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ABSTRACT

Acid mine drainage, produced from the oxidation of iron-sulfides, often contains elevated levels of dissolved Zn. To predict environmental hazards, it is important to understand the solubility relationships of Zn associated with acid mine drainage. Two eastern oil shales were leached under aerobic unsaturated environments using the humidity cell method. This study used a New Albany Shale (unweathered, 4.6% pyrite) and a Chattanooga Shale (weathered, 1.5% pyrite). The leachates from the humidity cells were filtered, and the filtrates were analyzed for total concentrations of cations and anions. From the total concentrations, ion activities were calculated, after correcting for significant solution complexes and ion pairs. The results show that the pH of the leachates decreased due to oxidation of pyrite. Furthermore, oxidation of pyrite increased the solubility of Fe^{3+} and Zn^{2+} in leachates. Above pH 7.00, the Zn^{2+} activity was supported by Zn_2SiO_4 (willemitite) in equilibrium with measured H_4SiO_4^0 activity. Below pH 5.00, Zn^{2+} activity for both shales appeared to be saturated by ZnFe_2O_4 (franklinite) in equilibrium with measured Fe^{3+} activity. The results in this study suggest that Zn^{2+} solubility in acid mine drainage, produced in an aerobic unsaturated environment, may be limited by ZnFe_2O_4 solid phase.

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 pyrite (FeS_2), which usually occurs in mining wastes, coal cleaning waste, mine spoil, and acid sulfate soils (Smith et al., 1974). The oxidation of pyrite and environmental problems associated with it are well documented (Stumm and Morgan, 1981; Martin, 1974; Griffin, 1980; Wahler, 1978). Sullivan et al. (1987) examined trace elements concentrations in eastern oil shales associated with soluble, adsorbed, organic, carbonate, and sulfide phases by selective dissolution methods. These authors reported the most of Zn was found to be associated with sulfide phases. Thus, acid mine drainage, produced from the oxidation of pyrite and Zn sulfides, often contains elevated concentrations of dissolved Zn. To understand the chemistry of Zn in acid mine waters, it is important to examine the solubility relationships of Zn minerals in an environment where pyrite will be oxidized. However, it has been shown by Sullivan et al. (1986) that disposal environments will influence the solid waste solution chemistry. Thus, the objective of the present study was to examine the solubility of Zn solid phases associated with acid mine drainage produced in an aerobic unsaturated environment.

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MATERIALS AND METHODS

Two eastern oil shales were used in this study: a New Albany shale (4.6% pyrite) and a Chattanooga Shale (1.5% pyrite). The new Albany Shale was collected from an unweathered stratum located in Bullit County, KY, and the Chattanooga Shale was collected from a weathered outcrop located in Smith County, TN.

The mineralogy of shale samples was determined by x-ray diffraction analysis. X-ray analysis was performed on randomly oriented ethanol slurried samples with a Scintag PAD V (Scintag, Inc., Santa Clara, CA) powder diffractometer and Ni filtered $\text{CuK}\alpha$ radiation. X-ray diffraction profiles were analyzed by manual interaction with Scintag software containing JCPDS (Joint Committee on Powder Diffraction Standards) files. The major minerals identified in shale samples are presented in Table 1. A 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 kilogram of each shale (<2.0 mm) was evenly spread in the bottom of the humidity cell, and the lid was tightly sealed. Dry air was passed over the samples for 3 d. From Day 4 to 7, humidified air was passed over the samples. On the 7th d, 1 L of distilled-deionized water was added to each cell and allowed to react for 1 h. After 1 h of reaction time, the suspensions were decanted. Decanted solutions were filtered with fiberglass vacuum filters and the sediments were returned to the respective cells. This cycle continued for 21 wk. A solution of *Thiobacillus ferrooxidans* and *T. thiooxidans* was added to each cell on the 15th wk to increase acid production. A more detailed description of the humidity cell is reported by Sobek et al. (1978). All leachate samples from the cells were analyzed for pH, Eh, Al, Ca, Mg, Na, K, Sr, Fe, Mn, Zn, Cu, Ni, Pb, HCO_3^- , CO_3^{2-} , Cl, SO_4^{2-} , Si, Mo, and Se. All experiments were conducted at 25 °C.

The pH was measured with a combination electrode. The Eh was measured with platinum electrodes. pe was calculated from Eh (Lindsay, 1979). Sulfate was measured by ion chromatography. Chloride was measured with a specific ion electrode. Bicarbonate and carbonate were measured by acid titration. All remaining elements were analyzed with inductively coupled plasma optical emission spectrometry. Total elemental concentrations of leachates, pH, Eh, and temperature were used as input parameters to the WATEQFC (Runnells and Lindburg, 1981) geochemical model to calculate ion activities.

Table 1. Relative abundance of minerals identified in shale samples listed in decreasing order.

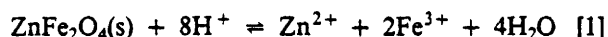
Shale	Minerals
New Albany	Quartz Illite Feldspars Pyrite Kaolinite Siderite Smectite Calcite
Chattanooga	Quartz Illite Feldspars Smectite Anhydrite Siderite Pyrite

RESULTS AND DISCUSSION

Data from the humidity cells were collected on a weekly basis. To simplify the graphical presentation of the data, results of the analyses are given for Days 7, 14, 21, 28, 56, 84, 112, and 147 for each shale. The results of all analyses are reported in Sullivan et al. (1987). Activities of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Zn^{2+} , H_4SiO_4^0 , and SO_4^{2-} , from the humidity cell extracts, are summarized in Table 2. Also included in this table are equilibrium times, $\text{pe} + \text{pH}$, and pH measurements.

For the New Albany Shale extracts (unweathered with no soluble acidity), the data show that initial pH increased from 4.69 to 7.66 and then decreased gradually from 4.64 to 2.47. However, for the Chattanooga Shale extracts (weathered with soluble acidity), the pH decreased gradually from 4.69 to 2.57. Furthermore, data in Table 2 show that addition of *T. ferrooxidans* and *T. thiooxidans* solutions to humidity cells decreased the leachate pH for both shales.

The relationship between the ion activity product (IAP) vs. pH for Zn^{2+} solid phases is shown in Fig. 1. Also included in this figure are $\log K_{\text{sp}}$ 6.87 and 15.33 for ZnFe_2O_4 (franklinite) and Zn_2SiO_4 (willemite), respectively. These values were taken from WATEQFC. The equilibrium solubility product (K_{sp}) for $\text{ZnFe}_2\text{O}_4(\text{s})$ and $\text{Zn}_2\text{SiO}_4(\text{s})$ is defined as follows:

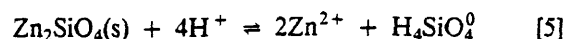


$$K_{\text{sp}}(\text{ZnFe}_2\text{O}_4(\text{s})) = (\text{Zn}^{2+})(\text{Fe}^{3+})^2(\text{H}_2\text{O})^4 / (\text{ZnFe}_2\text{O}_4(\text{s}))(\text{H}^+)^8 \quad [2]$$

where () refers to the thermodynamic activity of the species enclosed. Assuming activity of $\text{ZnFe}_2\text{O}_4(\text{s})$ and H_2O to be unity, Eq. [2] reduce to

$$K_{\text{sp}}(\text{ZnFe}_2\text{O}_4(\text{s})) = (\text{Zn}^{2+})(\text{Fe}^{3+})^2/(\text{H}^+)^8 \quad [3]$$

$$\log K_{\text{sp}}(\text{ZnFe}_2\text{O}_4(\text{s})) = \log \text{Zn}^{2+} + 2 \log \text{Fe}^{3+} + 8 \text{pH} \quad [4]$$



$$K_{\text{sp}}(\text{Zn}_2\text{SiO}_4(\text{s})) = (\text{Zn}^{2+})^2(\text{H}_4\text{SiO}_4^0) / (\text{Zn}_2\text{SiO}_4(\text{s}))(\text{H}^+)^4 \quad [6]$$

assuming activity of $\text{Zn}_2\text{SiO}_4(\text{s})$ to be unity, Eq. [6] reduce to

$$K_{\text{sp}}(\text{Zn}_2\text{SiO}_4(\text{s})) = (\text{Zn}^{2+})^2(\text{H}_4\text{SiO}_4^0)/(\text{H}^+)^4 \quad [7]$$

$$\log K_{\text{sp}}(\text{Zn}_2\text{SiO}_4(\text{s})) = 2 \log \text{Zn}^{2+} + \log \text{H}_4\text{SiO}_4^0 + 4 \text{pH} \quad [8]$$

The experimentally measured IAP for $\text{ZnFe}_2\text{O}_4(\text{s})$ and $\text{Zn}_2\text{SiO}_4(\text{s})$ in Eq. [1] and [5] is defined as follows:

$$\text{IAP}_{(\text{ZnFe}_2\text{O}_4(\text{s}))} = (\text{Zn}^{2+})(\text{Fe}^{3+})^2/(\text{H}^+)^8 \quad [9]$$

$$\log \text{IAP}_{(\text{ZnFe}_2\text{O}_4(\text{s}))} = \log \text{Zn}^{2+} + 2 \log \text{Fe}^{3+} + 8\text{pH} \quad [10]$$

and

$$\text{IAP}_{(\text{Zn}_2\text{SiO}_4(\text{s}))} = (\text{Zn}^{2+})^2(\text{H}_4\text{SiO}_4^0)/(\text{H}^+)^4 \quad [11]$$

$$\log \text{IAP}_{(\text{Zn}_2\text{SiO}_4(\text{s}))} = 2 \log \text{Zn}^{2+} + \log \text{H}_4\text{SiO}_4^0 + 4\text{pH} \quad [12]$$

If $\log(\text{IAP}/K_{\text{sp}})$ is equal to 0 for a given solid phase, the solution is saturated with respect to that solid phase. If $\log(\text{IAP}/K_{\text{sp}}) < 0$, the solution is undersaturated with respect to that solid phase. If $\log(\text{IAP}/K_{\text{sp}}) > 0$, the solution is supersaturated with respect to that solid phase.

Table 2. Ion activities of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Zn^{2+} , H_4SiO_4^0 , and SO_4^{2-} in humidity cell extracts from oil shales containing pyrite.

Sample no.	Time, d	pH	pe + pH	Log activity							
				Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe^{3+}	Zn^{2+}	SO_4^{2-}	H_4SiO_4^0
New Albany Shale											
1	7	4.69	9.03	-2.94	-3.07	-3.60	BD†	-12.72	-4.90	-2.88	-4.85
2	14	7.51	8.64	-3.14	-2.82	-3.47	BD	-18.14	-6.11	-2.74	-3.75
3	21	7.66	9.46	-3.30	-2.83	-3.48	BD	-17.58	-5.64	-2.72	-3.90
4	28	4.64	9.77	-3.16	-2.62	-3.57	BD	-12.91	-5.01	-2.40	-3.56
5†	56	2.95	7.82	-3.26	-2.77	-3.70	BD	-11.43	-4.42	-2.42	-3.48
6†	84	2.99	9.30	-3.35	-2.86	-4.66	BD	-9.74	-4.33	-2.37	-3.44
7†	112	2.15	9.85	-3.14	-2.74	-1.91	-2.40	-7.49	-4.33	-1.84	-5.34
8†	147	2.47	11.51	-3.39	-3.13	BD	BD	-6.32	-4.63	-2.05	-3.59
Chattanooga Shale											
9	7	4.69	9.12	-3.64	-4.18	BD	BD	-13.63	-4.83	-3.30	-5.18
10	14	4.66	9.17	-3.42	-3.67	-3.64	BD	-13.18	-4.12	-2.79	-3.73
11	21	4.36	9.60	-3.40	-3.59	-3.40	BD	-12.66	-3.86	-3.02	-3.62
12	28	2.79	12.37	-3.10	-3.30	-3.58	BD	-6.56	-3.42	-2.51	-3.24
13	56	2.66	12.43	-3.29	-3.26	-3.39	BD	-5.93	-3.35	-2.42	-3.47
14	84	2.78	12.68	-3.40	-3.37	-3.78	BD	-5.76	-3.70	-2.38	-3.57
15†	112	2.63	10.37	-3.60	-3.08	-1.87	-2.25	-9.35	-4.23	-1.90	-4.62
16	147	2.57	12.51	-3.50	-3.22	-3.33	-3.20	-5.65	-3.95	-2.29	-3.87

† Poor cation and anion balance due to complex solution matrix.

‡ BD = below detection limit of 0.04 mg/L.

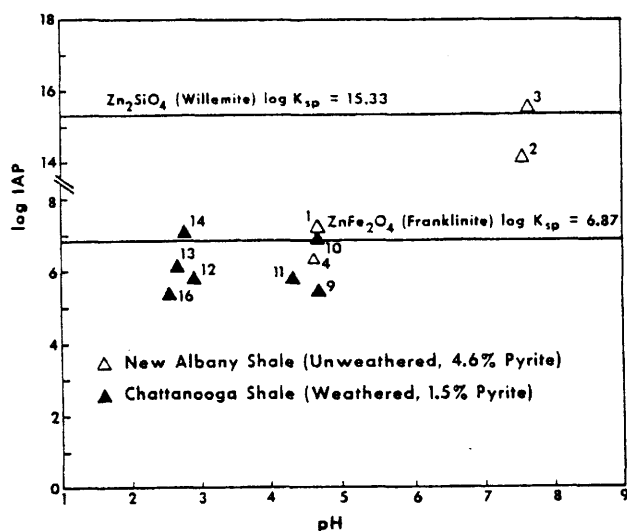


Fig. 1. Relationship between log IAP vs. pH with respect to Zn_2SiO_4 (willemite) and $ZnFe_2O_4$ (franklinite) in eastern oil shales containing pyrite.

The experimentally calculated IAP's are plotted in Fig. 1 to examine possible Zn solid phases controlling Zn^{2+} activities in acid mine waters (Note: ion activities in extracts with a poor ion balance were not plotted; see Table 1). For the New Albany Shale extracts, Zn^{2+} activity suggest saturation with respect to $ZnFe_2O_4$ (s) at a low pH. As leaching time increased, pH increased, and Zn^{2+} activity reached saturation with Zn_2SiO_4 (s). For the Chattanooga Shale extracts, all Zn^{2+} activities suggest saturation with $ZnFe_2O_4$ (s).

The log IAP's of Zn_2SiO_4 (s) and $ZnFe_2O_4$ (s), in Fig. 1, show slight undersaturation with respect to log K_{sp} values of these solid phases. However, Bohn and Bohn (1987) suggested that log (IAP/ K_{sp}) ratio between 0 to -1.00 are considered to be at equilibrium. Difference between log IAP and log K_{sp} values within that range are accounted for by the uncertainty of IAP measurements and K_{sp} in the chemical literature (Stumm and Morgan 1981). The observed log (IAP/ K_{sp}) ratios for Zn_2SiO_4 (s) and $ZnFe_2O_4$ (s) are within the range 0 to -1.00, except for samples 2, 9, and 16.

Several researchers have proposed precipitation of Zn with Fe oxides in soils and waters. White (1957) found evidence to suggest that 30 to 60% of Zn in soils of the eastern USA is tied up with hydrous ferric oxides. Jenne (1968) proposed that Zn and other heavy metals may be coprecipitated with hydrous oxides of Fe and Mn in soils and waters. Stanton and Burger (1970) examined precipitation of Zn at different pH values and reported that presence of Fe and Al ions in solutions rapidly lowered pH at which precipitation of Zn with Fe and Al oxides occurred. Lindsay (1979) reported $ZnFe_2O_4$ (s) as the most insoluble Zn solid phase, depending on the iron oxides controlling Fe^{3+} activity.

In conclusion, leaching oil shales (containing pyrite)

in an aerobic, unsaturated environment decreased pH and increased Fe^{3+} and Zn^{2+} activities in leachates due to pyrite oxidation. For the New Albany Shale extracts (unweathered with no soluble acidity), Zn^{2+} activity reached saturation with respect to $ZnFe_2O_4$ (s) below a pH of 6.00. Above pH 7.00, Zn^{2+} activity moved towards Zn_2SiO_4 (s) in equilibrium with measured $H_4SiO_4^0$ activity. For Chattanooga Shale (weathered with soluble acidity), Zn^{2+} activity suggested saturation with respect to $ZnFe_2O_4$ (s) in equilibrium with measured Fe^{3+} activity, below pH 5.00. The results of this study further suggest that Zn^{2+} activity in acid mine waters, produced in a leaching environment, as simulated by the humidity cell, may be regulated by $ZnFe_2O_4$ (s).

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