A METHOD FOR PREVENTION OF ACID MINE DRAINAGE

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ABSTRACT

The oxidation potential for the reaction of pyrite with ferric ions is studied. The limiting value for the voltage of the Fe^{+3}/Fe^{+2} cell is determined to be 0.41 v. The iron species are complexed and precipitated by phosphate species and tertiary sewage sludge in an effort to reduce the potential of this cell to below this limiting value. With this treatment, the oxidation reaction of pyrite with ferric ions is arrested in samples of "pure" pyrite and in overburden samples.

INTRODUCTION

The ecological impact of acid mine drainage (AMD) began when man first extracted coal commercially. During earth moving operations as in strip mining, millions of tons of rock overlaying the coal are removed to expose coal seams. This disturbance of the normal strata exposes minerals to oxidizing environments which accelerate weathering. During this process, iron sulfide minerals, mainly FeS 2, react with water and oxygen to produce soluble iron sulfates.(') These compounds first appear as white crusts of ferrous sulfate, occasionally accompanied by yellow-green ferric sulfate salt, which hydrolyze to produce sulfuric acid and iron oxides.

The exact weathering process of pyrite-containing overburden that produces AMD has not been well established; however, the commonly accepted reaction sequence is below: (2,3)

$$FeS_{2(s)} + 7/2O_{2} + H_{2}O = Fe^{++} + 2SO_{4}^{=} + 2H^{+} (1)$$

$$Fe^{++} + 1/4O_{2} + H^{+} = Fe^{+++} + 1/2H_{2}O (2)$$

$$Fe^{+++} + 3H_{2}O = Fe(OH)_{3}(s) + 3H^{+} (3)$$

$$FeS_{2(s)} + 14Fe^{+++} + 8H_{2}O = 15Fe^{++} + 16H^{+} {(*)} (4)$$

$$FeS_{2(s)} + 7/2 O_{2} + H_{2}O = Fe^{++} + 2 SO_{4}^{=} + 2H^{+}$$
(1)
$$Fe^{++} + 1/4 O_{2} + H^{+} = Fe^{+++} + 1/2 H_{2}O$$
(2)
$$Fe^{+++} + 3 H_{2}O = Fe(OH)_{3}(s) + 3H^{+}$$
(3)

$$\text{FeS}_{2(s)}$$
 + 14 Fe⁺⁺⁺ + 8 H₂0 = 15 Fe⁺⁺ + 2SO₄⁼ + 16 H⁺ (*) (4)

The process represented by equations (1) through (4) is a chain reaction. The product from Equation (2), ferric ion (Fe^{+3}), is used in Equation (4) to oxidize pyrite. During this step, it is subsequently reduced to

ferrous ion, Fe^{+2} . In Equation (2) ferrous ion is again oxidized to ferric ion to be used in Equation (4), etc., etc. The only reactant consumed is pyrite, and the only product cycled is sulfuric acid. Nature provides us with a perfect acid-generating system.

The purpose of this investigation is to determine a method by which this chain reaction can be broken. This method will then be extrapolated from pure chemical systems to overburden materials to determine its effect on AMD production.

EXPERIMENTAL

To determine the equilibrium solution potential of Fe^{+3} and FeS_2 we mixed 75 ml of various molar $FeCl_3$ solutions with 5 gm samples of -100 and -200 mesh pure pyrite. Nitrogen was bubbled through these suspensions for 10 minutes to minimize the concentration of dissolved oxygen. Once the samples were sealed to prevent oxygen absorption, they were shaken for two hours. This process was repeated each time measurements were taken. The pH and electrical potential were measured with a standardized glass electrode and a standardized platinum electrode at one month intervals. It was assumed that the system was in equilibrium when the voltage was constant for three months. This value, 0.41 v., was taken as the equilibrium voltage (Table I). When applied to the Nernst equation, this value establishes

*It is suspected that this is not the correct reaction in a non-aerated system. Our experiments indicate that $S_2O_3^{-2}$ is the oxidized sulfur product rather than SO_4^{-2} . This fact will not affect the results of this study because the oxidation of pyrite leading to AMD depends on the ferric ion concentration and is independent of sulfur species.

<u>-</u>4

the Fe⁺² /Fe⁺³ ratio at $1/10^{-6}$. The oxidation of pyrite with ferric ion can be eliminated if the concentration ratio of ferric to ferrous ion is kept at or below 10^{-6} :1. This ratio can be maintained if a precipitating and/or coordinating agent is added to the mixture.

This hypothesis has been tested by using PO_4^{-3} , which serves as both a coordinating and a precipitating agent. Five-gram samples of pyrite were mixed with 75 ml of various molar concentrations of FeCl₃. To these

mixtures were added three times the molar concentrations of $Ca_5(OH)(PO_4)^3$ These solutions were stored under N 2 and periodically shaken as before. After 6 months, the time normally required for a synthetic AMD' reaction to reach equilibrium, the samples showed no AMD and a solution potential of 0.23 v. Because these samples are idealized, no applicable conclusion can be reached except by using samples from an acidproducing environment. This effect was tested on overburden materials as described below.

Samples of overburden were obtained from Garrett County, Maryland, and Monongalia, County, West Virginia. A sample of Bakerstown overburden, one of Freeport overburden (both from Garrett County, Maryland), and one of Berea Sandstone from Monongalia County, West Virginia, were obtained. The Garrett County overburden is a known AMD producer, but the Berea sandstone is not suspected of producing AMID.

First, the samples were ground to -200 mesh in a porcelain mortar and pestle. Then weighed portions of the overburden were soaked overnight with 6M Hci to remove acid-soluble iron, such as $FeSO_4nH_2O$, $Fe_2(SO^4)_3$

 $Fe^2O_3H_2O$ and any iron which is leachable from clay mineral is dissolved. Once the mixture was filtered, the filtrate was analyzed for iron by atomic absorption spectroscopy. This concentration of iron is referred to as acid-soluble iron. The residue was soaked with 6M HNO₃ the samples were again filtered, and the filtrate was analyzed by AA to determine the amount of iron bound as pyrite. This process indicates acid-producing potential.

Several samples of the three overburden types were divided into three sample group tests.

Samples in Group la were used to demonstrate the acid producing potential of the overburden materials.

Samples in Group 1b were used to demonstrate the effect of $Ca_5(OH)(PO_4)^3$ in controlling the acid production of samples from tests of Group la.

Samples in Group 2a were used to show the possible extension of $Ca_5(OH)(PO_4)^3$ as a preventative technique.

Samples in Group 2b were used to test the preventative ability of $Ca_5(OH)(PO_4)^3n$ a simulated weathering environment.

Samples in Group 3 were used to test the ability of $Ca_5(OH)(PO_4)^3$ to eliminate and control AMD production through simulated wet and dry seasons.

The experimental procedures are below:

<u>Sample Group 1a.</u> 75 ml of distilled, deionized H_2O was added to 5gm of overburden samples of -200 mesh pyrite. The samples were sealed under N 2 and periodically stirred for two hours. After 6 months, they were tested for acid production, and the electrode potential was measured. The results can be seen in Table 2.

<u>Sample Group 2a.</u> To another portion of that sample (2a) $Ca_5(OH)(PO_4)^3$ was added at three times the molar concentration of acid-soluble iron. These samples were sealed under N 2 and periodically stirred for two hours. After 6 months, they were tested for acid production and oxidation potential. The results can be seen in Table 2.

<u>Sample Group 1b</u>. To samples in Group la which produce acid, $Ca_5(OH)(PO_4)^3$ was added at three times the original molar concentration of acid-soluble iron. They were again stored under N 2 and stirred periodically. After 3 months, they were tested for acid production and oxidation potential. The results can be seen in Table 2.

<u>Sample Group 2b.</u> The second sample, which was already treated with phosphate, was subjected to aeration to test the effect of oxygen on the system. Hydrated air was forced through the suspension daily for 10-minute periods for a week. The suspension was removed and exposed to hydrated air for 2 months, after which time it was tested for acidity and emf. The results can be seen in Table II.

<u>Sample Group 3.</u> Another overburden sample was permitted to produce acid mine drainage. It was then treated with phosphate and aerated as Sample 2b. Finally, it was filtered and the residues were permitted to stand exposed to air for one month. During this time, the samples were occasionally moistened to encourage the oxidation reaction. After 1 month, 75 ml of distilled, deionized H_2O was poured on the samples, and they were stirred for two hours. The pH and emf are shown in Table III.

RESULTS

The results of the Fe^{+3}/FeS_2 couple show that acid mine drainage production was an equilibrium potential of 0.41 v. Consequently, if the electrode potential of that couple can be reduced to below 0.41 v., no AMD will be produced because no pyrite oxidation can occur.

The role of $Ca_5(OH)(PO_4)^3$ is to reduce the concentration of ferrous to ferric to less than 1:10-6, resulting in an electrode potential for that cell of less than 0.41 v.

Tables II and III show the dramatic effect of $Ca_5(OH)(PO_4)^3$ on the AMD producing potential of that cell. The fact that the potential is less than 0.41 v. essentially eliminates the possibility of pyrite oxidation.

Table III also shows that upon vigorous aeration of samples treated with $Ca_5(OH)(PO_4)^3$, the voltage still

remains below 0.41 v.; thus, no acid can be produced subsequent to treatment.

Table III shows that after the system has been actually producing acid, addition of Ca 5 (OH)(PO 4)3 is still effective in eliminating the acid reaction. Subsequent vigorous aeration under optimum conditions does not seem effective in re-initiation of the reaction. Treatment of already active material by $Ca_5(OH)(PO_4)^3$ can arrest the acid production. 4 3

DISCUSSION

It is felt that the Fe^{+3}/FeS_2 reaction is the propagation step in the AMD reaction. This reaction is cyclic and could be the key to all AMD production methods. Micro-biological evidence for the oxidation of pure pyrite is controversial, (4,~,6) but the thiobacillus ferro-oxidans is known to oxidize Fe^{+2} to Fe^{+3} .⁽⁷⁾ Its role in AMD production may be the reoxidation of ferrous ion to ferric ion for continuous reaction with pyrite, which results in acid generation.

The lack of consistency between acid mine drainage production and pyrite concentration may in part be due to lack of acid soluble iron which, if in water-soluble form, could cause the potential of the Fe^{+2} / Fe^{+3} cell to be greater than the equilibrium voltage. Thus, the oxidation of pyrite would be initiated. If the acid soluble iron is not in a soluble form (see Berea sandstone), no high cell potential can occur. The important parameter is not the presence of acid soluble iron, but the electrochemical activity of the iron because it affects the voltage of the system and is thereby responsible for the oxidation of pyrite.

The lack of AMD production in calcareous overburden (8) may not be due to "neutralization" as in acid-base systems, but may be the result of chemically controlling the Fe^{+3}/Fe^{+2} voltage. In basic solutions the Fe^{+3} activity is much less than the Fe^{+2} activity.⁽⁹⁾ This causes a significant decrease in the electrode potential of the cell. If the resulting voltage is less than 0.41 v., the oxidation of pyrite cannot proceed. At high pH values, thiobacillus ferro-oxidans can't survive, ^(10,11,12) so the microbiological oxidation of ferrous to ferric ion is eliminated.

Treatment of acid-producing overburden by $Ca_5(OH)(PO_4)^3$ is shown to be effective in eliminating the AMD production of samples in the laboratory. This effect is due to lowering the electrode potential to below the equili brium voltage of the Fe⁺² /Fe₊₃ cell in the pyrite oxidation system, thus preventing the reaction.

Although the phosphate treatment may seem extreme because of cost, sewage sludge, containing high concentrations of precipitated phosphates, can be a substitute for phosphate rock. Because phosphate is frequently precipitated as $Ca_5(OH)(PO_4)^3$ by the addition of CaO in waste-water treatment systems, it is felt that the use of $Ca_5(OH)(PO_4)^3$ in our reaction tests indicates this possible application.⁽¹³⁾ Thus, the cost of treatment of acid mine drainage producing overburdens would be greatly reduced. Furthermore, this would also be a beneficial use for such sewage waste residue.

Table I

Emf and pH of Pyrite Fe⁺³ Solution (at equilibrium)

		pH	E	Initial [Fe ⁺³]
	150 mesh	3.35	+0.36	10-4
	5 gm/75 ml	3.00	+0.43	10-3
		2.45	+0.40	10 ⁻²
	200 mesh	3.35	+0.43	10-4
	5 gm/75 ml	3.10	+0.43	10-3
		2.35	+0.41	10 ⁻²
		3.50	+0.42	10-4
		3.0	+0.396	10-3
		2.8	+0.39	10-2
		3.0	+0.396	10-3
		2.6	+0.42	10 ⁻²
		2.95 avg	0.41 avg	
12.8	- · · ·			

Table II

Effect of Phosphate Trestment on Oxidation Potential and Acid Production of Overburden Material

Sample	Group	1a	Be	fore	Addition	of Ca ₅ (OH)	(PO4)	3
Bake	rstow	<u>n</u>	Fr	eepor	rt	Be	erea	-
E		pH	E		pH	Е		pH
0.498	-	2.9	0.66	-	2.3	0.264	-	4.0
0.54	-	2.8	0.612	-	2.5	0.27	-	4.1
0.498	-	3.2	0.63	-	2.5	0.282	-	4.1
0.456	-	3.9	0.51	-	2.7	0.30		4.2
Sample Group 1b		After Addition of Ca_(OH)(FO4)3						
Bake	rstow	<u>n</u>	Fr	eepor	rt	Ber	rea	
Е		PH	E		pH	E		pli
0.335	-	5.3	0.342	-	5.2	0.348	-	5.6
0.330	-	5.1	0.961	-	5.4	0.356	-	5.6
0.341	-	5.4	0.341	-	5.3	0.372	-	5.4
0.332	-	5.6	0.353	-	5.1	0.352	÷1	5.5
Sample Group 2a		Pretreatment by Ca ₅ (OH)(PO ₄) ₃						
Bake	rstown	<u>n</u>	Fr	eepor	t	Ber	rea	
E		pH	E		pH	E		pH
0.335	-	5.5	0.348	-	5.3	0.378	-	5.1
0.33	-	5.4	0.348	-	5.2	0.354	-	5.2
0.33	-	5.5	0.354	-	5.2	0.348	-	5.4
Sample	Group	2b	Af	ter A	ddition o	f Air and (a_(0	H)(P04)3
Bake	rstown	<u>1</u>	Fre	eepor	t	Ber	rea	
R		PH	Б		PH	E		PH
0.24	-	5.2	0.24	-	5.5	0.24	-	5.5
0.34	-	5.6	0.384	-	5.4	0.378	-	5.6
0.38	-	5.8	0.378	-	5.5	0.390	_	5.6

Table III

Effects of Simulated Scasonal Exposure on Treated Acid Producing Sample . Sample Group 3

Acid Producing Overburden	Before Phosphate Addition		After Phosp Aeration, & E	After Phosphate Addition, Aeration, & Extended Exposure		
	pH	E	pH	E		
Freeport	2.3	0.65	5.8	0.312		
	2.4	0.66	5.8	0.312		
	2.3	0.61	5.6	0.324		
Bakerstown	3.2	0.49	5.7	0.294		
	2.8	0.52	6.2	0.262		
	2.7	0.54	6.0	0.276		

Effects of Simulated Seasonal Exposure on Treated Acid Producing Sample

Sample Group 3

Acid Producing Overburden	Before Pl Addi	hosphate ition	After Phosphate Addition, Aeration, & Extended Exposure	
	pН	Е	pH	Ē
Freeport	2.3	0.65	5.8	0.312
	2.4	0.66	5.8	0.312
	2.3	0.61	5.6	0.324
Bakerstown	3.2	0.49	5.7	0.294
	2.8	0.52	6.2	0.262
	2.7	0.54	6.0	0.276

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