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In

Environmental Geological Water Science

Volume 11, No. 3

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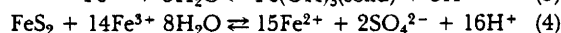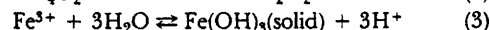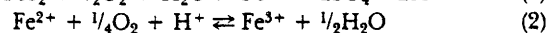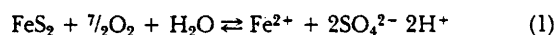Laramie, Wyoming 82071

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ABSTRACT / Acid mine drainage, produced from the oxidation of iron sulfides, often contains elevated levels of dissolved aluminum (Al), iron (Fe), and sulfate (SO_4) and low pH. Understanding the interactions of these elements associated with acid mine drainage is necessary for proper solid waste management planning. Two eastern oil shales were leached using humidity cell methods. This study used a New Albany Shale (4.6 percent pyrite) and a Chattanooga Shale (1.5 percent pyrite). The leachates from the humidity cells were filtered, and the filtrates were analyzed for total concentrations of cations and anions. After correcting for signifi-

cant solution species and complexes, ion activities were calculated from total concentrations. The results show that the activities of Fe^{3+}, Fe^{2+}, Al^{3+}, and SO_4^{2-} increased due to the oxidation of pyrite. Furthermore, the oxidation of pyrite resulted in a decreased pH and an increased pe + pH (redox-potential). The Fe^{3+} and Fe^{2+} activities appeared to be controlled by amorphous $Fe(OH)_3$ solid phase above a pH of 6.0 and below pe + pH 11.0. The Fe^{3+}, Fe^{2+}, and SO_4^{2-} activities reached saturation with respect to $FeOHSO_4$ solid phase between pH 3.0 and 6.0 and below pe + pH 11.0. Below a pH of 3.0 and above a pe + pH of 11.0, Fe^{2+}, Fe^{3+}, and SO_4^{2-} activities are supported by $FeSO_4 \cdot 7H_2O$ solid phase. Above a pH of 6.0, the Al^{3+} activity showed an equilibrium with amorphous $Al(OH)_3$ solid phase. Below pH 6.0, Al^{3+} and SO_4^{2-} activities are regulated by the $AlOHSO_4$ solid phase, irrespective of pe + pH. The results of this study suggest that under oxidizing conditions with low to high leaching potential, activities of Al and Fe can be predicted on the basis of secondary mineral formation over a wide range of pH and redox. As a result, the long-term chemistry associated with disposal environments can be largely predicted (including trace elements).

Introduction

Iron sulfide oxidation can be initiated by atmospheric oxygen and ferric iron. Stumm and Morgan (1981) suggest the following reactions for generating acidity from these two modes of oxidation.

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightleftarrows Fe^{2+} + 2SO_4^{2-}\ 2H^+ \qquad (1)$$
$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightleftarrows Fe^{3+} + \tfrac{1}{2}H_2O \qquad (2)$$
$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3(\text{solid}) + 3H^+ \qquad (3)$$
$$FeS_2 + 14Fe^{3+}\ 8H_2O \rightleftarrows 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

These reactions suggest that acid generation may occur in both unsaturated and saturated conditions. In addition to the degree of saturation, the time of contact between the leaching solution and the solid phases (i.e., equilibrium/nonequilibrium) will influence solution chemistry (Sullivan and others 1986).

In order to effectively manage wastes from geologic materials (e.g., oil shale and coal overburden containing iron sulfides), it is important to understand the reactions that will influence acid generation under low and high leaching environments. In a recent study by Sullivan and others (1987a), the chemistry of alu-

minum and iron was determined under low leaching oxidizing equilibrium conditions. The results of this study indicate that at equilibrium (1) a basic iron sulfate solid phase controls the solubility of Fe^{3+} and a basic aluminum sulfate solid phase controls the solubility of Al^{3+} below pH 6.0, and (2) amorphous iron and aluminum oxides control Fe^{3+} and Al^{3+}, respectively, above a pH of 6.0. Thus equation (3) likely does not control the activity of Fe^{3+} in low pH acid mine drainage environments. This study also showed that secondary mineral formation and acid hydrolysis of Fe^{3+} and Al^{3+} will determine the equilibrium pH. However, in those environments that may not attain equilibrium due to a short contact time between water and the solid phases, the chemistry of the system may not be similar to the equilibrium chemistry.

Thus, the objectives of the present study were to (1) evaluate iron sulfide oxidation and the reactions of Al^{3+}, Fe^{3+}, Fe^{2+}, and SO_4^{2-} under conditions of high leaching, (2) determine the composition of acid mine drainage under such conditions, and (3) utilize chemical equations to understand the management of geologic materials containing iron sulfides.

Materials and Methods

Two eastern oil shales were used in this study, a New Albany Shale that contains 4.6 percent pyrite, and a Chattanooga Shale that contains 1.5 percent pyrite. The New Albany Shale was collected from an unweathered stratum located in Bullit County, Kentucky, and the Chattanooga Shale was collected from a weathered outcrop located in Smith County, Tennessee.

Humidity Cell

The humidity cell, developed by Caruccio (1968), was used to simulate natural weathering of iron sulfides in an aerobic unsaturated environment. This procedure allowed acid production to occur while sequential leaching allowed oxidizing conditions to exist in a moist environment.

One kg of each shale (<2.0 mm) was spread evenly in the bottom of humidity cells, and the lids were tightly sealed. Dry air was passed over the samples for 3 d. From day 4 to day 7, humidified air was passed over the samples. On the seventh day, 1 l of distilled-deionized water was added to each cell and allowed to equilibrate for 1 h. After 7 d, the solutions were extracted, filtered, and the sediments were returned to the respective cells. This cycle continued for 21 wk. A solution of Thiobacillus ferrooxidans and Thiobacillus thiooxidans was added to each cell on the fifteenth week to increase acid production. All leachate samples from the cells were analyzed for pH, Eh, Cl, SO_4, Al, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sr, and Zn.

The pH was measured with a combination electrode. The Eh was measured with standard platinum and reference electrodes. Sulfate and chlorides were measured by ion chromatography. All remaining elements were analyzed with ICP-OES. Total elemental analyses were speciated with WATEQFC geochemical code (Runnells and Lindberg 1981) to calculate ion activities for Al^{3+}, Fe^{3+}, Fe^{2+}, Na^+, K^+, and SO_4^{2-}.

Quality Control

The following quality control methods were used in this study: (1) full set calibration was run with each sample set for each method, (2) one duplicate analysis was completed for every 10 samples run, (3) blanks were run with each sample set, and (4) spiking was performed for each analyte (all spiking was evaluated for 90–110 percent recovery of added analyte concentrations).
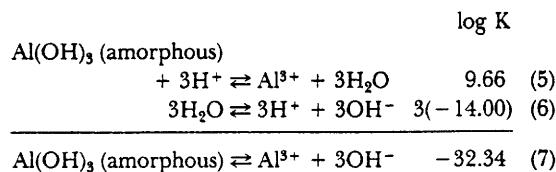
Results and Discussion

Data from the humidity cells were collected on a weekly basis. To simplify the graphical presentation of the data, results of analyses are given for day 7, 14, 21, 28, 56, 84, 112, and 147 for each shale. The results of all analyses (including trace element data) are reported in Sullivan and others (1987b). Activities of Al^{3+}, Fe^{3+}, Fe^{2+}, Na^+, K^+, and SO_4^{2-} from the humidity cell extracts are summarized in Table 1. Also included in this table are equilibration times, pH, and pe + pH measurements.

These data show that the New Albany Shale extracts (unweathered with no soluble acidity), the initial pH value increased from 4.69 to 7.66 and then decreased to 2.47. However, for the Chattanooga Shale extracts (weathered with soluble acidity), the pH value decreased gradually from 4.69 to 2.57. These data show that as the leaching time increased, the pH decreased, and the solubility of Al^{3+}, Fe^{3+}, and Fe^{2+} increased for both shales. Further, the data in Table 1 show that upon oxidation of pyrite, the redox (pe + pH) increased from 9.03 to 11.51 for the New Albany Shale and from 9.12 to 12.51 for the Chattanooga Shale.

The relationship between the ion activity product (IAP) vs. pH for Al^{3+}, Fe^{3+}, and Fe^{2+} solid phases are shown in Figures 1, 2, and 3, respectively. The data given in these figures include all samples except 1, 9, 10, 11, and 15. The calculated IAP values for the latter samples were excluded, because the leachate cation/anion balance exceeded 10 percent.

In Figure 1, the amorphous $Al(OH)_3$ line corresponds to a dissociation constant of $10^{-32.34}$ (equation 7). This constant was calculated from the following reactions:

log K

$Al(OH)_3$ (amorphous)

$$+ 3H^+ \rightleftharpoons Al^{3+} + 3H_2O \qquad 9.66 \quad (5)$$
$$3H_2O \rightleftharpoons 3H^+ + 3OH^- \quad 3(-14.00) \quad (6)$$

$$Al(OH)_3 \text{ (amorphous)} \rightleftharpoons Al^{3+} + 3OH^- \quad -32.34 \quad (7)$$

The equilibrium constant for $Al(OH)_3$ (amorphous) was taken from Lindsay (1979). The $AlOHSO_4$ equilibrium constant was taken from Van Breeman (1973). The experimental IAP's are plotted in this figure to examine possible Al solid phases controlling Al^{3+} activities in acid mine drainage. For the New Albany Shale extracts, the initial Al^{3+} activity shows saturation with respect to $Al(OH)_3$ (amorphous). As leaching time increased, Al^{3+} and SO_4^{2-} activities reached equilibrium with $AlOHSO_4$ solid phase. For the Chat-

Table 1.   Ion activities of Al^{3+}, Fe^{3+}, Fe^{2+}, Na^+, K^+, and SO_4^{2-} in humidity cell equilibrium extracts from oil shales containing pyrite.

Sample no.	Time (d)	pH	pe + pH	Log activity					
				Al^{3+}	Fe^{3+}	Fe^{2+}	Na^+	K^+	SO_4^{2-}
				New Albany Shale					
1	7	4.69	9.03	−5.29	−12.72	−4.05	−3.60	BD	−2.88
2	14	7.51	8.64	BD	−18.14	−6.25	−3.47	BD	−2.74
3	21	7.66	9.47	−13.53	−17.58	−6.38	−3.48	BD	−2.72
4	28	4.64	9.77	−6.02	−12.91	−5.03	−3.57	BD	−2.40
5	56	2.95	7.82	−4.47	−11.43	−3.28	−3.70	BD	−2.42
6	84	2.99	9.30	−4.16	−9.74	−3.03	−4.66	BD	−2.37
7	112	2.15	9.85	−4.13	−7.49	−2.17	−1.91	−2.40	−1.84
8	147	2.47	11.51	−4.15	−6.32	−2.35	BD	BD	−2.05
				Chattanooga Shale					
9	7	4.69	9.12	BD	−13.63	−5.04	BD	BD	−3.30
10	14	4.66	9.17	−5.03	−13.18	−4.68	−3.64	BD	−2.79
11	21	4.36	9.60	−4.45	−12.66	−4.90	−3.40	BD	−3.02
12	28	2.79	12.37	−4.03	−6.56	−3.14	−3.58	BD	−2.51
13	56	2.66	12.43	−3.91	−5.93	−2.68	−3.39	BD	−2.42
14	84	2.78	12.68	−4.06	−5.76	−2.65	−3.78	BD	−2.38
15	112	2.63	10.37	−4.63	−9.35	−4.07	−1.87	−2.25	−1.90
16	147	2.57	12.51	−4.01	−5.65	−2.57	−3.33	−3.20	−2.29

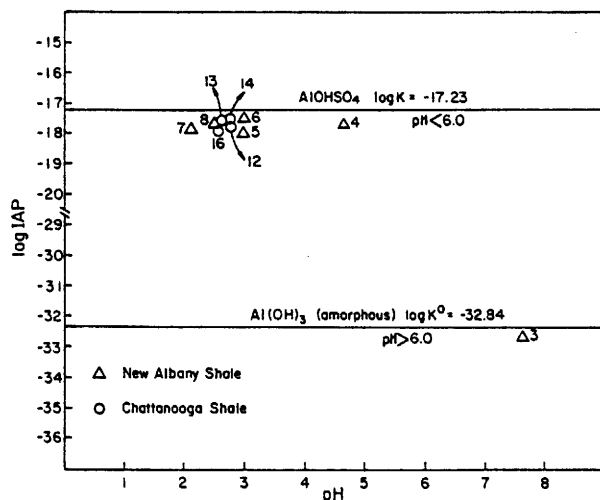BD = below detection limit of 0.04 mg/l.
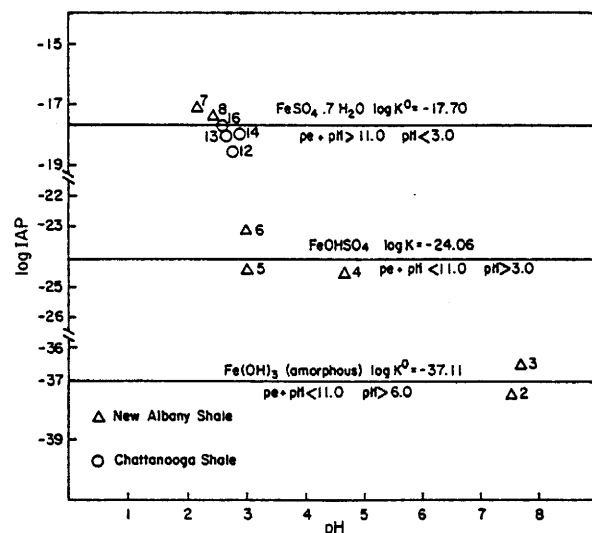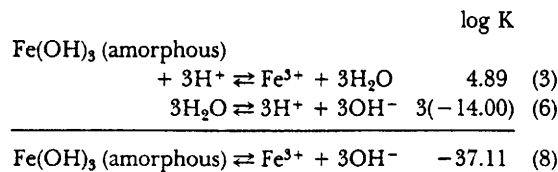

Figure 1. IAP vs. pH for aluminum.

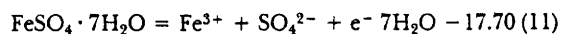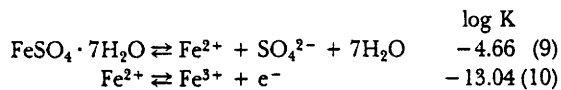Figure 2. IAP vs. pH for iron (based on equations 8 and 11).

tanooga Shale, all Al^{3+} and SO_4^{2-} activities show equilibrium with $AlOHSO_4$ solid phase. These results suggest that below pH 6.0, $AlOHSO_4$ may control the solubility of Al^{3+}. Similar results were reported by Van Breeman (1973) and Sullivan and others (1987a).

In Figure 2, the $Fe(OH)_3$ (amorphous) line corresponds to a dissociation constant of $10^{-37.11}$ (equation 8). This constant was calculated from the following reactions:

$$
\begin{array}{llr}
 & & \log K \\
Fe(OH)_3 \text{ (amorphous)} & & \\
\quad + 3H^+ \rightleftarrows Fe^{3+} + 3H_2O & 4.89 & (3) \\
\quad\quad 3H_2O \rightleftarrows 3H^+ + 3OH^- & 3(-14.00) & (6) \\
\hline
Fe(OH)_3 \text{ (amorphous)} \rightleftarrows Fe^{3+} + 3OH^- & -37.11 & (8)
\end{array}
$$

The equilibrium constant for equation (3) was taken from WATEQ3 (Ball and others 1981). The $FeOHSO_4$ line corresponds to an equilibrium constant

of $10^{-24.06}$ (Sullivan and others 1987a). The $FeSO_4 \cdot 7H_2O$ line corresponds to an equilibrium constant of $10^{-17.70}$ (equation 11). This constant was calculated from the following reactions:
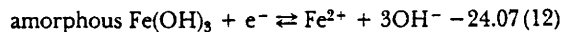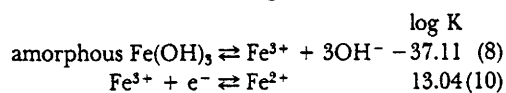
$$
\begin{array}{lr}
 & \log K \\
FeSO_4 \cdot 7H_2O \rightleftarrows Fe^{2+} + SO_4^{2-} + 7H_2O & -4.66 \quad (9) \\
Fe^{2+} \rightleftarrows Fe^{3+} + e^- & -13.04 \,(10) \\
\hline
FeSO_4 \cdot 7H_2O = Fe^{3+} + SO_4^{2-} + e^- \, 7H_2O & -17.70\,(11)
\end{array}
$$

The equilibrium constant for $FeSO_4 \cdot 7H_2O$ (equation 9) was taken from WATEQFC (Runnells and Lindberg 1981). The equilibrium constant for equation (10) was taken from Lindsay (1979).
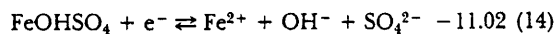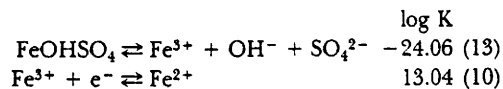
The experimental results in Figure 2 suggest that for the New Albany Shale extracts, the initial Fe^{3+} activity appears to be regulated by amorphous $Fe(OH)_3$. As the pH decreased, the pe + pH did not exceed 9.85, and the activities of Fe^{3+} and SO_4^{2-} approached saturation with respect to the $FeOHSO_4$ solid phase. With an increase of the pe + pH to 11.51, the activities of Fe^{3+} and SO_4^{2-} appear to be controlled by the $FeSO_4 \cdot 7H_2O$ solid phase. For the Chattanooga Shale extracts, the activities of Fe^{3+} and SO_4^{2-} show an equilibrium with $FeSO_4 \cdot 7H_2O$.

These results suggest that the solubility of Fe^{3+} is controlled by (1) $Fe(OH)_3$ above a pH of 6.0, (2) $FeOHSO_4$ above a pH of 3.0 and a pe + pH less than 11.0, and (3) $FeSO_4 \cdot 7H_2O$ below a pH of 3.00 and a pe + pH above 11.00. These results are also consistent with equilibrium data reported by Sullivan and others (1987a). However, in that study the equilibrium pH was always greater than 3.0 so that $FeSO_4 \cdot 7H_2O$ was not shown to control Fe^{3+} activity.

In Figure 3, amorphous $Fe(OH)_3$ line corresponds to a constant of $10^{-24.07}$ (equation 12). This constant was calculated from the following reactions:

$$
\begin{array}{lr}
 & \log K \\
\text{amorphous } Fe(OH)_3 \rightleftarrows Fe^{3+} + 3OH^- & -37.11 \quad (8) \\
Fe^{3+} + e^- \rightleftarrows Fe^{2+} & 13.04\,(10) \\
\hline
\text{amorphous } Fe(OH)_3 + e^- \rightleftarrows Fe^{2+} + 3OH^- & -24.07\,(12)
\end{array}
$$

The $FeOHSO_4$ line corresponds to a constant of $10^{-11.02}$ (equation 14). This constant was calculated from the following reactions:

$$
\begin{array}{lr}
 & \log K \\
FeOHSO_4 \rightleftarrows Fe^{3+} + OH^- + SO_4^{2-} & -24.06 \quad (13) \\
Fe^{3+} + e^- \rightleftarrows Fe^{2+} & 13.04\,(10) \\
\hline
FeOHSO_4 + e^- \rightleftarrows Fe^{2+} + OH^- + SO_4^{2-} & -11.02\,(14)
\end{array}
$$

The results suggest that for the New Albany Shale extracts, Fe^{2+} solubility shows an equilibrium with amorphous $Fe(OH)_3$. As the pH decreased, Fe^{2+} and SO_4^{2-} were supported by $FeOHSO_4$. A further in-
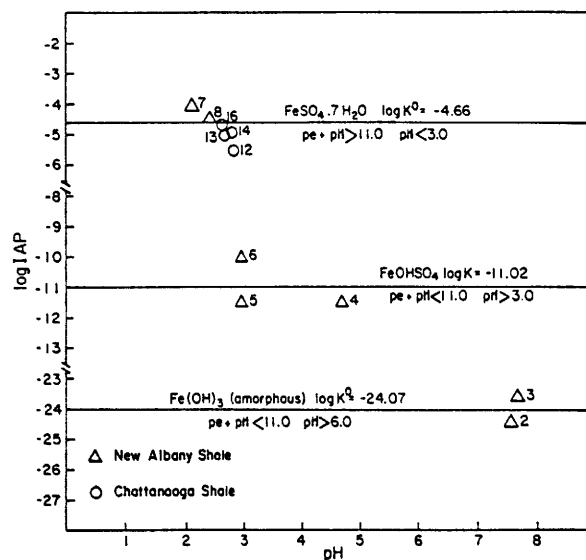

Figure 3. IAP vs. pH for iron (based on equations 12 and 14).

crease in leaching time resulted in a pH below 3.00, and Fe^{3+} and SO_4^{2-} activities approached equilibrium with $FeSO_4 \cdot 7H_2O$. In the Chattanooga Shale extracts, the Fe^{2+} and SO_4^{2-} activities show saturation with respect to $FeSO_4 \cdot 7H_2O$ solid phase below a pH of 3.00 and above a pe + pH of 11.00. Similar results were reported by Nordstrom and others (1979).

Other solid phases capable of forming were also examined. These phases are $KAl_3(SO_4)_2(OH)_6$ (alunite), K or Na $Fe_3(SO_4)_2(OH)_6$ (jarosite), $Fe_3(OH)_8$ (ferrosic hydroxide), and Fe_3O_4 (magnetite). However, none of the leachates examined in this study showed equilibrium with the above solid phases, except for sample 7, which showed saturation with respect to Na jarosite. This may have occurred because the sample had a low pH (2.15) and a high SO_4^{2-} activity $(10^{-1.84})$. This one data point suggests that possibly a fourth solid phase may control Fe^{3+} activity under extremely acidic conditions accompanied by high sulfate activity.

Chemistry of Acid Generation

The study by Sullivan and others (1987a) showed that at equilibrium of Al^{3+} and Fe^{3+} activities were controlled by amorphous hydroxides above pH 6.0 and by basic sulfates between pH 3.0 and 6.0. Their results indicate that in low leaching environments Al^{3+} and Fe^{3+} activities were determined by two different solid phases depending on pH and SO_4^{2-} activity.

The data in this study were collected under conditions simulating a greater leaching rate and availability of atmospheric oxygen for iron sulfide oxidation. Under such conditions, Al^{3+} activity was controlled by the solid phases reported previously. However, the ac-

tivity of Fe^{3+} was controlled by $FeSO_4 \cdot 7H_2O$ under very acid conditions. These results indicate that the prediction of acid generation and associated stoichiometry of iron sulfide oxidation is a function of the disposal environment.

On the basis of the results reported by Sullivan and others (1987a) and the result of this study, the chemistry of acid production associated with iron sulfide oxidation under high and low leaching environments can be described by the reactions given in Figure 4. In an environment that will produce acid mine drainage, iron sulfide oxidation (reactions 1, 4, and/or both) releases Fe^{2+}, SO_4^{2-}, and acidity into solution. After these initial reactions, the chemistry of acid generation is determined by the given reactions and environmental conditions (i.e., pH, pe + pH, and leaching conditions).

The results of this study also show that in a leaching environment (as simulated by the humidity cell) a contact time of one week may be adequate to establish the control of Al^{3+}, Fe^{2+}, Fe^{3+}, and SO_4^{2-} activities by various solid phases.

Management Applications

The Disposal Environment

The ability to predict the chemistry of acid mine drainage in a given disposal environment is important in evaluating long-term acid generation and water quality characteristics from materials containing iron sulfides. Accurate predictions of short-term and long-term water quality will be a function of the characteristics of the solid phases, initial water chemistry, and attainment of equilibrium. If a waste material generates acidity (e.g., a negative acid–base account and availability of oxygen), attainment of equilibrium or nonequilibrium in the disposal environment will determine water quality characteristics of the leachate. A leachate can attain equilibrium in the waste environment under either of the following conditions:

1. The rate of water flow through the waste environment is sufficiently slow to allow the chemical reactions to attain equilibrium.
2. The rate of water flow through the waste environment is too fast to allow chemical equilibrium but flow out of the disposal environment is retarded by a less permeable zone. This would result in establishing a saturated zone that will reduce the flow rate sufficiently to allow chemical reactions to attain equilibrium.

If the solid phases in a disposal environment vary to a large degree, it may be difficult to attain equilibrium (i.e., case 1). However, in an environment where flow is retarded, variations in solid phases are not so im-

portant. In the latter environment, the chemistry of the saturated system will determine the chemistry of the leachate leaving the disposal environment.

The present study shows that if water is in contact with waste materials for one week (and oxygen is available to the system), secondary minerals may precipitate and control the activities of Al^{3+}, Fe^{3+}, Fe^{2+}, and SO_4^{2-} and hydrolysis will determine the pH. This suggests that for a hydrologic environment, water quality characteristics can be predicted using the equations given in Figure 4 if the flow rate through the system is greater than one week in duration (assumes minimum variation in waste properties for case 1).

Predicting the Aqueous Chemistry

When secondary mineral formation controls the activity of Al^{3+}, Fe^{3+}, and Fe^{2+}, fundamental thermodynamic constants (i.e., conditional solubility products) can be used to predict leachate chemistry. As long as secondary mineral formation controls the leachate chemistry, long-term water quality predictions can be made. On the basis of the results of this study, the activity of Al^{3+}, Fe^{3+}, and Fe^{2+} can be predicted under the following conditions (this assumes that the necessary conditions exist for reactions 1, 2, and 4 in Figure 4 to occur):

1. When the pH is greater than 6.0 and pe + pH is less than 11.0, the SO_4^{2-} activity does not influence the activity of Al^{3+}, Fe^{3+}, and Fe^{2+}. In this case, the activity of Al^{3+} is controlled by reaction (5) and Fe^{3+} is controlled by reaction (3) in Figure 4. The equilibrium pH is a function of the hydrolysis reactions (i.e., 15, 16, 18, 19, 20, 22, 23, 24 reactions in Figure 4) and secondary mineral formation.
2. When the pH is less than 6.0 but greater than 3.0 and the pe + pH is less than 11.0, Fe^{3+} and Al^{3+} activities will be determined by basic sulfate secondary mineral formation (reactions 17 and 21 in Figure 4). The equilibrium pH will be a function of secondary mineral formation (note importance of SO_4^{2-} activity) and hydrolysis.
3. In a higher leaching environment there is the potential to generate a lower pH. This condition generated a pH less than 3.0 and a pe + pH greater than 11.0. In this environment the activities of Fe^{3+} and Fe^{2+} will be controlled by ferrous sulfate formation (reaction 9 in Figure 4). The equilibrium pH will be a function of secondary mineral formation and hydrolysis.

Depending on the environmental conditions described above, the long-term acidity and solution con-
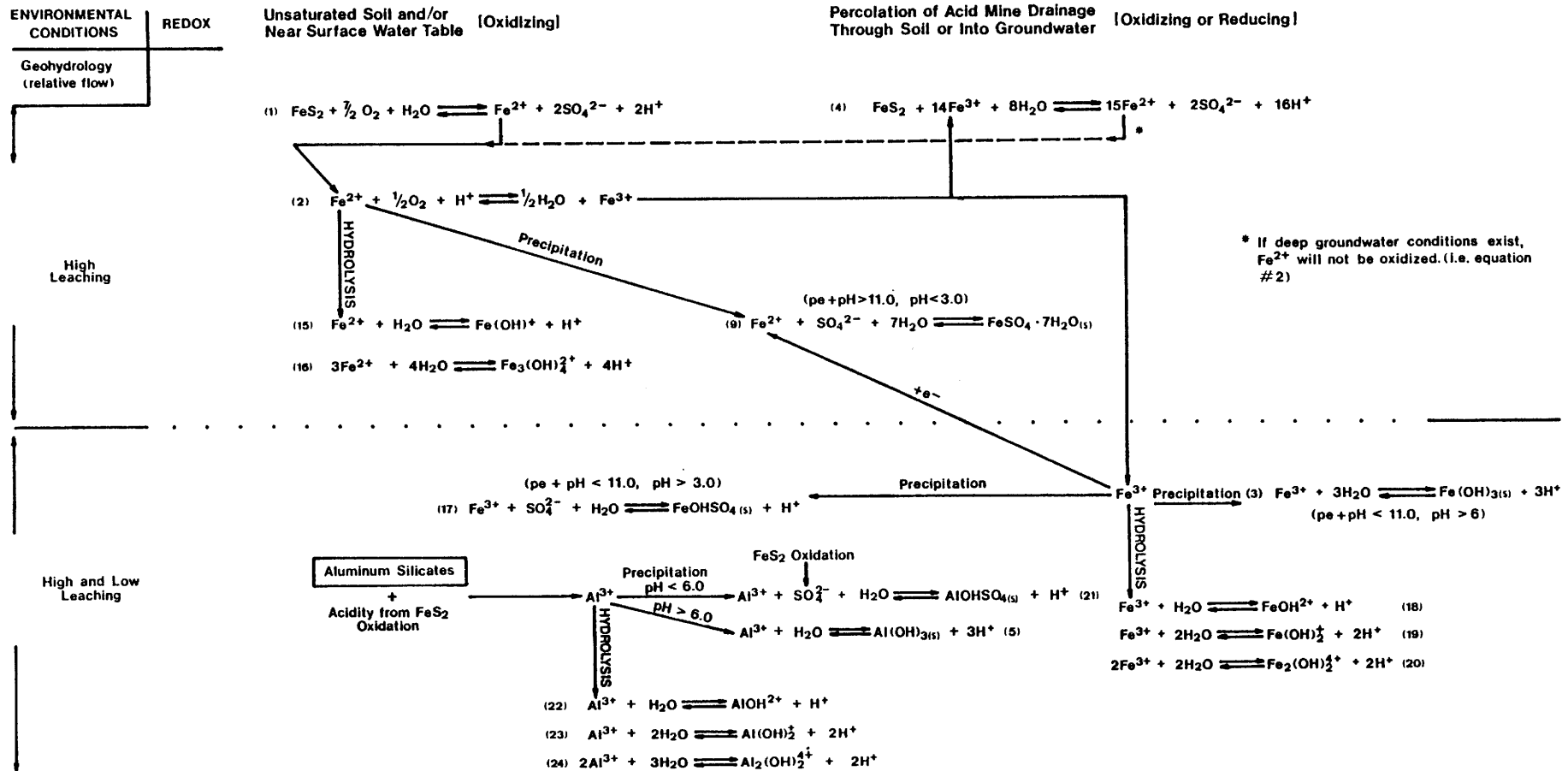
ENVIRONMENTAL CONDITIONS | **REDOX** | **Unsaturated Soil and/or Near Surface Water Table** [Oxidizing] | **Percolation of Acid Mine Drainage Through Soil or Into Groundwater** [Oxidizing or Reducing]

Geohydrology (relative flow)

(1) $FeS_2 + \frac{7}{2} O_2 + H_2O \rightleftharpoons Fe^{2+} + 2SO_4^{2-} + 2H^+$

(4) $FeS_2 + 14Fe^{3+} + 8H_2O \rightleftharpoons 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

(2) $Fe^{2+} + \frac{1}{2}O_2 + H^+ \rightleftharpoons \frac{1}{2}H_2O + Fe^{3+}$

HYDROLYSIS

Precipitation

High Leaching

* If deep groundwater conditions exist, Fe^{2+} will not be oxidized. (i.e. equation #2)

$(pe + pH > 11.0, \ pH < 3.0)$

(15) $Fe^{2+} + H_2O \rightleftharpoons Fe(OH)^+ + H^+$

(9) $Fe^{2+} + SO_4^{2-} + 7H_2O \rightleftharpoons FeSO_4 \cdot 7H_2O_{(s)}$

(16) $3Fe^{2+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{2+} + 4H^+$

$+ e^-$

$(pe + pH < 11.0, \ pH > 3.0)$

Precipitation

Fe^{3+} Precipitation (3) $Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_{3(s)} + 3H^+$

(17) $Fe^{3+} + SO_4^{2-} + H_2O \rightleftharpoons FeOHSO_{4(s)} + H^+$

$(pe + pH < 11.0, \ pH > 6)$

HYDROLYSIS

FeS_2 Oxidation

High and Low Leaching

Aluminum Silicates + Acidity from FeS_2 Oxidation

Precipitation pH < 6.0

Al^{3+}

$Al^{3+} + SO_4^{2-} + H_2O \rightleftharpoons AlOHSO_{4(s)} + H^+$ (21)

pH > 6.0

$Al^{3+} + H_2O \rightleftharpoons Al(OH)_{3(s)} + 3H^+$ (5)

HYDROLYSIS

$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$ (18)

$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+$ (19)

$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$ (20)

(22) $Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$

(23) $Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+$

(24) $2Al^{3+} + 3H_2O \rightleftharpoons Al_2(OH)_2^{4+} + 2H^+$

Figure 4. A summary of chemical reactions responsible for acid generation and secondary mineral formation as a function of environmental conditions.

centrations of Fe and Al can be predicted. The natural extension of this study will be to determine the activities of the major cations and anions and using geochemical models to predict the potential trace element chemistry associated with the given environmental conditions.

Because leachate chemistry will be a function of waste-specific/site-specific characteristics, test methods need to be developed that can determine potential leachate chemistry based on site characteristics. In addition, these tests need to be simple and completed in a relatively short period of time (unlike humidity cell methods).

Ultimately, the reactions suggested in this study to stimulate acid mine drainage chemistry in equilibrium or near equilibrium environment must be field validated. In addition to field validation, the chemistry of very high leaching environments needs to be determined (i.e., leachate contact times less than one week).

Acknowledgments

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