Silicate Covering Layer on Pyrite Surface in the Presence of Silicon–Catechol Complex for Acid Mine Drainage Prevention

Mutia Dewi Yuniati^{1,3}, Tsuyoshi Hirajima^{1,2,*}, Hajime Miki¹ and Keiko Sasaki¹

¹Department of Earth Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan

²Research and Education Center of Carbon Resources, Kyushu University, Fukuoka 816-8580, Japan

³Research Center for Geotechnology, Indonesian Institute of Sciences, Bandung 40135, Indonesia

In this paper, prevention of pyrite oxidation by carrier microencapsulation (CME) was investigated. A possible layer structure was suggested following analysis with electrochemical and surface analysis techniques. Electrochemical study of treated pyrite samples showed that treatment with silicon–catechol (Si-Cat) for 6 h at an initial pH of 9.5 gave the best barrier properties and suppression of the samples. Scanning electron microscopy with energy-dispersive X-ray, and Fourier transform infrared (FTIR) analyses confirmed the presence of a silicate layer on the surface of treated pyrite. X-ray photoelectron spectroscopy indicated that the coating layers on the treated pyrite samples consisted of a network of Fe–O–Si and Si–O–Si units bonded to the surface of pyrite. The Si–O–C asymmetric stretching mode was also observed in FTIR spectra. Detailed spectroscopic analyses confirmed the formation of a silicate polymer on a silica–quinone layer, which resulted in the effective suppression effect shown by Si-Cat-treated pyrite at increasing pH. [doi:10.2320/matertrans.M-M2015821]

(Received May 25, 2015; Accepted July 8, 2015; Published August 28, 2015)

Keywords: pyrite oxidation suppression, silicon-catechol complex, polymerization, silica-quinone layer

1. Introduction

Acid mine drainage (AMD) is produced when sulfide-bearing material is exposed to oxygen and water. The production of AMD usually, but not exclusively, occurs during mining of iron sulfide mineral (pyrite), which is the most abundant metal sulfide in nature. Although this process occurs naturally, mining and processing of metal ores can promote AMD generation simply through increasing the quantity of sulfides exposed to oxygen and water.¹⁾ Naturally occurring bacteria can accelerate AMD production by microbial oxidation of ferrous ions to ferric ones at low pH.^{2,3)}

A promising approach to prevent AMD is passivation, in which a thin organic or inorganic protective coating is formed on the surface of pyrite to prevent its contact with the atmosphere, water, and bacteria that promote oxidation. Numerous passivation agents have been investigated.^{4,5)} A method known as carrier microencapsulation (CME) that uses aqueous solutions of metal ions (Si^{4+} or Ti^{4+}) complexed with an organic carrier such as catechol (Cat), i.e., $\text{Si}[\text{Cat}]_3^{2-}$ or $\text{Ti}[\text{Cat}]_3^{2-}$, proposed by Satur *et al.*⁶⁾ and Jha *et al.*^{7,8)} has become a promising method for the practical suppression of pyrite oxidation.^{6–8)} In this method, complexed $\text{Si}[\text{Cat}]_3^{2-}$ or $\text{Ti}[\text{Cat}]_3^{2-}$ is decomposed selectively on the surface of pyrite to form a silicon or titanium oxide and/or hydroxide coating that protects against oxidation. There are many reports of the formation of silicate polymers when silica or its derivatives are used as coating agents.^{9–13)} However, the characteristics of the covering layers generated from Si-Cat complexes are poorly understood. Therefore, we decided to investigate the polymerization of the covering layer of pyrite. Another drawback of this method is the high cost of Cat.

As the utilization of low rank coal in Indonesia increases, it has been proposed to use hydrothermal treatment to upgrade

low rank coal.¹⁴⁾ It is known that the waste aqueous solution from hydrothermal treatment of low rank coal contains Cat. Utilizing this waste solution for CME of pyrite can reduce both the waste from hydrothermal treatment of low rank coal and the chemical cost of CME.

We previously reported suppression of pyrite oxidation using a Si-Cat complex formed using waste solution from hydrothermal treatment of low rank coal as the Cat source.^{14–16)} Our results indicated that a silica–quinone coating was formed and the oxidation rate of pyrite could be suppressed by pretreatment with Si-Cat. However, a more systematic investigation of the silica–quinone coating is needed to clarify the mechanisms involved in the formation of this coating. To address this issue, the morphological characteristics and chemical composition of the silica–quinone coating formed using Si-Cat were evaluated by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The ability of the silica–quinone coating to suppress oxidation of pyrite is also investigated by static potential measurements and electrochemical impedance spectroscopy (EIS).

2. Experimental Material and Methods

2.1 Material

Crystalline pyrite from Victoria mine, Navajún, La Rioja, Spain, was used as experimental material. The X-ray diffraction study of this material was carried out using XRD (Rigaku Ultima IV diffractometer, Tokyo, Japan) and the result is shown in Fig. 1. It can be seen that the sample was identical to pure pyrite.

For morphological analyses (FTIR, SEM-EDX, and XPS), a pyrite sample was ground to $-38\ \mu\text{m}$ in diameter on an agate mortar in a nitrogen-purged glove. After grinding, the washing method of Sasaki *et al.*¹⁷⁾ was adapted to remove the surface oxide. The sample was washed with ethanol in a beaker by an ultrasonic bath for 30 seconds. After removing

*Corresponding author, E-mail: hirajima@mine.kyushu-u.ac.jp

Fig. 1 XRD patterns of pyrite sample.

the supernatant, the pyrite was washed with 1 mol/L nitric acid solution for one minute, distilled water (two times) and acetone (four times). Finally, the washed pyrite was dried by freeze dehydration.

For electrochemical analysis, a working electrode was prepared from a pyrite sample by cutting it into cubes with working surfaces of approximately 1.10 cm^2 exposed to the electrolyte. One side of the pyrite electrode was used as the electrode surface and the other side was connected to a copper wire using silver conductive paste and cemented with epoxy resin. The electrode surface was polished with #400 to #4000 emery paper, a Texmet (Buehler, Illinois, USA) perforated non-woven pad, and a DP-Nap (Struers, Ballerup, Denmark) fine polishing cloth mounted on a plate using $3\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$ diamond sprays. After polishing, the electrode was rinsed with ethanol and distilled water to remove polishing residues.

2.2 Experimental

2.2.1 Preparation of coating solution

7.00 mmol/L Catechol ($\text{C}_6\text{H}_4[\text{OH}]_2$) (Wako, special grade) solution was prepared using ultrapure water. Subsequently, 2.34 mmol/L sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) (Wako, special grade) was added to the catechol solution. Solution pH was adjusted to the desired value using HCl and KOH, and used for pyrite surface treatment. This solution referred as silicon-catechol (Si-Cat) complex.

The concentration ratio of silicate solution to catechol was 1 : 3 because it is known that 1 mol of silicon forms a complex with 3 mol of catechol.⁸⁾ We used waste solution from hydrothermal treatment of low rank coal¹⁴⁾ with a catechol concentration of 7.00 mmol/L as the source of catechol in this work. Jha *et al.*⁸⁾ reported that the passivation effect of catechol on pyrite oxidation by CME is similar for Si-Cat concentrations of 1–10 mmol/L.

2.2.2 Electrochemical analysis

The pyrite working electrode was immersed in the coating solution (see section 2.2.1.), stirred with a magnetic stirrer at 100 rpm. After a predetermined stirring time (1, 6, and 12 h), the working electrode was air dried for 30 min, and used for electrochemical measurements in 0.10 mol/L sulfuric acid.

The electrochemical measurements were performed using three standard electrode cells consisting of a working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The three electrode cells and electrolyte (0.10 mol/L sulfuric acid) were placed in a glass container.

Static potential and electrochemical impedance spectroscopy (EIS) experiments of untreated and treated pyrite samples were performed at room temperature using an electrochemical instrument (Solartron Analytical 1280 C, Hampshire, UK).

Static potential experiments were carried out at 800 mV for 300 s and all the measured potentials were reported with respect to the standard hydrogen electrode. The EIS measurements were performed at open circuit potential in the frequency range of 0.1–20,000 Hz with peak-to-peak amplitude of 10 mV. The impedance data was modelled to an equivalent circuit (EC) using the data analysis program Zview[®] (Scribner Associates, Inc., North Carolina, USA), using iterative empirical data fitting combined with trial circuit elements chosen based on theoretical considerations.

2.2.3 Pretreatment of pyrite and morphological analysis

In a 250 mL bottle, 10.00 g of washed pyrite sample was added to 100 mL of Si-Cat solution. After predetermined stirring time (1, 6, and 12 h) at 100 rpm and 25°C , the solid residues from each treatment bottle were recovered by filtration and dried by freeze dehydration. Dry solid residue referred as Si-Cat treated pyrite samples.

SEM-EDX analyses were performed using (Keyence VE-9800, Osaka, Japan) and FTIR investigations were performed using FT-IR-670 Plus (JASCO, Tokyo, Japan [accumulation, 100 times; resolution, 4 cm^{-1} ; detector, triglycine sulfate; wave numbers, $400\text{--}4000\text{ cm}^{-1}$]).

XPS analyses were carried out using XPS ESCA 5800F (New York, USA) with Al $\text{K}\alpha$ X-ray source (1486.6 eV) operated at 200 W. The samples were cleaved under vacuum in the sample preparation chamber prior to delivery, without breaking vacuum, to the XPS analysis chamber. The vacuum in the sample preparation chamber is approximately 10^{-8} Torr when the sample is cleaved and the pressure in the analysis chamber is 10^{-9} Torr during the XPS measurements. The samples were first examined in wide scan (80 W of the analyzer pass energy) to identify all the elements present, the various elemental regions were scanned (40 W of the analyzer pass energy) in order to extract information on chemical bonding and oxidation stages. The collected data were analyzed with Casa XPS software (Ver. 2.3.16). Background corrections were made using the Shirley method for the Fe 2p, S 2p, O 1s, and Si 2p spectra.¹⁸⁾ Peak shapes were defined using a Gaussian–Lorentzian function. Binding energy (EB) calibration was based on C 1s at $E_B[\text{C1s}] = 284.6\text{ eV}$.

3. Results and Discussion

In our previous work (Kitagawa *et al.*¹⁴⁾) we investigated the direct leaching behavior of CME-treated pyrite and untreated pyrite for 30 days. Pyrite oxidation was suppressed by more than 50% following CME. In this study, oxidation effects over a shorter duration were investigated by electrochemical study to investigate silicate layer formation and the stabilization achieved by CME.

3.1 Effect of treatment time of silicate coating on pyrite oxidation suppression

Figure 2 shows static potential experiments data that

Fig. 2 Potentiostatic curves of untreated and Si-Cat treated pyrite samples initially pH 9.5 with different treatment time in 0.1 M H_2SO_4 .

completed to measure the oxidation rate of pyrite with and without pretreatment. Pretreatment were conducted initially at pH 9.5 (natural pH of Si-Cat) for 1, 6, and 12 h. These experiments were measured at 800 mV for 300 s. The average results of two times measurements are shown as curves of current density with time. Current density is the anodic current of the working electrode in the working area of 1.10 cm^2 .

From these results, the anodic currents of Si-Cat treated pyrite samples (1, 6, and 12 h) are lower than that of the untreated pyrite. Because the anodic current represents the oxidation rate, the lower anodic currents of Si-Cat treated pyrite samples mean that the oxidation rates of these samples are lower than that of the untreated pyrite. Figure 2 shows that pyrite sample treated for 6 h has the lowest oxidation rate and largest suppression effect. This result is consistent with the study conducted by Bessho *et al.*¹²⁾ that showed equilibrium pHs of silica solutions were reached after 6 h of stirring. Pyrite sample treated for 1 h shows the lowest suppression effect. It may be due to the shorter time that used to complete the coating process. Meanwhile, longer treatment time (12 h) also shows lower suppression effect than 6 h treatment. This might be caused by the formation of metal-catechol complex, where catechol can form stable complexes with various di- and trivalent metal ions such as iron.¹⁹⁾ Basic solutions of catechol react with iron(III) to give the red (catecholato)iron(III) complexes $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3]^{3-}$, and finally change to a black color on exposure to the air.²⁰⁾ It can be seen that the solution after 12 h treatment turned darker than other treatment times. This reaction caused the Si-Cat complex not to work completely during the coating process.

3.2 Effect of pH of silicate coating on pyrite oxidation suppression

A series of experiments (EIS, SEM-EDX, FTIR, and XPS) was conducted to evaluate the effect of initial pH of Si-Cat complex on pyrite oxidation suppression. EIS is often used to obtain information on the properties of systems, such as the presence of defects, reactivities of interfaces, adhesion, and barrier properties. In this work, EIS was used to study the barrier properties of pyrite surface in the presence of a silica-quinone layer.

Fig. 3 EIS spectra of Si-Cat treated pyrite samples initially pH (a) 3, (b) 7, (c) 9.5; compared with untreated pyrite.

Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Electrochemical impedance is usually measured by applying an alternating current (AC) potential to an electrochemical cell and then measuring the current through the cell. The technique is based on the measurement of current through an electrode when a sinusoidal potential is applied. The impedance is therefore expressed in terms of magnitude, Z_0 (ratio of voltage to current) and a phase shift, ϕ ; composed of a real part, Z' , and an imaginary part, Z'' . A Nyquist plot is obtained by plotting the real part on the x -axis and the imaginary part on the y -axis of a chart.

The EIS complex plane plots (Nyquist plots) of pyrite samples are shown in Fig. 3. The Nyquist plot for the

Fig. 4 EC models of pyrite samples.

untreated pyrite is a semicircle, and that of treated pyrite has a larger radius than that of untreated pyrite. The Z' value at the starting point of each semicircle indicates solution resistance, and a semicircle shape indicates the impedance of electrode, including both electrode resistance and capacitance.²¹⁾ The radius of the semicircle represents the resistance of the electrode. The flat semicircle shape indicates that the electrode surface is rough and contains defects, so for this fitting we used a constant phase element (CPE) instead of a capacitor. Using an alternating current frequency ω , imaginary unit j , and parameters T and P , the complex impedance of a constant phase element, Z_{CPE} , is defined by following equation.

$$Z_{CPE} = \frac{1}{T(j\omega)^P} \quad (1)$$

When the exponential parameter P is equal to 1, the impedance of a CPE, Z_{CPE} , becomes equal to the impedance of a capacitance by substituting C for T in the above equation.

Figure 4 presents a fitting for the circuit calculated from the Nyquist plot in Fig. 3. Figure 4(a) shows the fitting circuit for untreated pyrite, which consists of solution resistance (R_s) and a parallel of constant phase element (CPE1) and resistance (R_1) that represents an untreated pyrite electrode circuit (Z_1 part). For treated pyrite, the semicircle diameter is drastically increased compared with that of untreated pyrite (see Fig. 3). This result can be fitted as two parallel circuits in series (Fig. 4(b)). This indicates that in addition to the pyrite circuit, another coating layer exists as the Z_2 component, which consists of resistance (R_2) and capacitance (CPE2).²²⁾

This calculated circuit allowed the parameters of the EC elements for pyrite samples to be calculated; the values are listed in Table 1.

It is obvious that R_2 values of Si-Cat treated pyrite samples are higher than that of untreated pyrite. These results show the coating layer is created on the surface of treated pyrite samples. From the listed R_2 values, 6 h Si-Cat treated pyrite initially pH 9.5 has larger R_2 value and better barrier properties than other treatment conditions which confirm the results of the static potential measurements (effect of treatment time). At pH lower than 9 the formation of Si-Cat complexes might be incomplete and simple hydrolysis may predominate.^{23,24)} Based on those reports, silicate covering layer was not created completely and the suppression effect was lower than that of Si-Cat treated pyrite initially pH 9.5. These data also supported by Ultraviolet-visible (UV) absorption spectra studies conducted by Sever and Wilker²⁵⁾ that showed that at low pH (<7), catechol is reduced

Table 1 EC element parameters obtained by fitting experimental impedance data for untreated and Si-Cat treated pyrite samples with EC model shown in Fig. 4.

Pyrite	Treatment time, h	R_s , ohm	R_1 , ohm	R_2 , ohm
Untreated	—	9.46	1078	—
Treated pH 3	1	8.88	793.6	65323
	6	9.94	242.1	39621
	12	9.70	1217.0	45160
Treated pH 7	1	9.64	992.5	69842
	6	9.77	1545.0	69521
	12	10.73	1726.0	58489
Treated pH 9.5	1	10.29	678.3	58652
	6	11.55	1188.0	75192
	12	10.16	1855.0	69344

and coordination complexes are dissolved instead of cross linked.

Figure 5 show SEM-EDX images of 6 h Si-Cat treated pyrite samples initially pH 3, 7, and 9.5 compared with untreated pyrite.

All figures show that silica is present on pyrite surface of untreated and three treated pyrite samples, but the silica densities of the treated pyrite samples are much higher than that of the untreated sample. Si contents of the untreated pyrite, Si-Cat treated pyrite initially pH 3, 7, and 9.5 were 0.34%, 0.71%, 1.56% and 2.59%, respectively. These results confirm that silica adsorption occurred, and silicate coatings were formed on the surfaces of the treated pyrite samples.

The high silica density of treated pyrite initially pH 7 and 9.5 was probably caused by the formation of a silica polymer.^{26,27)} At pH > 4, the ferric hydroxide precipitated on the pyrite surface reacts with Si-containing species to form a ferric hydroxide-silica barrier.

Attenuated total reflectance Fourier transfer infrared spectroscopy (ATR-FTIR) has been used to study the adsorption of Si-Cat complex onto pyrite surface (Fig. 6). The presence of quinone was confirmed from the previous study.¹⁶⁾ In the present study, we investigated the presence of polymerization (via Si-O-Si linkages). Peaks observed at 955–960 cm^{-1} are present in the treated pyrite samples. These absorption peaks correspond to Fe-O stretching of the Fe-O-Si bond.²⁸⁾ The occurrence of Fe-O-Si bonds indicates that Si-OH groups (silanol) reacted with FeOOH on the surface of pyrite. FeOOH is produced on the surface of pyrite from released ferric ion as follows.

Fig. 5 SEM-EDX element mapping of (a) untreated pyrite; 6 hr Si-Cat treated pyrite initially pH (b) 3, (c) 7, (d) 9.5.

Fig. 6 FTIR spectra of untreated and 6 h Si-Cat treated pyrite samples.

The bonding mode near 1065 cm^{-1} is for the Si-O-C asymmetric stretching mode in a ring link.^{29,30} This bond shows that the aromatic ring attach to Si-O bonds. Besides, significant peaks are observed at $1154\text{--}1160\text{ cm}^{-1}$. According to Carlson and Schwertmann,³¹ the peaks observed at 1154--

1160 cm^{-1} were assigned to a shift of Si-O-Si in polymerized Si. As the Si-O-Si (siloxanes) chains become longer or branched, the Si-O-Si absorption becomes broader and more complex. As surface coverage increases with the pH, the presence of polymerized species becomes evident and the peak intensity due to adsorbed silicate shows the highest absorbance for Si-Cat treated pyrite initially pH 9.5.

To confirm the surface product, XPS analysis of pyrite samples have been conducted before and after 6 h Si-Cat treatment initially at pH 3, 7, and 9.5. The narrow scanned and corresponding decomposed of Fe 2p, S 2p, and O 1s spectra are shown in Fig. 7.

XP-spectra of Fe 2p, S 2p, O 1s, and Si 2p for untreated pyrite and treated pyrite samples were analyzed by peak separation and the results are summarized in Table 2.

The Fe 2p spectra of the four samples are presented in Fig. 7(a). This Fe 2p figure indicates that Si-Cat treatment decreased iron in pyrite peaks at 707.6 eV ³² and covered the treated pyrite surfaces with silicate coating as the peaks at around 711.3 eV attributable to iron/silicon oxide³³ were observed. As the pH increased, the peak area associated with iron/silicon dioxide increases in the Fe $2p_{3/2}$ spectra (Table 2). The shared peaks confirm the formation of Fe-O-Si bonds in the treated pyrite samples, which are consistent with

Fig. 7 XP spectra of untreated and 6 h Si-Cat treated pyrite samples with (a) Fe 2p peaks, (b) S 2p peaks, and (c) O 1s peaks.

Table 2 Comprehensive atomic allocation based on the measurement of narrow scan of Fe, S, O, and Si spectra of untreated and 6 h Si-Cat treated pyrite samples.

Pyrite		Fe 2p _{3/2}	Fe 2p _{3/2}	Fe 2p _{3/2}	Fe 2p _{3/2}	S 2p _{3/2}	S 2p _{1/2}	S 2p _{3/2}	S 2p _{1/2}	S 2p _{3/2}	S 2p _{1/2}	O 1s	O 1s	Si 2p	Si 2p
		a	b	c	d	a1	a2	b1	b2	c1	c2	a	b	SiO ₂	Si-O-Si
Untreated	<i>E_B</i> /eV	707.2	710.0	—	713.8	161.1	162.2	162.8	164.0	168.4	169.5	531.7	—	102.5	—
	AREA	6966.2	529.4		146.8	37.1	18.5	5276.9	2638.4	185.8	92.9	5399.0		75.8	
Treated pH 3	<i>E_B</i> /eV	707.7	710.0	711.1	—	161.9	163.1	162.9	164.1	—	—	532.3	533.6	—	103.5
	AREA	3625.7	366.9	207.0		194.0	97.0	2585.7	1292.9			1244.6	1071.2		110.8
Treated pH 7	<i>E_B</i> /eV	707.7	710.0	711.2	—	162.0	163.1	162.9	164.1	—	—	532.4	533.6	—	103.7
	AREA	3514.5	384.2	248.7		174.8	87.4	2350.2	1175.1			1162.8	1005.0		117.3
Treated pH 9.5	<i>E_B</i> /eV	707.7	710.0	711.2		161.9	163.0	162.9	164.1	—	—	532.2	533.4	—	103.8
	AREA	4230.4	442.8	291.3		215.4	107.7	2827.3	1413.7			1099.9	1258.3		130.8
Average	<i>E_B</i> /eV	707.6	710.0	711.1	713.8	161.7	162.9	162.9	164.1	168.4	169.5	532.2	533.5	102.5	103.7
STDEV		0.28	0.03	0.01	—	0.42	0.42	0.07	0.05	—	—	0.30	0.10	—	0.13

analysis of the FTIR spectra (Fig. 6). The peak observed at 710.0 ± 0.03 eV correspond to iron oxyhydroxide.³⁴⁾

The presented S 2p spectra consist of two major doublets representing bulk mono sulfide and disulfide.³⁵⁾ S 2p data (Fig. 7(b) and Table 2) are fitted with two S 2p doublets based on prior research on pyrite, which is the peaks at 162.9 eV and 163.78 eV were assigned to the disulfide group³⁶⁾ and the peaks at 161.65 eV and 162.83 eV feature to a monosulfide group.³⁷⁾ For S 2p peaks, sulfate peaks at 168.25

and 169.43 eV³⁷⁾ can be seen on the untreated pyrite which we believed were produced during exposure of the sample to air because untreated pyrite sample was not covered by coating layer. This result also supported by iron(III) sulfate peak at 713.25 eV³⁸⁾ that can be seen only on untreated pyrite. Natural oxidation of untreated pyrite might cause the following oxidation reaction to produce iron sulfate.

The first step involves hydrolysis of the Si-Cat complex, which yields reactive Si-OH groups (silanol) and quinone (eq. (4)). It has been reported that Si-Cat complex was selectively oxidized on the surface of pyrite, and such silanol groups can be present only on the surface of pyrite.¹⁵⁾

The proposed mechanism shows similar pathway with Diao *et al.*⁹ whereas the formation of covalent bonds (Fe-O-Si and Si-O-Si) were occur on the pyrite surface by using tetraethylorthosilicate (TEOS) and n-propyltrimethoxysilane (NPS). In Si-Cat treatment, the coating layer much more bulky than TEOS and NPS treatment. It caused by the attachment of 1 quinone molecule on the silanol group (eq. (4)). With this structure, the resulting coating layer probably could give bigger oxidation suppression effect.

In this study, we systematically examined Si-Cat adsorption and polymerization on the surface of pyrite. Treatment

Fig. 9 Proposed mechanism of pyrite oxidation suppression by Si-Cat complex.

of pyrite with Si-Cat under various conditions resulted in differences in the suppression of pyrite oxidation.

Electrochemical measurements demonstrated that treatment with Si-Cat for 6 h at an initial pH of 9.5 gave the best barrier properties and pyrite oxidation suppression effect of the samples. The coating formed was shown by SEM-EDX to be silica-rich. Evidence provided by FTIR and XPS analyses demonstrated that the coating layer on treated pyrite samples consisted of a network of Fe-O-Si and Si-O-Si units bonded to the surface of pyrite. The Si-O-C asymmetric stretching mode was also observed in FTIR spectra.

Detailed FTIR and XPS data revealed that (i) silicate polymerization occurs on the treated pyrite samples, (ii) Si-Cat-treated pyrite with an initial pH of 9.5 showed the highest degree of polymerization based on the intensity and peak area of Si-O-Si bonds. These results confirm that the Si-Cat complex is selectively oxidized on the surface of pyrite to produce silanol groups, followed by hydrolysis with hydroxide on the surface of pyrite, then formation of a protective layer by dehydration during drying. Overall, our results further confirm that it is the formation of silicate polymer

on the silica-quinone layer of treated pyrite samples that suppresses pyrite oxidation.

Acknowledgements

The authors would like to acknowledge the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and JSPS KAKENHI Grant Nos. 24246149 and 15H02333 for financial and other supports.

REFERENCES

- 1) A. Akcil and S. Koldas: *J. Clean. Prod.* **14** (2006) 1139–1145.
- 2) R. L. P. Kleinmann, D. A. Crerar and R. R. Pacelli: *Min. Eng. Littleton* **3** (1981) 300–305.
- 3) C. A. Backes, I. D. Pulford and H. J. Duncan: *Soil Use Manage.* **9** (1993) 30–34.
- 4) S. B. Lavani, B. A. DeNeve and A. Weston: *Fuel* **69** (1990) 1567–1569.
- 5) S. B. Lavani, B. A. DeNeve and A. Weston: *Corrosion* **47** (1991) 55–61.
- 6) J. Satur, N. Hiroyoshi, M. Tsunekawa and H. Okamoto: *Int. J. Miner. Process.* **83** (2007) 116–124.

- 7) R. K. T. Jha, J. Satur, N. Hiroyoshi, M. Ito and M. Tsunekawa: *Miner. Eng.* **21** (2008) 889–893.
- 8) R. K. T. Jha, J. Satur, N. Hiroyoshi, M. Ito and M. Tsunekawa: *Miner. Process. Extr. M.* **33** (2012) 89–98.
- 9) Z. Diao, T. Shi, S. Wang, X. Huang, T. Zhang, Y. Tang, X. Zhang and R. Qiu: *Water Res.* **47** (2013) 4391–4402.
- 10) H. Setyawan, F. Fajarah, W. Widiyastuti, S. Winardi, I. W. Lenggono and N. Mufti: *J. Nanopart. Res.* **14** (2012) 807.
- 11) P. J. Swedlund, S. Sivaloganathan, G. M. Miskelly and G. I. N. Waterhouse: *Chem. Geol.* **285** (2011) 62–69.
- 12) M. Bessho, T. Wajima, T. Ida and T. Nishiyama: *Environ. Earth Sci.* **64** (2011) 311–318.
- 13) D. M. Kargbo and S. Chatterjee: *J. Environ. Eng.* **131** (2005) 1340–1349.
- 14) K. Kitagawa, T. Hirajima and K. Sasaki: Proc. Spring Meeting of MMIJ, (MMIJ, 2011) pp. 119–120.
- 15) M. D. Yuniati, T. Hirajima, H. Miki and K. Sasaki: Proc. Int. Symposium on Earth Science and Technology, (CINEST, 2013) pp. 193–196.
- 16) M. D. Yuniati, T. Hirajima, H. Miki and K. Sasaki: Proc. Int. Symposium on Earth Science and Technology, (CINEST, 2014) pp. 108–111.
- 17) K. Sasaki, M. Tsunekawa, T. Ohtsuka and H. Konno: *Geochim. Cosmochim. Acta* **59** (1995) 3155–3158.
- 18) D. A. Shirley: *Phys. Rev. B* **5** (1972) 4709–4714.
- 19) N. Schweigert, A. J. B. Zehnder and R. I. L. Eggen: *Environ. Microbiol.* **3** (2001) 81–91.
- 20) B. F. Anderson, D. A. Buckingham, G. B. Robertson, J. Webb, K. S. Murray and P. E. Clark: *Nature* **262** (1976) 722–724.
- 21) V. F. Lvovich: *Impedance Spectroscopy, Application to Electrochemical and Dielectric Phenomena*, (John Wiley & Sons, Hoboken, New Jersey, 2012) pp. 26–34.
- 22) N. Hiroyoshi, S. Kuroiwa, H. Miki, M. Tsunekawa and T. Hirajima: *Hydrometallurgy* **74** (2004) 103–116.
- 23) H. Bartels: *Helv. Chim. Acta* **47** (1964) 1605–1609.
- 24) C. W. Correns: *Clay Miner. Bull.* **4** (1961) 249–265.
- 25) M. J. Sever and J. J. Wilker: *Dalton Trans.* **7** (2004) 1061–1072.
- 26) Y. L. Zhang and V. P. Evangelou: *Soil Sci.* **163** (1998) 53–62.
- 27) K. Fytas and P. Bousquet: *CIM Bulletin* **95** (2002) 1063.
- 28) U. Schwertmann and H. Thalmann: *Clays Clay Miner.* **11** (1976) 189–200.
- 29) L. J. Bellamy: *The Infrared Spectra of Complex Molecules*, (Chapman and Hall Ltd., London, 1975) p. 9.
- 30) L. J. Bellamy: *The Infrared Spectra of Complex Molecules*, (Chapman and Hall Ltd., London, 1975) p. 92.
- 31) L. Carlson and U. Schwertmann: *Geochim. Cosmochim. Acta* **45** (1981) 421–429.
- 32) H. W. Nesbitt, G. M. Bancroft, A. Pratt and M. Scaini: *Am. Mineral.* **83** (1998) 1067–1076.
- 33) M. Gettings and A. J. Kinloch: *J. Mater. Sci.* **12** (1977) 2511–2518.
- 34) A. P. Grosvenor, B. A. Kobe, M. C. Biesinger and N. S. McIntyre: *Surf. Interface Anal.* **36** (2004) 1564–1574.
- 35) K. Sasaki, K. Takatsugi, K. Ishikura and T. Hirajima: *Hydrometallurgy* **100** (2010) 144–151.
- 36) D. Brion: *Appl. Surf. Sci.* **5** (1980) 133–152.
- 37) H. W. Nesbitt and I. J. Muir: *Geochim. Cosmochim. Acta* **58** (1994) 4667–4679.
- 38) M. Descostes, F. Mercier, N. Thomat, C. Beaucaire and M. Gautier-Soyer: *Appl. Surf. Sci.* **165** (2000) 288–302.
- 39) A. I. Stadnichenko, S. V. Koshcheev and A. I. Boronin: *Moscow University Chem. Bull.* **62** (Allerton Press, Inc., 2007) pp. 343–349.
- 40) D. Pleul, R. Frenzel, M. Eschner and F. Simon: *Anal. Bioanal. Chem.* **375** (2003) 1276–1281.
- 41) E. Paparazzo: *Surf. Interface Anal.* **24** (1996) 729–730.