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Suppression of Pyrite Oxidation by Formation of Iron Hydroxide and Fe(III)-silicate Complex under Highly Oxidizing Condition

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Acid drainage generated by pyrite oxidation has caused the acidification of soil and surface water, the heavy metal contamination and the corrosion of structures in abandoned mine and construction sites. The applicability of Na-acetate (Na-OAc) buffer and/or Na-silicate solution was tested for suppressing pyrite oxidation by reacting pyrite containing rock and treating solution and by analyzing solution chemistry after the reaction. A finely ground Mesozoic andesite containing 10.99% of pyrite and four types of reacting solutions were used in the applicability test: 1) H_2O_2, 2) H_2O_2 and Na-silicate, 3) H_2O_2 and 0.01M Na-OAc buffer at pH 6.0, and 4) H_2O_2, Na-silicate and 0.01M Na-OAc buffer at pH 6.0. The pH in the solution after the reaction with the andesite sample and the solutions was decreased with increasing the initial H_2O_2 concentration but the concentrations of Fe and SO_4^{2-} were increased 10 – 20 times. However, the pH of the solution after the reaction increased and the concentrations of Fe and SO_4^{2-} decreased in the presence of Na-acetate buffer and with increasing Na-silicate concentration at the same H_2O_2 concentration. The solution chemistry indicates that Na-OAc buffer and Na-silicate suppress the oxidation of pyrite due to the formation of Fe-hydroxide and Fe-silicate complex and their coating on the pyrite surface. The effect of Na-OAc buffer and Na-silicate on reduction of pyrite oxidation was also confirmed with the surface examination of pyrite using scanning electron microscopy (SEM). The result of this study implies that the treatment of pyrite containing material with the Na-OAc buffer and Na-silicate solution reduces the generation of acid drainage.

Key words: Acid drainage, Na-silicate, Na-OAc buffer, Fe-hydroxide, Fe-silicate complex

Introduction

Pyrite is the most abundant sulfide mineral and generally occurs with coal, metallic ore, pyrophyllite ore and acid sulfate soil. It is also formed in a reducing environment with a continuous supply of sulfates and iron in the presence of easily decomposable organic matter (Barriga and Fyfe, 1988). The oxidation of pyrite generates acid drainage including acid mine drainage (AMD) and acid rock drainage (ARD) (Moses and Herman, 1991). The acid drainage acidifies soil, surface water and groundwater of the surrounding area and contaminates them with heavy metals (Moses and Herman, 1991). Ferric iron (Fe^{3+}) and oxygen (O_2) are known as the major oxidants for pyrite and the oxidation reactions are shown below.

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + H^+ + 1/4O_2 = Fe^{3+} + 1/2H_2O \qquad (2)$$

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

Oxidation of pyrite is initially a relatively slow process and most released iron ends up as iron hydroxide due to the relatively high pH on pyrite surface (Ivano, 1962; Fornasiero et al., 1992; Singer and Stumm, 1970). As the acid production continues and pH in the vicinity of pyrite surface drops below 3.5, the formation of iron hydroxide is hindered and the activity of free Fe^{3+} in solution increases. At the low pH, the oxidation of pyrite by Fe^{3+} is the main mechanism for acid drainage production since Fe^{3+} oxidizes pyrite approximately one order of magnitude faster than O_2 (Singer and Stumm, 1970). At the low pH, an acidophilic, chemoautotrophic and iron-oxidizing bacterium catalyzes and accelerates the oxidation of Fe^{2+} to Fe^{3+} by a factor lager than 10^6 comparing with the oxidation by O_2 (Singer and Stumm, 1970). The oxidation of Fe^{2+} to Fe^{3+} by microorganism accelerates the pyrite oxidation.

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Based on the oxidation mechanism, the rate of pyrite oxidation and the environmental contamination by the acid drainage can be reduced with reducing activity of free Fe^{3+}, depriving O_2, and neutralizing acidity. Acid drainage abatement technologies include physical barriers to prevent the contact of water and O_2 to pyrite surface. Plastic liner, clay liner and asphalt are the most commonly used physical barriers but their effectiveness is limited due to the tendency of the liners to be broken (Nicholson et al., 1989). Another technology for controlling acid drainage generation and mitigating environmental impact is the application of alkali production materials such as limestone and dolomite (Stiller et al., 1986). The alkaline materials neutralize the acidity and precipitate iron hydroxide. Application of bactericides has been used to suppress the activity of microorganism for the reduction of pyrite oxidation (Ericson et al., 1985). The relative short longevity and the secondary environmental contamination are raised for the uses of alkali production material and bactericide in terms of practical point, respectively. Organic matter also inhibits pyrite oxidation via several mechanisms including the consumption of O_2 due to bacterial growth and the removal of Fe^{3+} from solution by formation of Fe^{3+}-organic complex (Luther et al., 1992).

The environmental contamination in abandoned mine area is a worldwide current environmental issue due to the presence of AMD. Recently, ground excavation is a common construction work including slope cut and tunnel excavation for new roads, and residential and industrial areas in Korea. Nowdays, environmental problems associated with the ARD in the construction sites are frequently reported. Several technologies for the reduction of acid drainage generation and the remediation of contaminated soil by acid drainage have been developed and some of them are practiced in the field. The objective of this study was to test the effectiveness of Na-acetate (Na-OAC) buffer and Na-silicate solutions on the reduction of free Fe^{3+} activity and the pyrite surface coating for the reduction of pyrite oxidation.

Materials and Methods

A fresh Mesozoic andesite containing a significant amount of pyrite was collected form Yangsan, Korea. The sampling site was laid out for a residential land and there has been an acid rock drainage problem due to the exposure of the pyrite-rich andesite and the subsequent oxidation of pyrite (Lee et al., 2005). The collected sample was finely ground with a cup mill and passing through a 200 mesh sieve. The ground sample was analyzed with an X-ray diffractometer (XRD, MAC Science MXP 18A Rint-2500) for the mineralogical composition. The chemical composition was determined with an X-ray fluorescence spectrometer (Shimadzu XRF-1700). The sulfur (S) content was determined with a sulfur analyzer (Leco S-analyzer S600C) and the pyrite content was calculated based on the S content assuming that all S occurred as pyrite.

The suspensions of 10 g of the finely ground sample and 100 ml of various solutions containing H_2O_2, Na-OAc at pH 6.0 and/or Na-silicate in 250 ml flask were shaken using a rotational shaker at 200 rpm for 24 hrs. Four types of solution were used in the reaction: 1) 0.01 - 0.1M H_2O_2, 2) 0.01 − 0.1M H_2O_2 and 0.0001 − 0.01M Na-metasilicate, 3) 0.01 − 0.1M H_2O_2 and 0.01M Na-OAc at pH 6.0, and 4) 0.01 − 0.1M H_2O_2, 0.0001 − 0.01M Na-metasilicate and 0.01M Na-OAc at pH 6.0. Sodium hydroxide (NaOH) was used for the pH adjustment of the Na-OAc buffer. All chemicals used for this study were reagent grade and distilled water used for preparation of the reacting solution. After 24 hrs reaction, the suspensions were filtered with a 0.45 μm membrane filter. The pH and concentration of SO_4^{2-} of the filtrates were measured with a pH meter (Horiba pH meter F-23) and an ion chromatography (IC, Dionex DX-120), respectively. A portion of the filtrate was acidified with a few drops of concentrated HNO_3 for the determination of total Fe and the concentrations was determined with an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jobin Yvon JY70Plus). Morphology of pyrite was examined with scanning electron microscopy (SEM, JEOL JS5610LV) before and after the reaction between the andesite and the solutions.

Results and Discussion

Characteristics of the studied andesite Quartz, kaolinite, sericite and pyrite were the major minerals of the studied andesite sample and the andesite did not contain the minerals with high acid neutralizing potential such as calcite and dolomite (Table 1). The sample contained 5.88% of S and 10.99% of pyrite (FeS2). The mineralogical composition and the pyrite content indicated that the studied andesite had a high potential for the generation of acid drainage.

Table 1. Chemical composition and mineralogy of the studied andesite.

Chemical composition determined with XRF											
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_5	I.L.[†]	Total
%											
70.71	15.04	6.17	0.14	0.01	0.03	0.20	0.51	<0.01	0.15	6.60	99.56
Sulfur content						Mineralogy					
S: 5.88 %, pyrite: 10.99%						Quartz, kaolinite, sericite, pyrite					

[†] ignition loss.

Table 2. pH and concentrations of total Fe and SO_4^{2-} of the solutions after reacting with H_2O_2 solutions.

Initial concen. of H_2O_2	pH	Concen. of total Fe	Concen. of SO_4^{2-}
M		mg L^{-1}	mg L^{-1}
0.01	3.55	0.50	60.75
0.02	3.35	1.05	129.87
0.05	3.02	4.43	279.41
0.08	2.86	8.91	407.10
0.10	2.79	12.10	506.73

Table 3. pH and concentrations of total Fe and SO_4^{2-} of the solutions after reacting with H_2O_2 solutions buffered at pH 6 with Na-OAc.

Initial concen. of H_2O_2	pH	Concen. of total Fe	Concen. of SO_4^{2-}
M		μg L^{-1}	mg L^{-1}
0.01	5.83	10	20.07
0.02	5.79	11	30.27
0.05	5.70	14	45.50
0.08	5.65	18	65.25
0.10	5.62	20	74.15

Effect of H_2O_2 solution without buffer and silicate Table 2 shows the pH and the concentration of total Fe and SO_4^{2-} in the solution after 24 hrs reaction between the ground andesite and the highly oxidizing solutions with various concentrations of H_2O_2. The pH of the solutions ranged from 2.79 to 3.55 and decreased with increasing initial H_2O_2 concentration. The concentrations of total Fe and SO_4^{2-} increased by 10 to 20 times with increasing initial H_2O_2 concentration. The oxidation of pyrite can be described as following:

$$FeS_2 + H_2O_2 + 2H_2O = Fe^{3+} + 2SO_4^{2-} + 6H^+ \quad (4)$$

$$FeS_2 + Fe^{3+} + 8H_2O = 2Fe^{2+} + 2SO_4^{2-} + 8H^+ \quad (5)$$

$$Fe^{2+} + H_2O_2 + 2H^+ = Fe^{3+} + 2H_2O \quad (6)$$

The inhibition of pyrite oxidation did not occur the formation $Fe(OH)_3$ at below pH 4 in the presence of H_2O_2 (Zhang and Evangelou, 1996).

Effect of H_2O_2 solution buffered with 0.01M Na-OAc buffer at pH 6.0 The pH of solution decreased with increasing the initial H_2O_2 concentration with Na-OAc at pH 6.0 but the concentrations of total Fe and SO_4^{2-} increased as they did for the H_2O_2 solution without buffer (Table 3). However, the variation ranges of Fe and SO_4^{2-} concentrations were much smaller than those for H_2O_2 without the buffer. The concentration of total Fe was three times smaller than those of the H_2O_2 solution without the buffer. The SO_4^{2-} concentration indicated that 3 to 8 times less amount of pyrite was oxidized comparing with the H_2O_2 solution without the buffer at the same concentration of H_2O_2. The solution pH (5.62 - 5.83) indicated that Fe-hydroxide can be formed in the solution (Zhang and Evangelou, 1996):

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (7)$$

The formation of Fe-hydroxide reduced the active surface area of pyrite by surface coating as well as the

Table 4. Initial concentrations of Na-silicate and H_2O_2 without pH 6 Na-OAc buffer and the pH and concentrations of total Fe and SO_4^{2-} after 24 hrs reaction.

Initial con. of Na-silicate	Initial Con. of H_2O_2	pH	Con. of total Fe	Con. of SO_4^{2-}
M	M		mg L^{-1}	mg L^{-1}
0.0001	0.01	3.52	0.62	94.05
	0.02	3.30	1.28	128.06
	0.05	3.15	2.21	165.53
	0.08	3.10	6.12	223.96
	0.10	2.86	8.20	285.53
0.001	0.01	3.49	0.81	120.42
	0.02	3.28	1.64	132.54
	0.05	3.14	2.63	158.93
	0.08	2.83	9.21	280.65
	0.10	2.78	12.51	330.37
0.01	0.01	3.45	1.28	101.39
	0.02	3.27	5.49	123.18
	0.05	2.98	18.43	156.94
	0.08	2.84	22.86	221.63
	0.10	2.80	31.70	238.23

activity of Fe in the solution. The decreased Fe^{3+} activity reduced the amount of oxidant for pyrite in the solution. The Fe-hydroxide coating reduced the accessibility of oxidants such as Fe^{3+} and H_2O_2 to the pyrite surface.

Effect of H_2O_2 and silicate solution The pH and SO_4^{2-} concentration, indicators of pyrite oxidation, of the solution containing H_2O_2 and Na-silicate were controlled by the concentration of H_2O_2 (Table 4). The Fe concentration increased but the pH decreased with increasing initial silicate concentration at the same H_2O_2 concentration. The concentration of SO_4^{2-} was not significantly affected by the initial silicate concentration at the same initial concentration of H_2O_2. However, the solutions in the presence of silicate showed the lower concentration of SO_4^{2-} comparing with those of H_2O_2 solution without the buffer and silicate at the same concentration of H_2O_2 (Table 2 and 4). The lower SO_4^{2-} concentration of the solution indicates that the silicate inhibited the pyrite oxidation at the same H_2O_2 concentration. The formation Fe^{3+}-monomeric silicic acid complex [$FeSiO(OH)_3^{2+}$] in a Si-Fe^{3+} solution system was reported by Olson and Omelia (1973), Porter and Weber (1971), and Weber and Stumm (1965). The Fe^{3+}-monomeric silicic acid complex was reported as a chemically inert species in solution (Olson and Omelia, 1973). The formation of Fe-silicate complex in the reacting solution reduced activity of Fe^{3+}, a strong oxidant for pyrite, and it leaded the reduction of pyrite oxidation and the decrease of the SO_4^{2-} concentration. The point of zero charge of pyrite was reported to be pH 1.2 (Fornasiero et al., 1992) and the pyrite surface should be negatively charged in the solution of pH 2.8 − 3.5. Therefore, a portion of Fe-silicate complex might be adsorbed on the negatively charged pyrite surface by electrostatic force. The adsorption of Fe^{3+}-silicate complex on the pyrite surface also reduced the contact of H_2O_2 and free Fe^{3+} to the pyrite surface.

Effect of H_2O_2 and silicate buffered with 0.01M Na-OAc at pH 6.0 The solution pH after 24 hours reaction ranged from 5.6 to 5.9 which were similar with the pH values of the buffered solution without silicate (Table 5). The solution showed the lowest SO_4^{2-} concentration among the reacting solutions at the same concentration of H_2O_2. The solution had much lower Fe concentration comparing with those of H_2O_2 solution and H_2O_2-silicate solution without the buffer regardless H_2O_2 concentration. The 0.001M silicate solution with the buffer had a similar Fe concentration with those of the buffered solution at the same H_2O_2 concentration. The Fe concentration increased with increasing silicate concentration at H_2O_2 concentration but the SO_4^{2-} concentration decreased. As discussed in previous section, the formation of Fe-hydroxide and Fe-silicate complex and their surface

Table 5. Initial concentrations of Na-silicate and H_2O_2 of reacting solutions with pH 6 Na-OAc buffer and the pH and concentrations of total Fe and SO_4^{2-} after 24 hrs reaction.

Initial con. of Na-silicate	Initial Con. of H_2O_2	pH	Con. of total Fe	Con. of SO_4^{2-}
M	M		μg L^{-1}	mg L^{-1}
0.0001	0.01	5.85	13	16.08
	0.02	5.81	12	20.58
	0.05	5.75	14	29.17
	0.08	5.70	16	38.75
	0.10	5.64	19	46.43
0.001	0.01	5.84	116	18.74
	0.02	5.79	161	20.91
	0.05	5.72	206	30.80
	0.08	5.67	304	35.60
	0.10	5.64	276	34.94
0.01	0.01	5.87	334	13.76
	0.02	5.82	385	16.49
	0.05	5.75	625	22.85
	0.08	5.70	768	29.19
	0.10	5.66	757	33.18

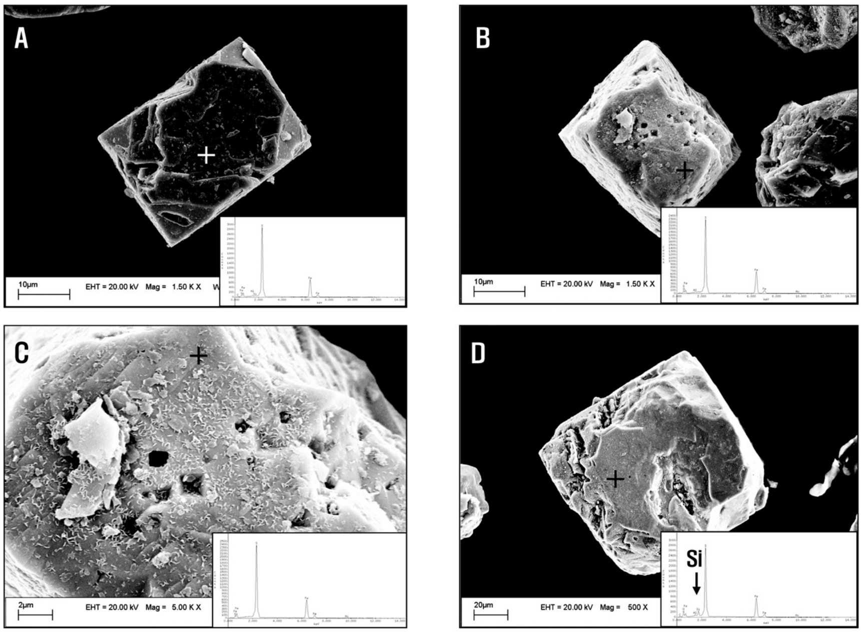

Fig. 1. The SEM micrographs of pyrite before and after the reaction between the andesite and the solution. A: before the reaction, B: after the reaction with 0.1M H_2O_2 solution, C: after reaction with 0.1M H_2O_2 and 0.01M Na-silicate solution, and D: after the reaction with 0.1M H_2O_2, pH6 Na-OAc buffer and 0.01M Na-silicate solution.

coating reduced the oxidation of pyrite oxidation.

SEM micrographs The micrographs of pyrite examined with SEM revealed the smooth surfaces of pyrite for the reaction with the H_2O_2, Na-OAc buffer and Na-silicate solution, and before the reaction (Fig. 1). The surface of pyrite after the reaction with the solution containing H_2O_2, and H_2O_2 and Na-silicate showed dissolution pits. The chemical composition determined with EDX showed the presence of Si on the surface of pyrite reacted with H_2O_2, Na-OAc buffer and Na-silicate solution. The SEM micrograph confirmed that the Na-OAc buffer and Na-silicate reduced the pyrite oxidation.

Conclusion

The oxidation of pyrite indicated by the pH and the concentrations of Fe and SO_4^{2-} increased with increasing H_2O_2 concentration. However, the pyrite oxidation was suppressed in the presence of 0.01M Na-OAc buffer at pH 6.0 and with increasing the Na-silicate concentration of treating solution. The reduced pyrite oxidation in the presence of 0.01M Na-OAc buffer at pH 6.0 might be due to the formation of Fe-hydroxide resulting in reducing Fe^{3+} activity and Fe-hydroxide coating on the surface. The SiO_4^{4-} in the reacting solution reacted with Fe^{3+} derived from pyrite oxidation to form Fe-silicate complex. The formation of Fe-silicate complex reduced the Fe^{3+} activity in the solution resulting in the reduction of pyrite oxidation. The smooth surface of pyrite reacted with the solutions containing the Na-OAc buffer and the Na-silicate comparing with the pyrite reacted with the H_2O_2 solution also confirmed their reduction capacity for pyrite oxidation. The results of this study indicate that the treatment with the Na-OAc buffer and Na-silicate solution reduces the production of acid drainage by pyrite surface coating and reducing Fe^{3+} activity.

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