indicate a fundamental change in the stoichiometric equations used to predict acidity from iron sulfide oxidation. The results of this study also indicate that water quality predictions associated with acid mine drainage can be based on fundamental thermodynamic relationships. As a result, waste management decisions can be based on waste-specific/site-specific test methods.

## Introduction

In a natural aerobic environment, there is a potential for iron sulfide compounds to oxidize and produce acidity. The best example of this natural process is the oxidation of  $\text{FeS}_2$  (pyrite) that usually occurs in mining wastes, coal cleaning waste, spoil and acid sulfate soils (Smith and others 1974). It is suggested by Stumm and Morgan (1981), that the oxidation of pyrite in a natural environment is indicated by the following reactions:



The environmental problems associated with the oxidation of pyrite are well documented (Martin 1974; Griffin and others 1980; Wahler 1978). In order to manage acid mine drainage production effectively, it is important to understand the solubility relationships of

Al and Fe minerals and the stoichiometry of acid generation in environments where pyrite will be oxidized.

Several studies have been conducted on the solubility relationships of Al and Fe minerals in acid sulfate soils and acid mine waters (VanBreeman 1973; Adams and Rawajfih 1977; Rhodes and Lindsay 1979; Nordstrom and others 1979; Nordstrom 1982a; Nordstrom 1982b; and Filipek and others 1987). However, it has been shown by Sullivan and others (1986) that the disposal environment will influence the solution chemistry. Thus, the objective of this study was to evaluate the equilibrium chemistry of Al and Fe to predict the long-term effects of acid mine drainage from low leaching aerobic saturated disposal environments.

## Materials and Methods

Two eastern oil shales were used in this study, a New Albany Shale, and a Chattanooga Shale. The

New Albany Shale is an unweathered shale that contains 4.6 percent pyrite, and the Chattanooga is a weathered shale that contains 1.5 percent pyrite.

Two 150-g of each sample were placed into 500-ml Nalgene plastic bottles. Two hundred fifty ml of distilled-deionized water were added to each of these bottles and capped tightly. The bottles were equipped with a plastic tube running through the cap to the bottom of the bottle and were supplied with a constant flow of compressed air. Each sample bottle was placed into a water shaker bath at a constant temperature of 25°C. The samples were shaken at a constant rate of 60 rpm, and were agitated manually four times a week. One bottle for each shale was removed from the water bath for analysis after 1, 4, 8, 16, 32, 64, 128, and 180 days of equilibration. The samples were filtered, and the clear filtrates were analyzed for different chemical constituents. The pH was measured with a combination electrode and Eh was measured with standard platinum and reference electrodes. Aluminum, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sr, and Zn were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The discussion of the trace element chemistry will be the subject of a future paper. Sulfate was measured by ion chromatography. Chloride was measured with a specific ion electrode. Carbonates were determined by titration and with a carbon analyzer. Chemical analyses of the total elemental contents were coded and speciated using the WATEQFC geochemical code (Runnells and Lindberg 1981) to calculate ion activities.

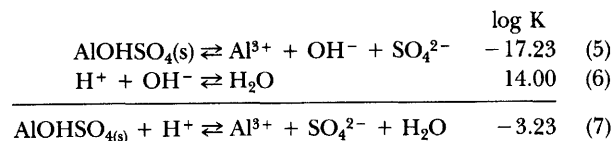
## Results and Discussion

Activities of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$ , from the oxidizing equilibration extracts are presented in Table 1. Also included in this table are equilibration times, pH and  $p_e + \text{pH}$  (oxidation-reduction). These data show that for the New Albany Shale extracts (unweathered with no soluble acidity) the initial pH increased from 5.47 to 7.90 and then decreased to 3.73. However, for the Chattanooga Shale extracts (weathered with soluble acidity) the pH decreased gradually from 4.62 to 2.44. These data also show that as equilibration times increased the solubilities of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  increased.

### $\text{Al}^{3+}$ Solubility

The relationship between ( $\log \text{Al}^{3+} + \log \text{SO}_4^{2-}$ ) and  $\log \text{Al}^{3+}$  versus pH are developed and shown in

Figure 1. In this figure, the  $\text{AlOHSO}_4$  (solid phase) solubility line corresponds to an acidic dissociation constant of  $10^{-3.23}$ . This constant was calculated from the following reactions:



The  $\log K^\circ$  for  $\text{AlOHSO}_4(\text{s})$  was taken from Van Breeman (1973). The acidic dissociation constant for amorphous  $\text{Al}(\text{OH})_3$  was taken from Lindsay (1979).

Activities of  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  for each shale extract are plotted in Figure 1 (note: extracts with a poor ion balance are not plotted, see Table 1). For the New Albany Shale, the initial  $\text{Al}^{3+}$  activity was in equilibrium with amorphous  $\text{Al}(\text{OH})_3$ . As equilibration time increased,  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  activities approach the  $\text{AlOHSO}_4(\text{s})$  solubility isotherm. The activities of  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  for the Chattanooga Shale approach equilibrium with  $\text{AlOHSO}_4(\text{s})$ . In general, above pH 6.0 the activity of  $\text{Al}^{3+}$  appear to be controlled by amorphous  $\text{Al}(\text{OH})_3$ , and below pH 6.0 the  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  activities are regulated by  $\text{AlOHSO}_4(\text{s})$ . Similar results were reported by VanBreeman (1973).

### $\text{Fe}^{3+}$ Solubility

Acid mine waters resulting from the oxidation of iron sulfides may precipitate a large number of secondary iron phases (Nordstrom, 1982) such as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (melanterite),  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  (rozenite),  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  (ferrohexahydrate),  $\text{Fe}(\text{II})\text{Fe}_4(\text{III})(\text{SO}_4)_6(\text{OH})_2$  (copiapite),  $(\text{K},\text{Na})\text{Fe}_3(\text{S})_4(\text{OH})_6$  (jarosite), and  $\text{Fe}(\text{OH})_3$  (amorphous iron). All of these solid phases are very soluble except jarosite and amorphous iron. Several studies have been completed on the solubility relationships and precipitation of jarosite in acid mine waters (Nordstrom and others 1979 and Filipek and others 1987). These studies showed supersaturation to jarosite. In the present study, we also observed that  $\text{Fe}^{3+}$  activities are not controlled by jarosite.

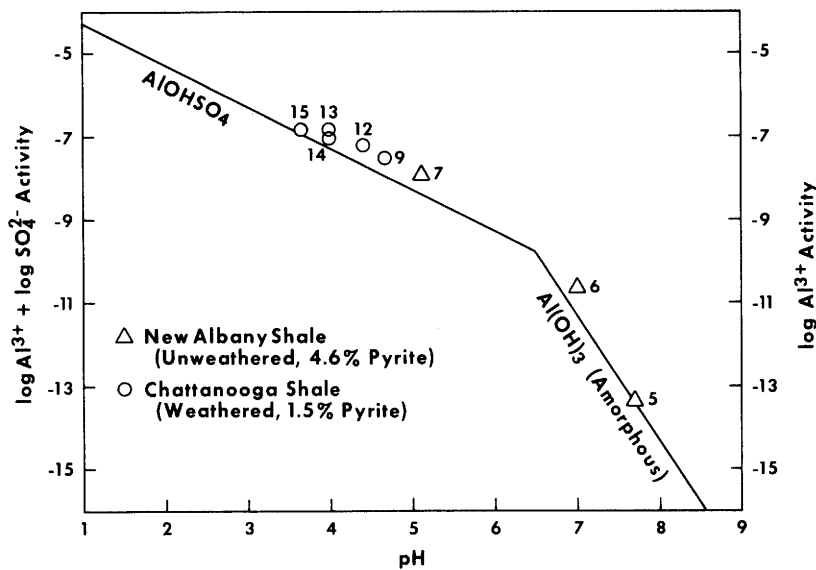
It is evident from Table 1 that  $\text{Fe}^{3+}$  activity increases as pH decreases. If  $\text{Fe}^{3+}$  activity was controlled by a ferric hydroxide, a one unit decrease in pH would correspond to a 1,000-fold increase in the  $\text{Fe}^{3+}$  activity. Instead, the  $\text{Fe}^{3+}$  activity increased approximately 10-fold for each unit decrease in pH, except for samples 5 and 6. This suggests that  $\text{Fe}^{3+}$  activity may be controlled by ferric iron solid phases other than ferric hydroxides. Given the pH range between

Table 1. Activities of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$  in distilled-deionized water equilibrium extracts from oil shales containing pyrite.

Sample no.	Equilibration time (d)	pH	pe + pH	log activity				
				$\text{Al}^{3+}$	$\text{Fe}^{3+}$	$\text{Na}^+$	$\text{K}^+$	$\text{SO}_4^{2-}$
New Albany Shale								
1+	1	5.47	9.07	-6.89	-15.08	-3.11	-3.22	-1.90
2+	4	6.23	8.71	-6.72	-15.20	-3.47	-2.98	-2.48
3+	8	6.33	6.66	BD	BD	-3.14	-3.40	-1.95
4	16	7.90	9.91	BD	BD	-3.15	BD	-1.99
5	32	7.67	9.14	-13.39	-17.34	-2.71	-2.65	-2.15
6	64	7.00	10.06	-10.63	-15.80	-3.11	-3.25	-2.17
7	128	5.11	10.72	-5.68	-12.78	-2.86	-3.28	-2.26
8+	180	3.73	8.00	-6.70	-14.83	-3.19	-3.33	-2.13
Chattanooga Shale								
9	1	4.62	8.74	-5.06	-13.45	-3.59	-3.05	-2.45
10+	4	4.66	8.83	-6.41	-14.20	-3.14	-3.37	-2.06
11+	8	3.26	8.23	-4.19	-12.35	-3.17	-2.95	-4.00
12	16	4.41	9.38	-4.93	-12.38	-3.25	-3.09	-2.26
13	32	4.02	9.54	-4.63	-11.69	-3.26	-3.06	-2.19
14	64	4.00	8.94	-4.54	-12.04	-3.28	-2.94	-2.35
15	128	3.64	9.32	-4.60	-11.30	-3.21	-2.77	-2.27
16+	180	2.44	10.00	-4.10	-10.09	-3.25	-3.09	-2.51

BD = below detection limit of 0.04 mg/L.

+ = poor cation and anion balance (&gt;10%).

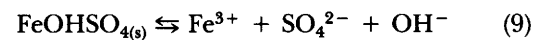
Figure 1. The solubility of  $\text{Al}(\text{OH})_3$  (amorphous) and  $\text{AlOHSO}_4$  solid phases in equilibrium extracts.

sample 7 (5.11) and sample 15 (3.64), the relationship of  $\log \text{Fe}^{3+} + \log \text{SO}_4^{2-}$  versus pH gives a regression slope of  $-1.00$ . Assuming this slope, the observed relationship can be expressed as:

$$\log \text{Fe}^{3+} + \log \text{SO}_4^{2-} + \text{pH} \rightleftharpoons -10.06 \quad (8)$$

This suggests an equilibrium between dissolved  $\text{Fe}^{3+}$

and a basic ferric sulfate solid phase with the stoichiometric formula of  $\text{FeOHSO}_4$  as follows:



The average equilibrium constant for equation (9) is calculated to be  $10^{-24.06}$  with an acidic dissociation constant of  $10^{-10.06}$ .

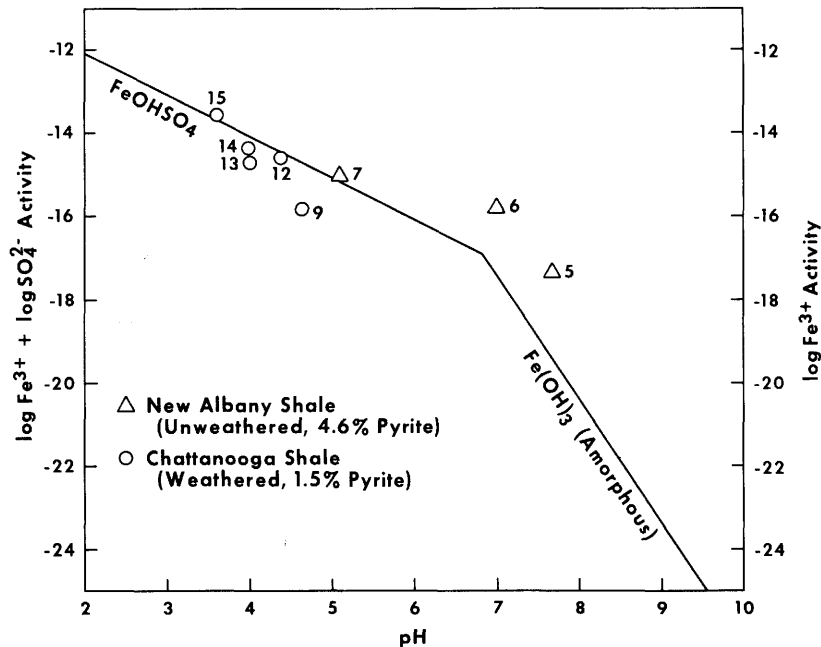
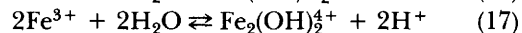
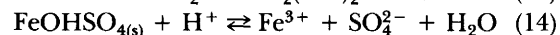
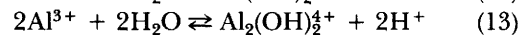
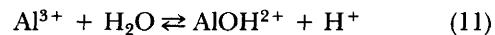
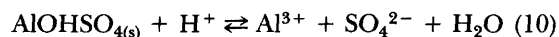


Figure 2. The solubility of  $\text{Fe}(\text{OH})_3$  (amorphous) and  $\text{FeOH}_4\text{SO}_4$  solid phases in equilibrium extracts.

The acidic dissociation constant of equation (9) was used to develop the relationship between  $\log \text{Fe}^{3+} + \log \text{SO}_4^{2-}$  versus pH for  $\text{FeOH}_4\text{SO}_4$  in Figure 2. The equilibrium constant used to determine the solubility line for amorphous  $\text{Fe}(\text{OH})_3$  was obtained from Lindsay (1979). The activities of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  are plotted in Figure 2 to examine the possibility that  $\text{FeOH}_4\text{SO}_4$  may control  $\text{Fe}^{3+}$  solubility. For the New Albany Shale, the initial  $\text{Fe}^{3+}$  activity showed slight supersaturation with respect to amorphous  $\text{Fe}(\text{OH})_3$ . However,  $\text{Fe}^{3+}$  activity approached equilibrium with the  $\text{FeOH}_4\text{SO}_4$  as pH decreased. The activities of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  for the Chattanooga Shale reached equilibrium with  $\text{FeOH}_4\text{SO}_4$  except for samples 9 and 13, which showed slight undersaturation. These results suggest that the  $\text{FeOH}_4\text{SO}_4$  is very likely controlling the activity of  $\text{Fe}^{3+}$  in solution below pH 6.00.

#### Acid Reactions

The results of this study demonstrate that below pH 6.00 the activities of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are controlled by basic sulfate solid phases. This shows that equation (3) is not valid below pH 6.00. In addition, there will be a significant interaction between  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{H}_2\text{O}$  (hydrolysis) influencing acid generation. Thus, the equations describing acid production associated with pyrite oxidation below pH 6.00 (most acid mine drainage is well below pH 6.00) should include the following reactions:



In aqueous solutions below pH 6.00,  $\text{AlOH}^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{FeOH}^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$  and  $\text{Fe}_2(\text{OH})_2^{4+}$  are the predominant ionic species. This suggests that at chemical equilibrium pH will be a function of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  hydrolysis.

## Management Applications

### Predicting Aqueous Chemistry

In a disposal environment, the rate of infiltration or groundwater flow will influence the aqueous chemistry. If water flow is slow enough to allow contact times necessary to establish equilibrium (i.e., rate of reaction faster than the flow rate through the system), the water quality characteristics will reflect the influence of secondary mineral formation. With increased leaching rates and rapid removal of reaction products, the kinetics of mineral dissolution-precipitation and adsorption will determine water quality characteristics. This may result in a nonequilibrium or metastable equilibrium conditions influencing the aqueous chemistry.

If the waste/water system is at chemical equilibrium and the aqueous chemistry can be defined by secondary mineral reactions, then any leachate that leaves the disposal environment can be predicted using fundamental thermodynamic constants. With these fundamental relationships established, waste-specific/site-specific test methods can be used to predict water quality as a function of disposal site design (i.e., design with influence waste composition and flow rate). If water quality predictions are not acceptable, then treatment options can be included in the test procedure.

### Acknowledgments

The work upon which this report is based was completed for the U.S. Department of Energy, Morgantown Energy Technology Center, as directed by the Laramie Project Office, under contract DE-AC20-85LC11062.

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