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SUPPRESSION OF PYRITE OXIDATION WITH IRON-PHOSPHATE COATING : TECHNIQUE FOR PREVENTION OF ACID MINE DRAINAGE

การยับยั้งกระบวนการเกิดออกซิเดชันของแร่ไพไรต์ด้วยการเคลือบเหล็กฟอสเฟต : เทคนิคการป้องกันน้ำทิ้งจากเหมืองเป็นกรด

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Abstract

This study was aimed to evaluate the feasibility of an iron-phosphate coating on pyrite surfaces for inhibiting an oxidation that is expected to prevent acid mine drainage (AMD). Prior to the experiments, pyrite samples (av. 425-850 μm in size) were mixed with sand (av. 1-2 mm in size) with a ratio of 1:4. Coating process was conducted in batch experiments that were treating with various concentrations of coating solutions, i.e., hydrogen peroxide (H_2O_2), sodium acetate (NaAc) and potassium dihydrogen phosphate (KH_2PO_4) at different contact times. Subsequently, leaching test was performed in columns (10 mm in diameter) using 0.145 M of the oxidizing solution (H_2O_2) at different times. Remaining phosphate, releasing iron and pH were recorded to estimate the degree of pyrite oxidation.

Treating with the coating solution, a mixture of 0.3 M KH_2PO_4 + 0.2 M H_2O_2 + 0.2 M NaAc, with 20 min contact time appeared to be the optimum condition to create iron-phosphate formation on pyrite surfaces. Phosphate remains in the solution is the lowest concentration after coating process (0.497-0.745 mg/L). The treated pyrite yielded leaching solution with pH ranging from 6.45 to 7.23 and low iron concentration releasing (0.008-0.151 mg/L). In addition, phosphate coated on the pyrite surface was quantitatively analyzed using Electron Probe Micro Analyzer (EPMA);

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consequently, the highest amount was also detected from the samples treated by such solution.

Keywords: acid mine drainage, pyrite oxidation, iron-phosphate coating

บทคัดย่อ

การศึกษาครั้งนี้ต้องการทดสอบกระบวนการเคลือบเหล็กฟอสเฟตบนผิวแร่ไพไรต์ สำหรับยับยั้งการเกิดออกซิเดชัน เพื่อป้องกันการเกิดสภาพกรดในน้ำทิ้งจากเหมือง ในการเตรียมตัวอย่างแร่ไพไรต์ให้มีขนาดประมาณ 425-850 ไมโครเมตรก่อนผสมกับทรายขนาด 1-2 มม. ด้วยสัดส่วน 1 ต่อ 4 กระบวนการเคลือบผิวด้วยปฏิกริยาหมู่ของสารละลายเคลือบผิวที่องค์ประกอบความเข้มข้นแตกต่างกัน ประกอบด้วย ไฮโดรเจนเพอร์ออกไซด์ (H_2O_2) โซเดียมอะซิเตรด (NaAc) และโปแทสเซียมไฮโดรเจนฟอสเฟต (KH_2PO_4) ที่ระยะเวลาต่างกัน จากนั้นนำไปทดสอบการชะในคอลัมม์ขนาดเส้นผ่านศูนย์กลาง 10 มม. ด้วยสารละลายออกซิเจนไดซิง (H_2O_2) ความเข้มข้น 0.145 M ที่ระยะเวลาต่างๆ โดยปริมาณฟอสเฟตที่เหลือค้าง เหล็กที่ถูกชะ และค่า pH จะถูกบันทึกเพื่อนำไปประเมินความรุนแรงการเกิดกระบวนการออกซิเดชันของแร่ไพไรต์

ผลการศึกษา พบว่า การเคลือบผิวด้วยสารละลายผสมระหว่าง 0.3M KH_2PO_4 กับ 0.2M H_2O_2 และ 0.2M NaAc ที่เวลาเคลือบ 20 นท. ให้ผลการสร้างเหล็กฟอสเฟตเคลือบผิวไพไรต์ได้เหมาะสมที่สุด มีฟอสเฟตเหลือค้างต่ำสุด (0.497-0.745 มก./ล.) โดยแร่ไพไรต์ที่ถูกเคลือบผิวด้วยสภาวะดังกล่าวหลังจากทดสอบการชะจะให้สารละลายมีค่า pH ประมาณ 6.45 ถึง 7.23 และมีปริมาณความเข้มข้นของเหล็กถูกชะออกมาต่ำ (0.008-0.151 มก./ล.) นอกจากนี้ปริมาณฟอสเฟตที่เคลือบบนผิวไพไรต์จากการวิเคราะห์เชิงปริมาณ ด้วยเครื่องอิเล็คตรอนไมโครโพรบ (EPMA) ให้ค่าสูงสุดจากการเตรียมด้วยสารละลายเคลือบผิวดังกล่าว

คำสำคัญ: น้ำทิ้งจากเหมืองเป็นกรด, กระบวนการออกซิเดชันของไพไรต์, การเคลือบเหล็กฟอสเฟต

Introduction

Acid Mine Drainage (AMD) is a serious environmental impact resulting from chemical weathering of sulfur-bearing minerals that have been exposed by mining activity. Percolation of water through these minerals may lead to a discharge with low pH that can leach out metals from the surrounding earth. As the results, AMD will contaminate surface water and groundwater threatening the human, plants and animal. Pyrite, FeS_2, is one of the most common metal-sulfides occurred in coal mining waste. It often exists in association with other heavy metals such as arsenic, cadmium, copper, zinc and lead(1). Pyrite undertaken oxidizing reaction is the major cause of AMD impairing surface water and groundwater qualities. The reactions of pyrite oxidation are described by Singer and Stumm(2) as following. Reaction (1) is weathering of pyrite. Disulfide is oxidized to sulfate, while ferrous iron and acid are released. This reaction generates two moles of acid for each mole of pyrite oxidized. The second reaction involves the conversion of ferrous iron to ferric iron consuming one mole of acidity; besides, certain bacteria can increase the rate of oxidation from ferrous iron to ferric iron. The reaction rate is pH dependent; the reaction is proceeding slowly under acidic conditions (pH 2-3) without bacteria present but several orders of magnitude faster rate may occur at about pH 5. Thus, it is referred as the "rate determining step" in the overall acid-generating sequence. Reaction (3) is the hydrolysis of iron which splits water molecule. Acidity is generated as a by product and many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate, commonly known as yellow boy, is pH dependent. Solids form when the pH is above 3.5 while solids will not precipitate below pH 3.5. Reaction (4) is the oxidation of additional pyrite by ferric iron which is generated in reactions (1) and (2). This is the cyclic and self propagating part of the overall reaction and takes place very rapidly, then continues until either ferric iron or pyrite is depleted. In this reaction iron is the oxidizing agent, not oxygen. In conclusion, an overall summary reaction of pyrite oxidation is shown in Equation (5).

$$2FeS_2+7O_2+2H_2O \rightarrow 2Fe^{2+}+4SO_4^{2-}+4H^+ \quad (1)$$

$$4Fe^{2+}+O_2+4H^+ \rightarrow 4Fe^{3+}+2H_2O \quad (2)$$

$$4Fe^{3+}+12H_2O \rightarrow 4Fe(OH)_3+12H^+ \quad (3)$$

$$FeS_2+14Fe^{3+}+8H_2O \rightarrow 15Fe^{2+}+2SO_4^{2-}+16H^+ \quad (4)$$

$$4FeS_2+15O_2+14H_2O \rightarrow 4Fe(OH)_3+8H_2SO_4 \quad (5)$$

General remediation methods of AMD are categorized into two ways as described as active and passive treatments. Active treatment involves adding a neutralizing agent such as $CaCO_3$ or NaOH directly to streams that have been impacted whereas passive treatment includes a variety of techniques to raise the stream pH values and reduce heavy metals loading. For example, open limestone channels, diversion wells, anoxic limestone drains and aerobic wetlands may be selectively operated within the impacted area. However, these approaches for preventing AMD have short-term of effectiveness because of the fact that the surfaces of metal-sulfides remain exposed to the oxygen after treatment. Consequently, another approach on using other chemicals to coat or encapsulated has been introduced(3-5). The pyrite coating process is based on the hypothesis that when pyrite is treated with a phosphate solution containing H_2O_2, oxidation will take place and ferric ions released will react with the phosphate ions. Passive coating on the pyrite surface is the result and then pyrite oxidation and acid production will stop(6). The method was firstly applied on framboidal or pulverized mineral pyrite particles. When hydrogen peroxide (H_2O_2), a strong oxidizing agent, is added into pyrite, the oxidation reaction is initiated(2) as present in equation (6). The process is an autocatalytic process which Fe^{3+}, an oxidation product, can also oxidize pyrite. If phosphoric acid along with FeS_2 react with H_2O_2 into the system, the oxidation reaction with unbalanced equation (7) can be written. Finally, iron phosphate will precipitate as a coated surface of pyrite. This reaction depends on the degree of supersaturation. Therefore, the main aim of this study is to find out experimentally optimum conditions of iron-phosphate coating on pyrite surfaces for inhibiting an oxidation that is expected to prevent.

$FeS_2+4H_2O_2 \rightarrow Fe^{3+}+2SO_4^{2-}+8H^+$ (6)

$FeS_2+H_2O_2+H_2PO_4 \rightarrow FePO_4+SO_4^{2-}+H^++H_2O$ (7)

Materials and Methods

Natural pyrite (FeS_2) available for this study was obtained from a gold mine in Phichit Province, Northern Thailand. In order to verify the feasibility of an establishment of iron phosphate coating on pyrite surface, experiments were carried out under laboratory scale. The methods in this study were divided into four main parts as described below.

Pyrite sample preparation

Pyrite samples were crushed and sieved to retain grain size between mesh numbers 20 and 40, equivalent to 425 µm to 850 µm. The prepared pyrite samples were then mixed with cleaned sand (1-2 mm in grain size) with a ratio of 1 to 4. Sand mixing in pyrite (later called pyrite sand) is aimed to promote the hydraulic conductivity of the system and hence the completion in reaction within the system is expected to increase.

Coating process

The optimum conditions of coating process were investigated by varying the concentrations of coating solutions (H_2O_2, KH_2PO_4 and NaAc) and different contact times of reaction between the coating solution and pyrite sand. The whole coating processes were divided into five steps as recommended by Evangelou and Huang(3) for the pyrite coating. This process was conducted in batch experiments containing coating solutions at different concentrations of KH_2PO_4 and H_2O_2. Coating processes are detailed as following:

1) Loading 10 g pyrite sand in the glass vials with a total of thirty vials.

2) Surface preconditioning in each vial was performed using 15 ml of 2 M hydrochloric acid solution (HCl solution) with constantly and regularly agitation for a period of length of time. The vials were then agitated to allow the contact of the chemical and the pyrite sand samples in order to clean the sample surface. The spent hydrochloric solution was then discharged from the vials. Any oxide or hydroxide component that might have formed on the surface of pyrite would be cleaned and ready for further reaction.

3) All samples were rinsed repeatedly by distilled water until the pH value of the rinsed solution raised to about 5. The pH value ranging form 5 to 6 is suitable for iron-phosphate precipitation on the pyrite particles(7).

4) Five coating solutions A, B, C, D and E, were prepared as mixture of various concentrations of KH_2PO_4 and H_2O_2 with constant concentration of NaAc with their compositions of all coating solutions described below. The solutions A, B and C are expected to compare the effect of KH_2PO_4 while the solution A, D and E is designed for determine the affect of H_2O_2.

Solution A = 0.2 M KH_2PO_4 + 0.2 M H_2O_2 + 0.2 M NaAc
Solution B = 0.3 M KH_2PO_4 + 0.2 M H_2O_2 + 0.2 M NaAc
Solution C = 0.1 M KH_2PO_4 + 0.2 M H_2O_2 + 0.2 M NaAc
Solution D = 0.2 M KH_2PO_4 + 0.33 M H_2O_2 + 0.2 M NaAc
Solution E = 0.2 M KH_2PO_4 + 0.01 M H_2O_2 + 0.2 M NaAc

Chemically, hydrogen peroxide (H_2O_2) in the coating solution strongly oxidizes the pyrite surface to produce ferric ion (Fe^{3+}) to be ready to react with potassium dihydrogen phosphate (KH_2PO_4) to form surface coating substance of iron phosphate ($FePO_4$). Sodium acetate (NaAc) is an important reagent in this coating process by playing a role as a buffer reagent.

Subsequently, 15 ml of these coating solutions were added into the prepared pyrite sand samples. Six contact times were applied to each type of coating solution allowing different periods of reaction including (a) instantaneous reaction for 0-1 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min and (g) 60 min. The reactions were carried on effectively by agitating motion in shakers. The solutions tapped from the vials after coating reaction of each experiment were taken to measure pH value and analyze phosphate concentration remaining. In addition, some treated samples were selected to analyze chemical composition on the coated pyrite using Electron Probe Micro-Analyzer (EPMA). EPMA is an electron beam technique applied for micro-scale analyses including qualitative/quantitative chemical compositions and electron images of material. EPMA used in this study belongs to Geology Department, Faculty of Science, Chulalongkorn University. It was operated with focused beam (<1μm) at 15 kV about 20 nA for applications of quantitative analysis and Secondary Electron Image (SEI). In addition, standardization using natural minerals and pure metals was carried out prior to quantitative analysis.

5) Stabilization of coated pyrite was performed by adding 20 ml of 800 mg/L concentrated calcium hydroxide solution [$Ca(OH)_2$] into the iron phosphate coated pyrite. Then the mixture of coated pyrite-$Ca(OH)_2$ was agitated in the shaker for ten minutes. This procedure would firmly stabilize the existence of the coated substance. Spent $Ca(OH)_2$ solution was subsequently discharged.

Leaching Test

The effectiveness of the coated substance, $FePO_4$, to prevent the pyrite oxidizing and AMD generating was determined by leaching test method. The coated pyrite was fed intermittently by hydrogen peroxide solution (H_2O_2) to simulate the oxidation process in natural hydraulic cycles. H_2O_2 reagent was chosen for leaching study because it creates an extremely oxidizing environment. In the H_2O_2 solution, the concentration of dissolved oxygen is much higher than that occurs naturally(8). The sequences of the leaching study are described below.

1) After coating process, air dry was applied to all pyrite sand samples.

2) Subsequently, 10 g of dried pyrite sand samples were loaded into the glass columns with 10 mm in diameter and 400 mm in length which were underlain by glass wool to filter leachate through the bottom of the column.

3) All samples were leached with a series of steps. Hydrogen peroxide (H_2O_2) solution, 20 ml of 0.145 M, was fed in each step for a period of 60 min. Therefore, the series of time are: t = 0, 60, 120, 180, 240, 300 and 360 min (t0 to t360), respectively. This step was designed by putting solution into the column and then waiting for solution passing through the column until the final drop of leachate was collected. In the next 60 min, the H_2O_2 solution was put into the column again and the leachate was then collected. This leaching process was continued until 360 min.

4) Leachates from each leaching test were collected into plastic bottles for subsequent analyses of the released iron and measurement of pH value.

Analytical Methods: Leachates collected at different times of feeding were measured for pH using PHM 83 Autocal pH meter and analyzed for total iron released by Flame Atomic Absorption Spectrometry (AAS) while the phosphate content was analyzed by Ascorbic acid method.

Result and Discussion

Coating results

Different mixtures of coating solutions were designed to determine the quantity and the quality of coating product, iron-phosphate ($FePO_4$), on the surface of the pyritic mineral. It is, therefore, essential to quantify the optimum condition of the formation of coating material and also the resistance of this coating product inhibiting oxidation process.

Figure 1 illustrates pH (Figure 1a) and concentrations of remaining phosphate (Figure 1b) in solutions A, B, C, D and E after the coating process. For all solutions, after 10 min, the pH was increased from around 4.8 to around 5.7. However after 10 min to 60 min, for all solution pH was slightly different and varied in the range of 5.4 to 5.8. It can be seen clearly in the graph (Figure 1b) that treating pyrite with the solutions A, C and E exhibited lower quantity of phosphate consumed to form the coating substance whereas the possibility of phosphate consumption for surface coating in the solutions B and D is apparently better. In addition, the contact time seems to be less affect in most of coating process of almost solution, except, that the phosphate remaining concentration increased at the time 40 and 50 min and then decreased at time 60 min.

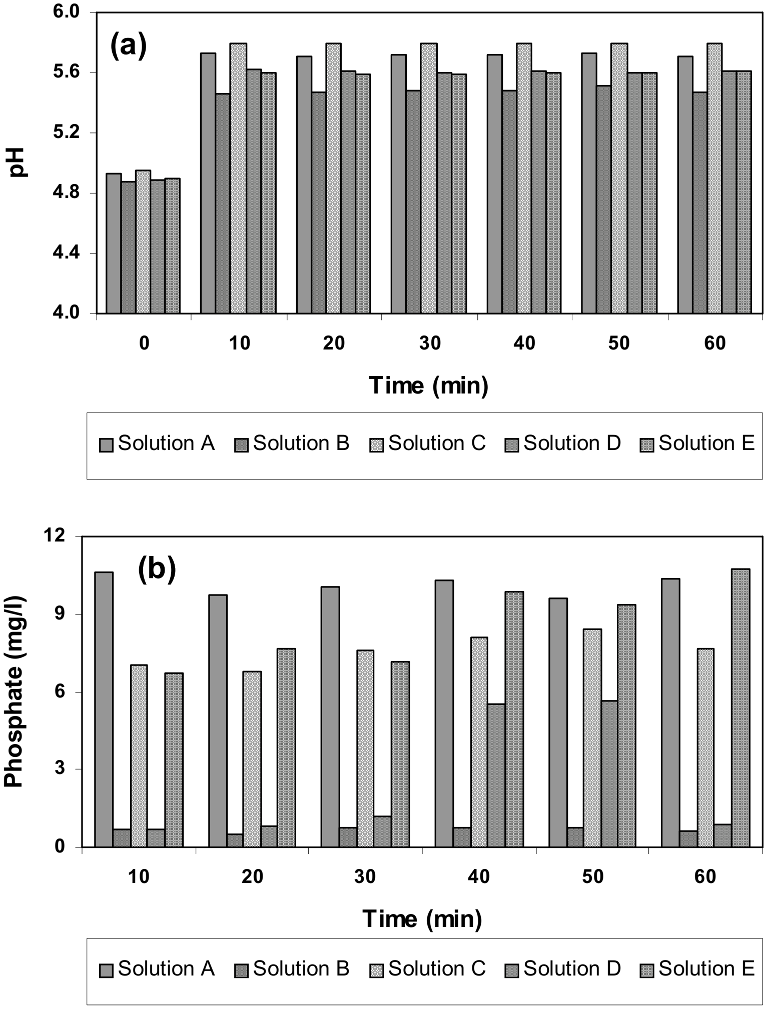

Figure 1 Variation of (a) pH and (b) remaining phosphate concentrations after treating with various coating solutions at different contact times.

From the coating result, some coating pyrite samples were selected to study the physical properties of coating by Electron Probe Micro-Analyzer (EPMA). Table 1 shows the result of the atomic proportion of elements analyzed by EPMA from the surface of coated pyrite. It is illustrated by the atomic ratio of S:P that is the lowest ratio yielded from the coated surface of sample B (t20). It could probably suggest that the coated substance on the surface of pyrite in sample B (t20) is relatively better than other samples.

Table 1 Average of atomic proportion on pyrite surfaces after coating with solutions B, C, D and E.

Sample	Atomic Proportion				
	Fe	S	P	Fe : S	S : P
Non-coated pyrite	0.136	0.269	0.000	0.504	-
B (t20)	0.120	0.234	0.052	0.514	59.240
C (t20)	0.145	0.281	0.004	0.517	112.452
D (t10)	0.144	0.281	0.005	0.514	95.201
E (t10)	0.139	0.268	0.024	0.517	80.251

Surface of uncoated pyrite was visualized under Scanning Electron Image (SEI), an application of EPMA, which is associated with some clay mineral (Figure 2a). However, clay mineral is obviously disappeared on the surface of coated pyrite; it may be mostly washed during the coating process. On the other hand, irregular cloudy grains of iron-phosphate ($FePO_4$) are increased on the coated surface (Figure 2b).

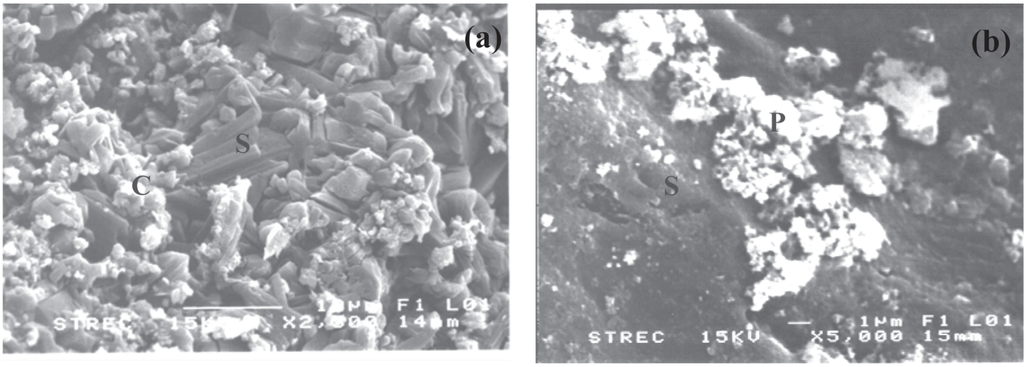

Figure 2 Secondary Electron Image (SEI) of pyrite surface taken from EPMA; (a) uncoated pyrite and (b) coated pyrite (C = clay mineral, S = pyrite, P = iron-phosphate).

Leaching results

For each coating result, one of each suitable coated pyrites based on the coating result and properties are selected for leaching experiments namely: Solution A, t-50; Solution B, t-20, Solution C, t-20, Solution D, t-10 and Solution E, t-60. The pH and cumulative iron concentration of leachates from each leaching at various time is shown in most effective coated results of each coating solution with different the optimum coating time are shown in Figure 3. The amount of iron released from leaching test of the coated samples show significantly decreasing from the experiment at t5 to t60, after that iron concentration decreases gradually and stays almost at the same concentration throughout t120 to t360. Oxidation rate of pyrite would be decreased in accordant to declination of iron concentration released in leachates.

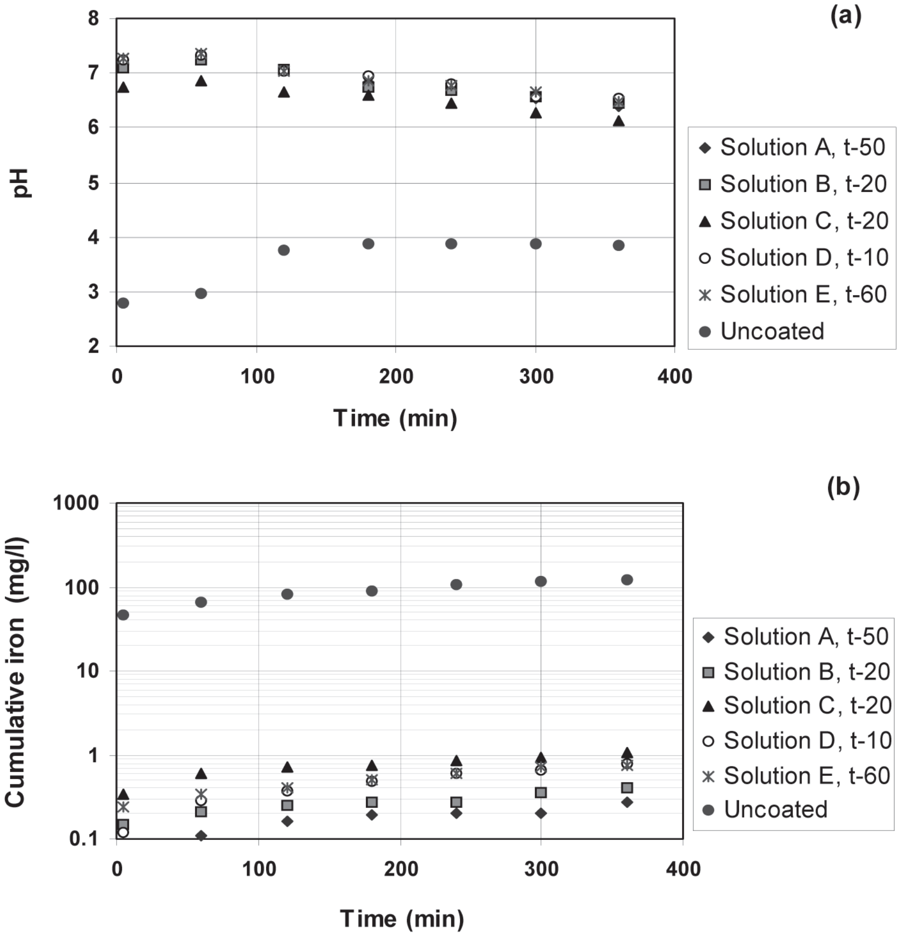

Figure 3 Trends of pH and cumulative iron released after leaching with 0.145 M H_2O_2 at various times; all samples undertaken coating process at the optimum times compared with uncoated pyrite.

The amount of iron released from the coated samples appears to be considerably small. They, however, show also the tendency of decreasing trend. From this experiment, the coated pyrite sample obtained from Solution B (0.3 M KH_2PO_4 + 0.2 M H_2O_2 + 0.2 M NaAc) at contact or coating time 20 min (t-20) can be considered to be the optimum of the coating condition.

Conclusion

It could be summarized, based on the results of the coating process, the leaching test and EPMA analyses, that the optimum condition of treating pyrite is coating solution B (0.3 M KH_2PO_4 + 0.2 M H_2O_2 + 0.2 M NaAc) at the optimum time of 20 min for the coating process to maximize the formation of an iron-phosphate coating on pyrite surfaces. This condition yield lowest quantity of remaining phosphate (0.497 mg/L) left after the coating process. Coated pyrite surface in sample B (t20) is relatively better than other samples. In addition, iron concentration released after leaching test is exceptionally low quantity ranging from 0.008 to 0.151 mg/L. Iron-phosphate formation on the surfaces of pyrite by treating with this optimum coating solution can efficiently reduce the pyrite oxidation rate and prevent the formation of AMD.

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