

Development of silica coating on pyrite particles using Si-catechol complexes

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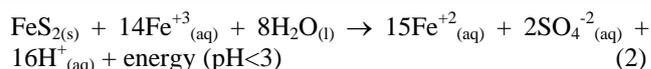
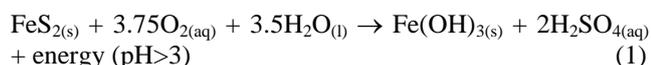
Abstract

The release of acidic mine waters in the environment constitutes a major problem faced by the mining industry. These acidic waters, known as Acid Mine Drainage (AMD), are related to the oxidation of sulphide minerals and especially pyrite (FeS₂) in the presence of oxygen, water and bacteria. An innovative and environmentally friendly alternative to prevent the generation of acidic waters is related to the formation of artificial coatings around pyrite grains. In this way, the direct contact between pyrite and oxidizing agents is avoided and thus the oxidation reactions are inhibited. Batch-type coating experiments were carried out with solutions contained Si-catechol complexes. In order to evaluate the stability of coating, oxidative leaching tests were conducted on samples previously subjected to the Si-catechol coating procedure. The investigated parameters included the FeS₂-particle size (-250+125, -125+75, -75+45 μm), the pH (3, 5, 6, 7, 9) and the treatment duration (up to 6 hours). Based on the results obtained by the oxidative leaching tests, it was found that an efficient silica layer can be developed within 6 hours using a coating solution with pH 6, as the release of SO₄⁻² was reduced by 40% compared to the fresh, non-treated pyrite (control test).

Keywords: Acid Mine Drainage, Sulphidic wastes, Pyrite, Silica coating, Si-catechol complexes

1. Introduction

The exposure of iron sulphides-bearing mine wastes to the atmospheric conditions causes their oxidative dissolution, which is catalyzed by Fe- and S- oxidizing bacteria. This complex geochemical process results finally to acid generation and toxic metal release to the environment, a phenomenon known as Acid Mine Drainage (AMD). The AMD is one of the major problems faced by the mining industry, in both abandoned and operating mine sites. Pyrite (FeS₂) is the most abundant of the sulphides and significantly contributes to AMD (Blowes *et al.*, 2014; Rickard, 2012). Pyrite oxidation has been studied extensively and can be summarized by the following reactions (Lottermoser, 2007):



The conventional AMD prevention and remediation techniques include wet and dry covers, alkaline additives, the use of bactericides, the desulphurization, as well as passive and active systems for water treatment (Flynn, 1969; Ford, 2003; Johnson and Hallberg, 2005; Mylona *et al.*, 2000; Öhlander *et al.*, 2012; Pérez-López *et al.*, 2007; Rastogi, 1996; Robertson *et al.*, 1997; Spotts and Dollhopf, 1992; Xenidis *et al.*, 2002). An emerging technique for the environmentally safe management of potentially acid generating wastes is related to the formation of artificial coatings on the pyrite grains in order to inhibit the direct contact of oxidizing agents (BREF, 2009). Several inorganic and organic compounds have been used for the development of artificial coating including phosphates, silicates, humic acids, polyamines, organosilanes, etc. (Açai *et al.*, 2009; Belzile *et al.*, 1997; Diao *et al.*, 2013; Evangelou, 2001; Huminicki and Rimstidt, 2009; Kargbo and Chatterjee, 2005; Kollias *et al.*, 2015, 2014; Liu *et al.*, 2013; Ouyang *et al.*, 2015). An interesting approach applied to the formation of coatings is based on the use of an organic agent, i.e. catechol (C₆H₄(OH)₂) as in-situ carrier for transporting soluble metals (i.e. Si or Ti) to the surface of pyrite. This process is reported as carrier microencapsulation, CME (Jha *et al.*, 2012, 2008; Satur *et al.*, 2007). Jha *et al.* (2012) performed shaking flask tests on pure pyrite grains, with size -75+53 μm, using coating solutions of 0-10 mM Si-catechol complexes at initial pH 3.5. The tests were carried out with liquid to solid ratio (L/S) equal to 10 mL/g and the duration was up to 1 month. The treated samples were subjected to leaching with solutions of variable pH values (0-6), as well as in the presence of *acidithiobacillus ferrooxidans* bacteria, in order to investigate the effectiveness of the silica coating. The first set of experiments indicated that S oxidation was reduced by 80-95% compared to non-treated samples (control samples) in the range of pH examined. The second set showed that S oxidation was inhibited by 55% compared to the control samples. Yuniati *et al.* (2015) applied treatment on pure pyrite of -38 μm grain size with a solution containing 2.34 mM Si and 7 mM catechol at variable pH values (3, 7 and 9.5) up to 6 hours. The best performance of the coating solution was observed at an initial pH 9.5 and 6 hours treatment time. FTIR and XPS analyses showed that the coating around pyrite grains consisted of a network of Fe-O-Si and Si-O-Si units. In the

present study, batch-type tests were performed to investigate the effectiveness of this coating procedure. The parameters investigated included the effect of grain size of FeS₂, the pH of coating solution, and the duration of treatment.

2. Materials and Methods

2.1. Material

The experimental work was conducted using pyrite tailings (Py) originating from Kassandra mines (Chalkidiki peninsula). In order to remove any previous oxidized phases, a pretreatment procedure was applied as described by Kollias *et al.* (2014). A representative amount of the sample, approximately 100 g, was finely ground and subjected to chemical and mineralogical analyses. The results of chemical analyses following aqua-regia digestion are presented on **Table 1**. Chemical analysis was carried out in duplicate and the relative percent difference was low (i.e. <4%). Based on X-Ray Diffraction (XRD) analysis (Bruker D8 Focus), the crystalline phases contained in the pyrite tailing include pyrite (FeS₂) and quartz (SiO₂).

Table 1. Chemical composition of pyrite tailings, Py (%), Mean values)

Major Elements	-250+125 μm	-125+75 μm	-75+45 μm
Fe	43.82	45.60	44.41
S	45.30	47.33	47.10
Insoluble			
SiO ₂	6.89	6.18	6.49

2.2. Coating experiments

The methodology used for the formation of silica coating around pyrite particles involved treatment of the samples with a solution containing Na₂SiO₃·5H₂O, as source of silicate ions, and catechol. HCl (1 N) was used as buffer for adjusting the pH at the appropriate values. The examined parameters are presented in **Table 2**. The experiments were carried out using constant liquid to solid ratio (L/S) equal to 100 mL/g. The experimental procedure included the preparation of 5 suspensions, containing 0.9 g of Py and 90 mL of coating solution for each pH value. Each suspension was removed from the shaker after a predetermined time period, i.e. 0.5, 1, 2, 4, and 6 hours. The solution was separated from the solids by filtration through a filter paper with 0.45 μm pore size. The filtrates were analyzed for Fe, Si and SO₄²⁻. The aqueous elements were measured by means of Atomic Absorption Spectrometry-Flame Emission (2100 Perkin Elmer), whereas the soluble sulphates were determined gravimetrically (Rice *et al.*, 2012). The solid residues were washed with deionized water, air dried and stored under anoxic conditions (N₂ atmosphere). The coating experiments were conducted under controlled conditions (T=20±5°C).

2.3. Evaluation of coating

2.3.1 Characterization of pyrite surfaces by SEM/EDS

The residual solids were examined by scanning electron microscopy (SEM) using a Jeol6380LV microscope at 20 kV accelerating voltage under high vacuum conditions for maximum resolution. The surface elemental composition was determined by the Oxford INCA Energy Dispersive Spectrometer (EDS), connected to the microscope.

Table 2. Experimental conditions

Parameter	Value
Size fraction (μm)	-250+125
	-125+75
	-75+45
Si (mM)	50
Catechol (mM)	150
L/S (mL/g)	100
pH	3, 5, 6, 7, 9
Agitation	Rotary shaker (10 rpm)
Time (h)	0.5, 1, 2, 4, 6

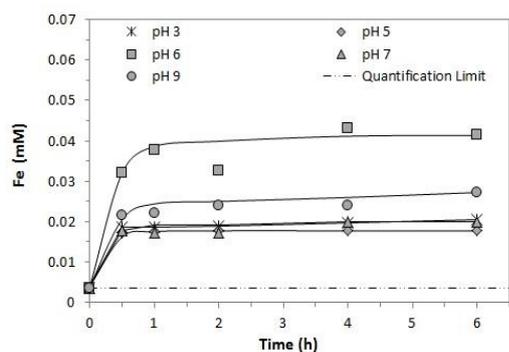
2.3.2 Oxidative leaching tests

In order to investigate the effectiveness of silica coating as far as the prevention of further oxidation is concerned, a series of post-coating oxidative leaching tests were conducted on treated Py samples. In this stage, 1 g of Py was mixed with 100 mL of solution containing 0.1 M H₂O₂ under natural pH. The suspensions were placed for agitation on a rotary shaker (10 rpm). At 24 hours the suspensions were filtered through a 0.45 μm filter and the filtrate was analyzed for Fe, SO₄²⁻ and Si. The remaining solids were washed and air dried. For comparison reasons, a fresh, non-treated Py sample was tested with the above procedure. The oxidative leaching tests were carried out in duplicate in a controlled laboratory environment (T=20±5°C).

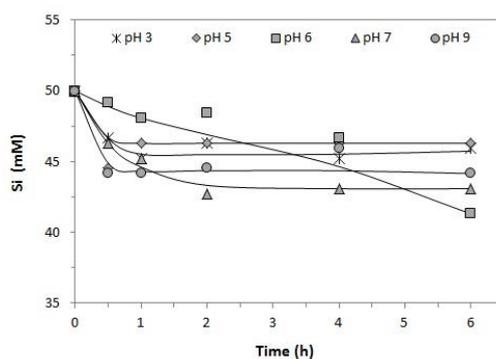
3. Results and discussion

3.1. Quality of aqueous phase

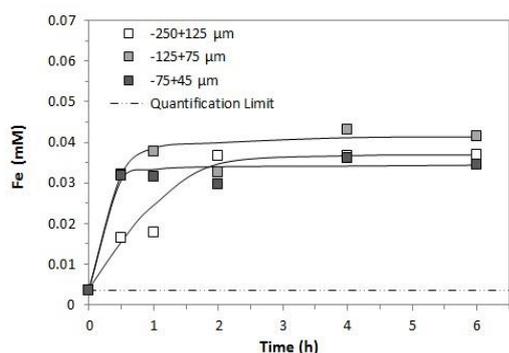
The concentrations of Fe and Si are presented in **Figures 1** and **2**. The concentrations of dissolved sulphates were below the quantification limit of gravimetric method (0.1 mM). The pH of the coating solution was found to affect the dissolution of Fe. The highest levels, 0.036-0.041 mM, were recorded at the value of 6. At the other tested pH values, the final Fe dissolution varied between 0.015 and 0.028 mM (**Fig. 1a**). The amount of Fe released to the aqueous phase did not vary significantly with the decrease of size fraction (**Fig. 1b**). It is also noted that after 1 hour of treatment, the amount of dissolved Fe reached a quasi-equilibrium concentration in the three fractions at all operating pHs. The results suggest that the evolution of the surface phenomena on pyrite is rapid. The evolution of Si



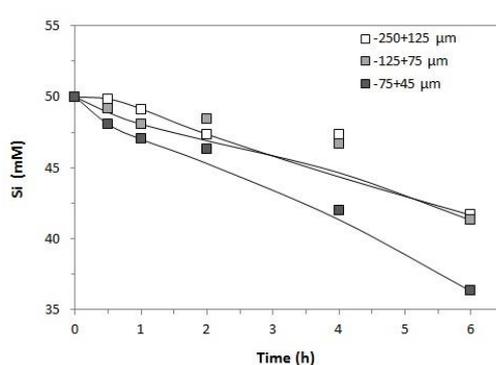
(a)



(a)



(b)



(b)

Figure 1. Evolution of aqueous Fe (a) effect of pH for the size fraction: -125+75 μm and (b) effect of size fraction at pH 6

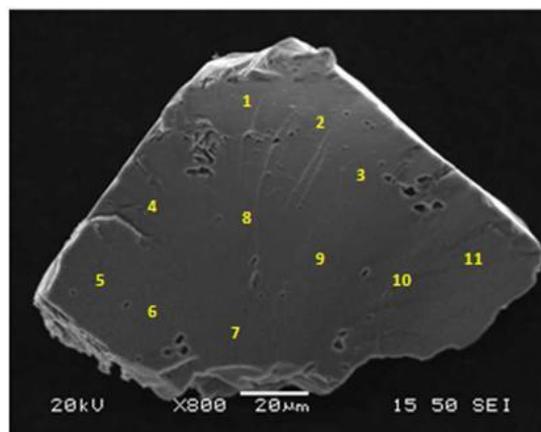
Figure 2. Evolution of aqueous Si (a) effect of pH for the size fraction: -125+75 μm and (b) effect of size fraction at pH 6

in the aqueous phase with respect to the pH of the coating solution and the size fraction is presented in Figure 2. The pH was seen to affect the precipitation process of Si. At pH 6, the removal of Si from the aqueous solution followed an almost linear kinetics during the whole duration of treatment and the final removal was approximately 17%. At the other tested pHs (i.e. 3, 5, 7 and 9), the precipitation of Si was completed within the first 30-60 minutes and varied between 7 and 14% (Fig. 2a). The size of grains at pH 6 had significant effect on the precipitation of Si only for the fine-sized fraction, i.e. -75+45 μm , with final removal equal to 27%. On the contrary, the evolution of the precipitation process had a similar trend for the coarser fractions (i.e. -250+125, -125+75 μm). At the end of 6 hours, the precipitation was about 16% (Fig. 2b).

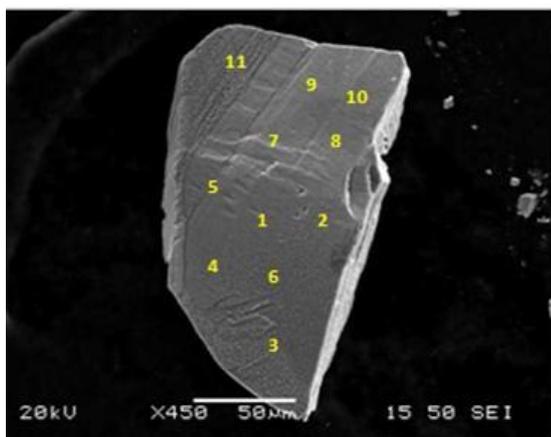
3.2. SEM/EDS analysis of coated particles

The treated Py samples were observed with SEM/EDS in order to investigate the chemical composition of the modified surfaces, as well as the morphological features, as a function of the operating pH. Representative results are shown in Figure 3. It is necessary to mention that the EDS spectrum represents the mean composition of a depth of about 1.5-2 microns and therefore, the analyses of Fe and S cannot be directly attributed to surface protective layer due to the FeS_2 background. Consequently, EDS analyses can be simply used to verify the presence of O- and Si- rich phases on the examined surfaces.

The EDS indicated the presence of oxygen in all the spots analyzed, suggesting the presence of oxidized phases in all the examined surfaces of treated particles. As seen in Figure 3, an extended silica protective layer is formed around pyrite grains treated at pH 6 and pH 7. More particularly, the EDS analyses of the pyrite grains treated at pH 6 indicated that the atomic % Si ranged from 0.11 to 0.77% and the % O varied between 5.68 and 25.94% (Fig. 3a). The treatment at pH 7 resulted in the detection of 0.11-0.95% Si and 4.10-7.61% O (Fig. 3b). It is noted that the silica coating was partial in grains treated at pHs 3, 5 and 9 (data not shown).



Element	Atomic%											Mean
	1	2	3	4	5	6	7	8	9	10	11	
O K	23.32	25.94	16.50	17.40	10.71	5.68	10.50	11.24	12.27	11.36	17.91	14.80
Si K	0.63	0.34	0.29	0.32	0.43	0.12	0.22	0.52	0.77	0.37	0.11	0.37
S K	51.58	50.56	59.66	56.02	63.49	67.20	62.02	61.77	59.80	62.06	56.92	59.19
Fe K	24.47	23.17	23.55	26.26	25.38	27.00	27.26	26.47	27.16	26.21	25.06	25.64
Totals	100.00											



Element	Atomic%											Mean
	1	2	3	4	5	6	7	8	9	10	11	
O K	4.31	6.84	6.10	4.10	6.62	5.05	5.45	6.63	5.35	5.76	7.61	5.802
Si K	0.34	0.17	0.16	0.34	0.19	0.60	0.11	0.65	0.61	0.39	0.95	0.41
S K	57.31	57.55	63.43	60.68	57.08	47.33	49.35	54.53	51.50	55.43	38.30	53.86
Fe K	38.04	35.44	30.31	34.88	36.10	47.02	45.09	38.19	42.54	38.42	53.13	39.92
Totals	100.00											

Figure 3. SEM microphotographs and EDS analyses of pyrite grains at 6 h of silica treatment for pH (a) 6 and (b) 7

3.3. Effectiveness of silica coating

The effectiveness of the coating formed around the pyrite particles under variable pH values was estimated based on the amount of sulphates released from the solids to the aqueous phase, during post coating oxidative leaching tests. The same test was applied to a non-treated Py sample for comparison reasons. It is mentioned that the pH value after the completion of the tests dropped to approximately 3, while the initial pH was ~5. **Figure 4** presents the dissolved amount of sulphates per kg of Py for the samples treated at pH 3, 5, 6, 7 and 9. It is seen that most effective coating was formed at pH 6. In this sample the dissolution of SO_4^{2-} was about 40% lower, compared to the non-treated sample. The concentration of dissolved Si was below the quantification limit of AAS.

4. Conclusions

Based on the results of this study, the following conclusions can be drawn:

- During the coating treatment of FeS_2 with the Si-catechol method, the concentration of SO_4^{2-} in the aqueous phase was constantly below detection limit, indicated limited oxidation of the pyrite grains (less than 0.3%). The highest dissolution of Fe was in the order of 0.05% and was observed at pH 6.

- The maximum precipitation of Si, 16-27%, was observed at pH 6.
- The SEM/EDS analysis of all solid residues indicated that an extended silica coating was formed around the pyrite grains treated at pH 6 and 7. The treatment at pH 3, 5 and 9 resulted in the formation of a partial coating.
- The oxidative leaching tests showed that the best performance was obtained at pH 6. The silica coating formed at pH 6 reduced the dissolution of S by 40% compared to the non-treated Py sample.

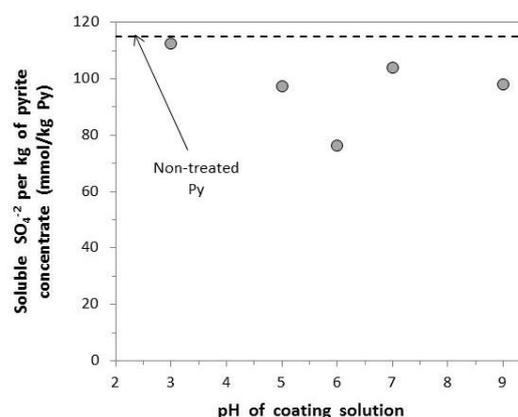


Figure 4. Dissolution of sulphates from the oxidative leaching tests in order to evaluate the effect of pH on the formation of a silica coating around FeS_2 (mean values of duplicate)

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References

- Ačai P., Sorrenti E., Gorner T., Polakovič M., Kongolo M. and de Donato P. (2009), Pyrite passivation by humic acid investigated by inverse liquid chromatography, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 337, 39–46.
- Belzile N., Maki S., Chen Y.-W. and Goldsack D. (1997), Inhibition of pyrite oxidation by surface treatment, *Science of The Total Environment*, 196, 177–186.
- Blowes D.W., Ptacek C.J., Jambor J.L., Weisener C.G., Paktunc D., Gould W.D. and Johnson D.B. (2014), The Geochemistry of Acid Mine Drainage, in: Turekian, Holland (Eds.), *Treatise on Geochemistry*, Elsevier, 131–190.
- BREF (2009), Reference Document on Best Techniques for the Management of Tailings and Waste-Rock in Mining Activities, European Commission.
- Diao Z., Shi T., Wang S., Huang X., Zhang T., Tang Y., Zhang X. and Qiu R. (2013), Silane-based coatings on the pyrite for remediation of acid mine drainage, *Water Research*, 47, 4391–4402.
- Evangelou V.P. (2001), Pyrite microencapsulation technologies: Principles and potential field application, *Ecological Engineering*, 17, 165–178.

- Flynn J.P. (1969), Treatment of Earth Surface and Subsurface for Prevention of Acidic Drainage from the Soil. U.S. Patent 3,443,882.
- Ford K.L. (2003), Passive Treatment Systems for Acid Mine Drainage. Technical Note 409. U.S. Department of the Interior. Bureau of Land Management, National Science and Technology Center.
- Huminicki D.M.C. and Rimstidt J.D. (2009), Iron oxyhydroxide coating of pyrite for acid mine drainage control, *Applied Geochemistry*, 24, 1626–1634.
- Jha R.K.T., Satur J., Hiroyoshi N., Ito M. and Tsunekawa M. (2012), Suppression of Pyrite Oxidation by Carrier Microencapsulation Using Silicon and Catechol, *Mineral Processing and Extractive Metallurgy Review*, 33, 89–98.
- Jha R.K.T., Satur J., Hiroyoshi N., Ito M. and Tsunekawa M. (2008), Carrier-microencapsulation using Si-catechol complex for suppressing pyrite floatability, *Minerals Engineering*, 21, 889–893.
- Johnson D.B. and Hallberg K.B. (2005), Acid mine drainage remediation options: a review, *Science of The Total Environment*, 338, 3–14.
- Kargbo D.M. and Chatterjee S. (2005), Stability of Silicate Coatings on Pyrite Surfaces in a Low pH, *Journal of Environmental Engineering*, 131, 1340–1349.
- Kollias K., Mylona E., Adam K., Papassiopi N. and Xenidis A. (2014), Suppression of Pyrite Oxidation by Surface Silica Coating, *Journal of Geoscience and Environment Protection*, 2, 37–43.
- Kollias K., Mylona E., Papassiopi N. and Xenidis A. (2015), Conditions favoring the formation of iron phosphate coatings on the pyrite surface, *Desalination and Water Treatment*, 56, 1274–1281.
- Liu Y., Dang Z., Xu Y. and Xu T. (2013), Pyrite Passivation by Triethylenetetramine: An Electrochemical Study. *Journal of Analytical Methods in Chemistry*, 2013, 1–8.
- Lottermoser B. (2007), Mine Wastes, 2nd ed. Springer-Verlag Berlin Heidelberg, Berlin, Heidelberg, New York.
- Mylona E., Xenidis A. and Paspaliaris I. (2000), Inhibition of acid generation from sulphidic wastes by the addition of small amounts of limestone, *Minerals Engineering*, 13, 1161–1175.
- Öhlander B., Chatwin T. and Alakangas L. (2012), Management of Sulfide-Bearing Waste, a Challenge for the Mining Industry, *Minerals*, 2, 1–10.
- Ouyang Y., Liu Y., Zhu R., Ge F., Xu T., Luo Z. and Liang L. (2015), Pyrite oxidation inhibition by organosilane coatings for acid mine drainage control, *Minerals Engineering*, 72, 57–64.
- Pérez-López R., Nieto J.M. and de Almodóvar G.R. (2007), Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste: Column experiments, *Chemosphere*, 67, 1637–1646.
- Rastogi V. (1996), Water quality and reclamation management in mining using bactericides, *Minerals Engineering*, 48, 66–71.
- Rice E.W., Baird R.B., Eaton A.D. and Clesceri L.S. (2012), Standard Methods for the Examination of Water and Wastewater, 22nd ed. American Public Health Association, American Water Works Association, Water Environment Federation.
- Rickard D. (2012). Sulfidic Sediments and Sedimentary Rocks, 1st Edition. ed. Elsevier.
- Robertson J.D., Tremblay G.A. and Fraser W.W. (1997). Subaqueous tailing disposal: A sound solution for reactive tailings, in: Forth International Conference on Acid Rock Drainage. 1029–1041.
- Satur J., Hiroyoshi N., Tsunekawa M., Ito M. and Okamoto, H. (2007), Carrier-microencapsulation for preventing pyrite oxidation, *International Journal of Mineral Processing*, 83, 116–124.
- Spotts E. and Dollhopf D.J. (1992), Evaluation of Phosphate Materials for Control of Acid Production in Pyritic Mine Overburden. *Journal of Environmental Quality*, 21, 627.
- Xenidis A., Mylona E. and Paspaliaris I. (2002), Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. *Waste Management*, 22, 631–641.
- Yuniati M.D., Hirajima T., Miki H. and Sasaki K. (2015), Silicate Covering Layer on Pyrite Surface in the Presence of Silicon and Catechol Complex for Acid Mine Drainage Prevention, *Materials Transactions*, 56, 1733–1741.