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Conditions favoring the formation of iron phosphate coatings on the pyrite surface

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ABSTRACT

The feasibility and conditions for the establishment of phosphate coating on a pyrite concentrate material to inhibit acid generation were studied. Batch tests involving the treatment of pyrite samples with H_2O_2 (control tests) and coating solution (H_2O_2, KH_2PO_4) buffered to pH 5.0–6.0 with sodium acetate were performed. The concentration of H_2O_2 and the liquid to solid ratio were characterized as critical factors for the formation of coating. A coating consisting of Fe–K phosphate phases and mixed Fe–K phosphate/Fe^{3+} oxyhydroxide phases was effectively developed on the surface of pyrite particles treated with H_2O_2 0.1 M, KH_2PO_4 0.4 M, buffered at pH 5.5 with CH_3COONa 0.2 M.

Keywords: Acid mine drainage; Mine wastes; Pyrite; Iron phosphate coatings; Surface reactions

1. Introduction

Acid generation from sulfidic wastes constitutes a significant environmental problem in coal, lignite, and polymetallic sulfide mining [1,2]. The sulfide minerals, especially pyrite, FeS_2, and pyrrhotite, $Fe_{1-x}S$, contained in the wastes, when exposed to atmospheric conditions and in the presence of bacteria are oxidized resulting in the generation of acidic waters, with high concentrations of sulfate anions, heavy metals, and metalloids (e.g. Fe, Cu, Pb, Zn, Cd, Ni, As, etc.).

The overall pyrite oxidation process can be described by the following equation [3,4]:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{-2} + 4H^+ \tag{1}$$

An emerging and appealing technique to prevent acid generation from sulfide wastes is the formation of coatings on the surface of sulfides that inhibit the direct contact between sulfide phases and water (and/or O_2), thus, inhibiting the progress of acid drainage generation. This geochemical process is known as pyrite microencapsulation. The technology of phosphate

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coating involves leaching of the sulfidic material with a solution containing an oxidant (mainly H_2O_2) to produce Fe^{3+} ions, a phosphate source (KH_2PO_4, NaH_2PO_4), and a buffer (CH_3COONa). The process results in the formation of iron phosphate ($FePO_4$) phases on pyrite surfaces, according to reaction (2) [5–7]:

$$FeS_2 + 7.5H_2O_2 + H_2PO_4^- \rightarrow FePO_4 + 2SO_4^{-2} + 3H^+ + 7H_2O \quad (2)$$

Based on Evangelou [7], iron phosphate coating can be established on pyritic coal wastes under a wide range of conditions, i.e. H_2O_2 concentration can range from 0.017 to 0.173 mol/L, KH_2PO_4 concentration can vary from 10^{-4} to 10^{-2} mol/L, and CH_3COONa concentration can be as low as 0.02 mol/L. In all cases, pH of the solution is necessary to be above pH 5 to ensure $FePO_4$ precipitation. To improve the stability of the phosphate coating, Fytas and Evangelou [8] treated pyritic tailings with $Ca(OH)_2$ aiming at the formation of calcium phosphate complexes on the surface of pyrite particles. Based on the results, phosphate coating inhibited pyrite oxidation by 75% as compared to the uncoated material.

Based on Harris and Lottermoser [9,10], the application of KH_2PO_4-H_2O_2/$KMnO_4$ solutions to partly oxidized, polymineralic mine wastes suppresses sulfide oxidation and is effective in inhibiting Pb, Cu, and Zn release. However, the technique appears ineffective in preventing metalloid (As, Sb) leaching from tetrahedrite- and arsenopyrite-bearing wastes. Short-term laboratory experiments showed that the application of water-soluble phosphate fertilizer MKP (KH_2PO_4) to sulfidic waste rocks results to the formation of phosphate coatings and precipitates that inhibited acid and metal release (Cd, Mn, Ni, Pb, and Zn) [11].

Ji et al. [12] investigated the effectiveness of KH_2PO_4 coating agent to inhibit acid generation from coal mine (S: 1.27%) and gold mine (S: 0.60%) samples by conducting laboratory-scale and field tests. The application of phosphate coating on laboratory scale resulted in the reduction of the sulfate production by 71–93%, as compared to the control test. Based on field-scale pilot tests at the gold mine site, the application of KH_2PO_4 resulted in the decrease of sulfate production from 200 to 13 mg/L and minimized Cu and Mn dissolution (<0.05 mg/L).

In this study, a series of experiments were undertaken in order to investigate the feasibility and conditions favoring the formation of phosphate coating on a pyrite concentrate material. The kinetics of pyrite oxidation with H_2O_2 under pH conditions used for the establishment of phosphate coating, i.e. pH 5.5 were also studied.

2. Materials and methods

A pyrite concentrate material produced in the past from Stratoni mines at Chalkidiki peninsula (Greece) was used. The pyrite sample assaying 50% S was screened and three fractions were selected for the experiments, i.e. (−250 + 125), (−125 + 75), and (−75 + 45) μm. To remove any previous oxidation products, the selected fractions were washed with HCl 1 M for 24 h (liquid to solid ratio, L/S = 20 mL/g), thereafter, rinsed repeatedly with deionized water. The samples were then dried at 40˚C for 24 h and finally, rinsed once with acetone. The pyrite's purity was confirmed by scanning electron micrograph (SEM)/EDS and powder-XRD.

Two series of batch-type tests were executed and the experimental conditions are given in Table 1.

Set of experiments No. 1 aimed at studying the kinetics of pyrite oxidation with H_2O_2 under pH conditions used for the establishment of phosphate coating, i.e. pH 5.5. The parameters investigated during this set of tests included (a) the size of FeS_2 particles, i.e. the size fractions (−250 + 125), (−125 + 75), and (−75 + 45) μm and (b) reaction time. The experimental procedure involved the preparation of 16 suspensions containing 0.4 g of pyrite and 40 mL of solution for each size fraction. The suspensions were placed for agitation on a rotary shaker (10 rpm). Two suspensions were removed for analyses after 0.5, 1, 2, 4, 6, 24, 48, and 72 h. At each sampling event, one suspension was filtered through a 0.45 μm filter and the filtrate was analyzed for Fe, SO_4^{-2}, and H_2O_2. The second suspension was acidified with 4 mL of concentrated HCl to obtain a final concentration of approximately 1 M HCl. After 24 h, the acidified sample was filtered and the HCl extract was analyzed for Fe and SO_4^{-2}. Acidification procedure aimed at determining iron and sulfate that may precipitate at the relatively high pH 5.5.

The second series of experiments aimed at investigating the conditions favoring the formation of phosphate coating on the pyrite grains. For the establishment of phosphate coating on the pyrite surface, the general methodology reported in the literature, involving leaching with a solution containing a coating agent (KH_2PO_4), an oxidizing agent (H_2O_2), and a buffer (CH_3COONa), was followed [7]. The batch tests were carried out using one size fraction,

Table 1
Experimental conditions

Parameter	Series of experiments No. 1 Kinetics of FeS_2 oxidation	 No. 2 Phosphate treatment
Size fraction (μm)	(−250 + 125) (−125 + 75) (−75 + 45)	(−125 + 75)
H_2O_2 (M)	0.1	0.01, 0.1
KH_2PO_4 (M)	–	0.0, 0.01, 0.1, 0.4
CH_3COONa (M)	0.2	0.2
L/S (mL/g)	100	1, 10, 100
Agitation	Rotary shaker (10 rpm)	–
Time (h)	1/2, 1, 2, 4, 6, 24, 48, 72	24

i.e. (−125 + 75) μm, and had 24 h duration. The suspensions were not agitated in order to favor the formation of coating and avoid potential removal of surface precipitations by the development of local shear strengths. Examined parameters included two levels of H_2O_2 concentration, 0.01 and 0.1 M, three levels of liquid/solid (L/S) ratios, 1, 10, and 100 mL/g, and three concentrations of KH_2PO_4, which were added as coating reagent, i.e. 0.01, 0.1, and 0.4 M. For comparison reasons, similar experiments were carried without addition of KH_2PO_4. In all the experiments, solutions were buffered with sodium acetate (CH_3COONa) 0.2 M to pH 5.5 and temperature was maintained close to normal atmospheric conditions (T = 23 ± 1˚C).

Iron concentration in the aqueous solutions and in the HCl extracts was determined by means of Atomic Absorption Spectrophotometry (2100 Perkin Elmer). Sulfate concentrations were measured gravimetrically [13]. The concentration of residual hydrogen peroxide in the aqueous solution was determined by volumetric titration with $KMnO_4$ 0.02 M. The surfaces of solid residues were examined and characterized by SEM/EDS.

3. Results and discussion

3.1. Pyrite oxidation by H_2O_2 at pH 5.5

The concentration of aqueous Fe in the solutions produced from the oxidation of pyrite samples with H_2O_2 0.1 M buffered at pH 5.5 was very low, ranging from 0.02 to 0.09 mM. This was expected given that under experimental conditions (pH 5.5), Fe is oxidized to ferric iron and precipitates in the form of amorphous and/or poorly crystalline Fe^{3+} phases. Fig. 1(a) shows Fe concentration in the 1 M HCl extract vs. time. As seen in the figure, Fe which is recovered in the acidic extract is about 2 orders of magnitude higher, ranging between 1.3 and 3.4 mM. However, the shape of the curves in Fig. 1(a) indicates that the acidic treatment with 1 M HCl is not able to dissolve all the Fe^{3+} solid phases. The concentration of HCl extractable Fe was increasing in the slurries corresponding to the initial 2–4 h of leaching and reached the maximum value of 1.8, 2.6, and 3.4 mM for the fractions (−250 + 125), (−125 + 75), and (−75 + 45) μm, respectively. Afterward, the HCl extractable Fe decreased and reached a quasi-equilibrium concentration of 1.4, 1.8, and 2.1 mM in the three fractions. The results suggest that the mineral phases of iron, which are formed after the initial 2–4 h of FeS_2 oxidative leaching are very stable and cannot be quantitatively dissolved in the 1 M HCl solution. The formation of stable iron phases like maghemite, γ-Fe_2O_3, during pyrite oxidation in carbonate buffered solutions has been reported by Nicholson et al. [14].

The evolution of HCl extractable SO_4^{-2} is shown in Fig. 1(b). It is seen that extractable SO_4^{-2} follows a trend similar to that observed for HCl extractable Fe. The maximum concentrations were recorded in the initial 4–6 h and were equal to 3.5, 4.0, and 6.1 mM for the fractions (−250 + 125), (−125 + 75), and (−75 + 45) μm, respectively. Afterward, there was a gradual decrease and the concentrations of HCl extractable SO_4^{-2} were stabilized close to 2.3, 2.7, and 2.2 mM for the coarse-, medium-, and fine-sized fractions, respectively. It is noted that, contrary to what happens with Fe, the concentrations of sulfates measured in the aqueous solutions were almost equal to the concentrations measured in the HCl extracts. The form of SO_4^{-2} kinetic curves suggests that a considerable part of produced sulfates is retained in the solids either by adsorption on the iron oxide phases or by formation

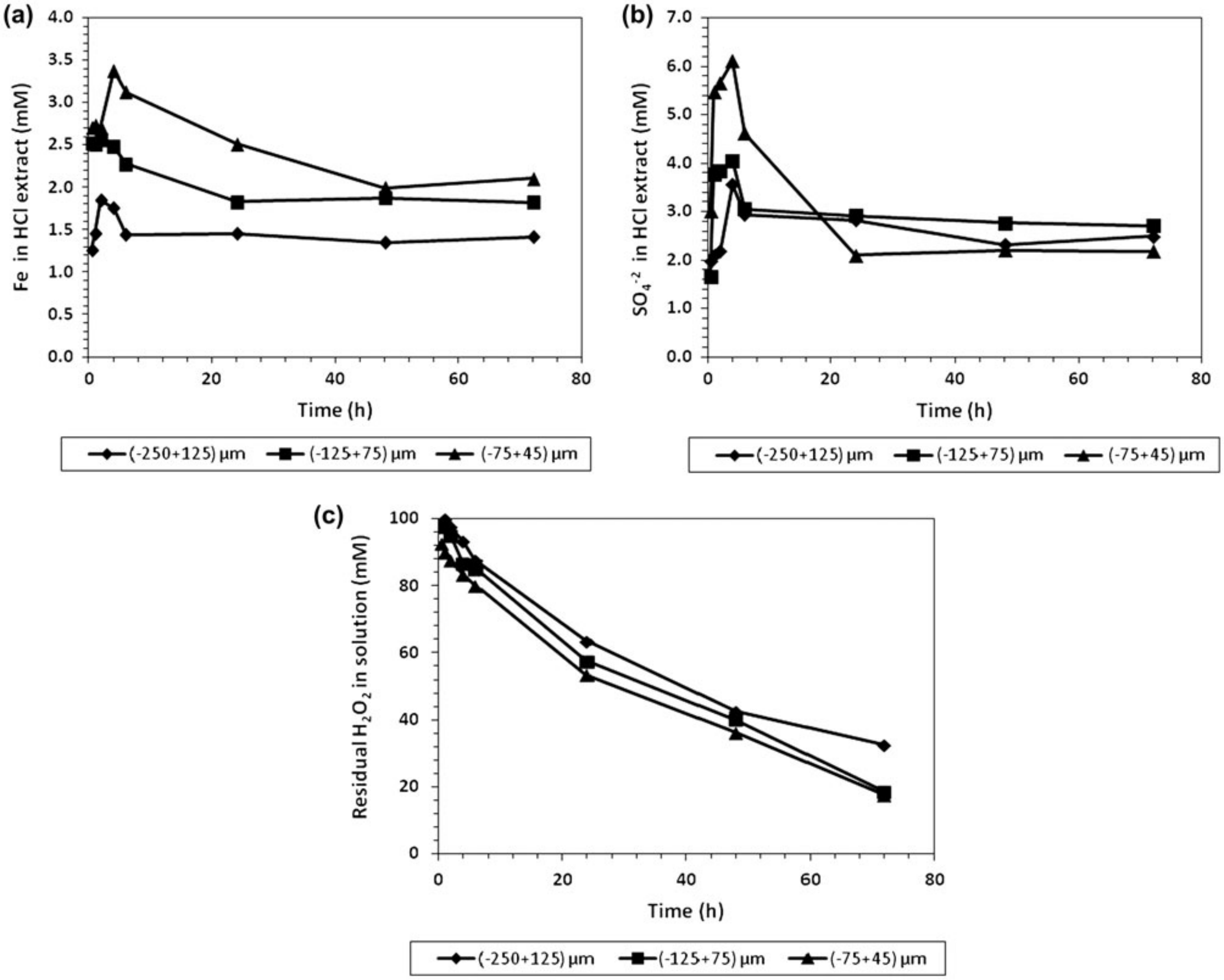


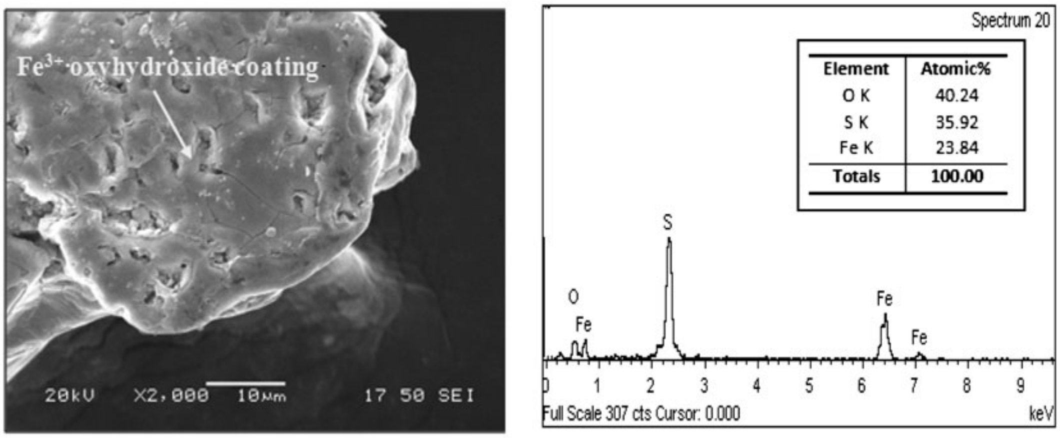
Fig. 1. (a) Concentration of Fe in HCl extract (mM), (b) concentration of SO_4^{-2} in HCl extract (mM), and (c) residual amount of H_2O_2 (mM) in the solutions vs. time for the pyrite oxidation tests.

of distinct iron sulfate solid compounds, like K- or H_3O-jarosites. The sulfates which are bound in the solid phases could not be mobilized with the acidic treatment using 1 M HCl.

Precipitation reactions that take place in parallel with the oxidation of pyrite particles do not allow an accurate estimation of the final oxidation degree obtained in the three size fractions. From the maximum amounts of HCl extractable Fe and SO_4^{-2}, it can be calculated that the oxidation obtained under the specific experimental conditions, i.e. H_2O_2 0.1 M, pH 5.5, liquid to solid ratio L/S = 100 mL/g, and gentle agitation 10 rpm, was at least equal to 2.3, 3.2, and 4.2% of pyrite for the size fractions (−250 + 125), (−125 + 75), and (−75 + 45) μm, respectively. As expected, oxidation percentage increases as the particle size diminishes, due to the larger specific surface area of the finer size fraction.

The curves of HCl extractable iron and sulfate (Fig. 1(a) and (b)) suggest that the progress of coupled oxidation/precipitation reactions is suppressed after approximately 24 h and a kind of equilibrium conditions are established. This is probably due to the precipitation reactions, which are forming a protective layer of iron oxides and oxyhydroxides around the pyrite grains.

SEM/EDS analysis of the solid residues confirmed the formation of Fe oxidized phases on the surface of pyrite particles that covered the clean relatively homogeneous pyrite surfaces, as illustrated in Fig. 2. According to EDS, the elemental analysis of the coating solid phase corresponds to 24% Fe, 36% S, and



Element	Atomic%
O K	40.24
S K	35.92
Fe K	23.84
Totals	100.00

Fig. 2. SEM and EDS spectrum of the pyrite particle after leaching with a solution consisting of H_2O_2 0.1 M buffered at pH 5.5 with CH_3COONa 0.2 M.

40% O. It is not clear, however, if measured sulfur corresponds to oxidized sulfates, adsorbed or precipitated, or to the underlying sulfides of FeS_2. The results of current work are in agreement with previous studies, which indicated that an iron oxyhydroxide coating can be established rapidly on the surfaces of pyrite by leaching with a solution containing H_2O_2 and a pH buffer (pH 4.0–6.0) [14,15]. This coating acts as a physical barrier preventing H_2O_2 from attacking the pyrite surface, thereby inhibiting further pyrite oxidation.

The residual H_2O_2 concentration in the solution of the pyrite oxidation tests vs. time is shown in Fig. 1(c). The consumption of the oxidizing agent was higher in the tests involving the finer size fraction, i.e. (−75 + 45) μm. It is seen, however, that after 6 h of leaching, when oxidation of the three pyrite size fractions studied is significantly retarded as indicated by iron and sulfate analysis, a significant percentage of hydrogen peroxide, i.e. 75–80% still remains in the solution. The concentration of hydrogen peroxide in the solutions decreased with time and after 72 h of leaching corresponded to 19–35% of the initial amount. The decrease of hydrogen peroxide in the solutions may be attributed to its decomposition. Under conditions of pH 5.5, the decomposition of hydrogen peroxide is mainly catalyzed by pyrite surfaces and to a lesser extent by the residual iron ions in the solution. The presence of amorphous or crystalline iron oxide phases on the pyrite surfaces may also catalyze heterogeneously the decomposition of hydrogen peroxide [16].

3.2. Phosphate treatment

The second series of experiments was carried out using the fraction of pyrite particulates with medium size, i.e. (−125 + 75) μm and aimed at investigating the conditions favoring the formation of phosphate coating on the pyrite grains. The performance of treatment was evaluated based on the amount of oxidized sulfate anions released in the aqueous solution per kg of treated pyrite. The results which were obtained using H_2O_2 concentration equal to 0.1 M are presented in Fig. 3. As seen in the figure, for the experiments that were carried out at liquid to solid ratio L/S = 1 mL/g and 10 mL/g, the addition of KH_2PO_4 at 0.01 and 0.1 M has a very limited effect on the amount of sulfates released in the solution. The concentration of SO_4^{-2} in solution when pyrite was treated without

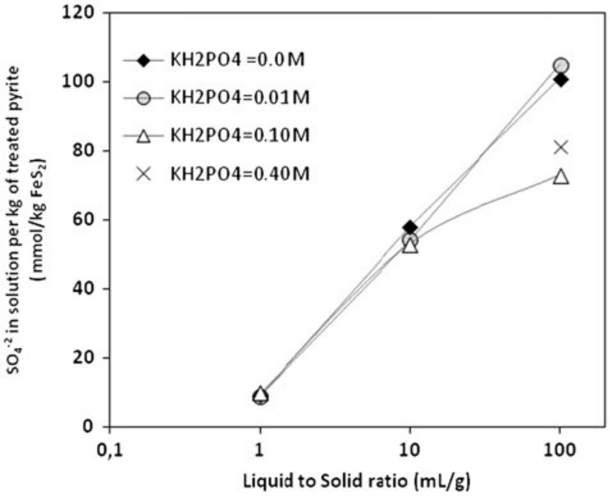
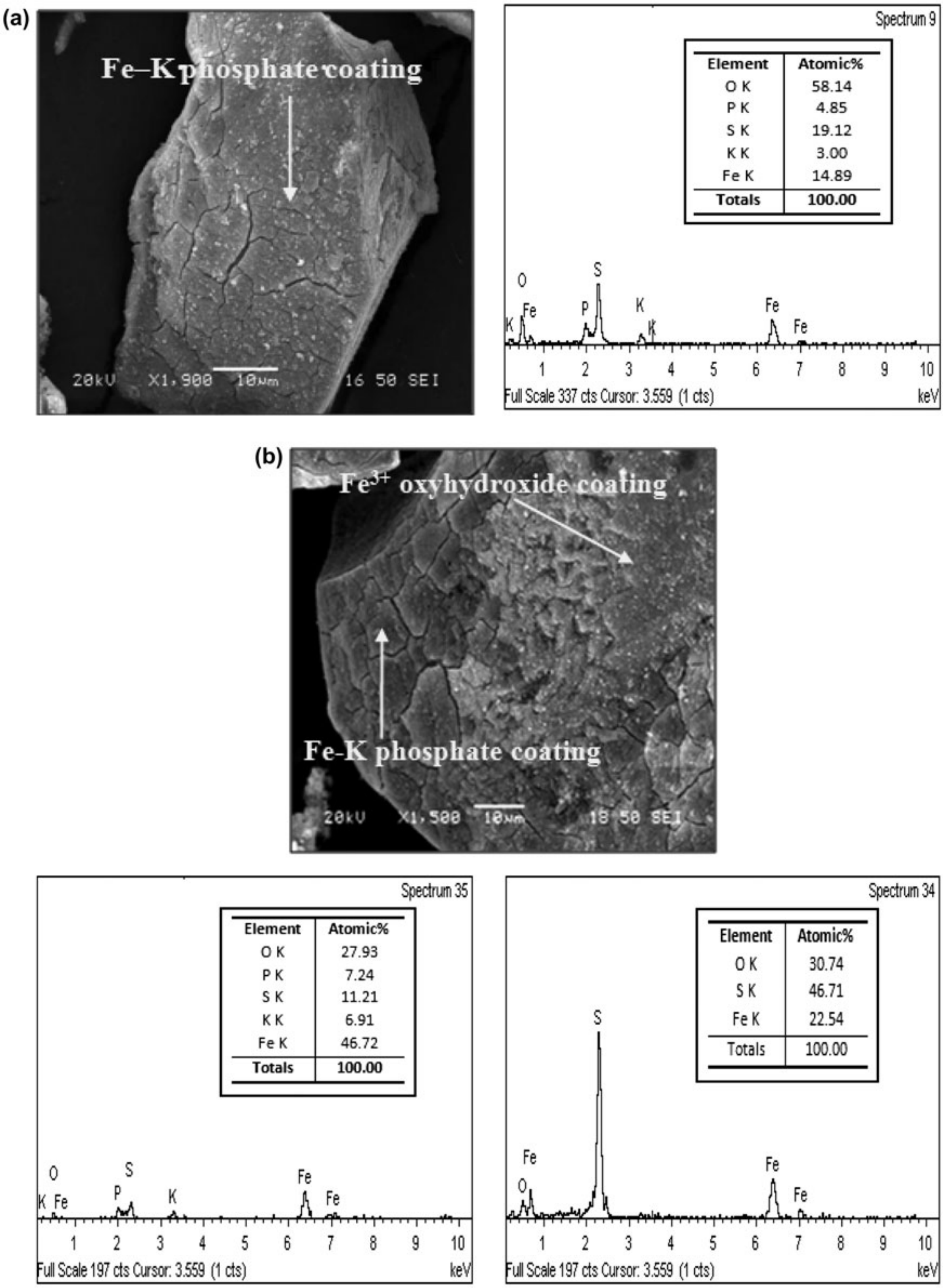


Fig. 3. Effect of liquid to solid ratio (mL/g) and KH_2PO_4 concentration on the amount of SO_4^{-2} released in solution per kg of treated pyrite (mmol S/kg FeS_2). Treatment conditions: H_2O_2 0.1 M, particle size fraction (−125 + 75) μm, pH 5.5, duration t = 24 h.



Spectrum 9

Element	Atomic%
O K	58.14
P K	4.85
S K	19.12
K K	3.00
Fe K	14.89
Totals	**100.00**

Spectrum 35

Element	Atomic%
O K	27.93
P K	7.24
S K	11.21
K K	6.91
Fe K	46.72
Totals	**100.00**

Spectrum 34

Element	Atomic%
O K	30.74
S K	46.71
Fe K	22.54
Totals	100.00

Fig. 4. SEM and EDS spectra of pyrite particles, treated with H_2O_2 0.1 M, KH_2PO_4 0.4 M, buffered CH_3COONa 0.2 M, covered by: (a) Fe–K phosphate coating and (b) mixed Fe–K phosphate/Fe^{3+} oxyhydroxide coating.

phosphate was almost the same with the values measured in the presence of phosphates. These concentrations were equal to 8.8–9.7 mmol/kg FeS_2 at L/S = 1 mL/g and 53–58 mmol/kg FeS_2 at L/S = 10 mL/g. Under these conditions, it seems that the pyrite grains are covered by simple Fe-oxyhydroxide layers without formation of any additional protective $FePO_4$ coating.

During the tests that were carried out with high liquid to solid ratio, L/S = 100 mL/g, addition of KH_2PO_4 at 0.01 M does not improve the protection of pyrite grains from oxidation, since the amount of sulfates release is equivalent to that observed without phosphates, i.e. 101–105 mmol/kg FeS_2. Addition of KH_2PO_4 at 0.1 M seems to favor the formation of a $FePO_4$ layer which is more effective in reducing the oxidation of FeS_2 and the subsequent dissolution of SO_4^{-2}. The release of sulfates decreases from 101–105 to 73 mmol/kg FeS_2. Increase of added KH_2PO_4 concentration to 0.4 M does not improve the performance of phosphate layer, since the amount of released sulfates is slightly higher, i.e. 81 mmol/kg FeS_2.

In the experiments that were conducted using a lower concentration of H_2O_2, i.e. 0.01 M, addition of KH_2PO_4 at all tested concentrations did not improve the protection of FeS_2 from oxidation.

The treated pyrite surfaces were observed under SEM/EDS in order to specify the surface reaction products. In some cases, the SEM micrograph and EDS analysis suggested a significant change on the surface morphology, due to the formation of amorphous and/or poorly crystalline phases. Based on the results of chemical analysis and SEM/EDS, it was deduced that no phosphate coating was detected in experimental conditions involving leaching of the pyrite particles with H_2O_2 0.01 and 0.1 M in the presence of KH_2PO_4 0.01 and 0.1 M, for liquid/solid ratio of 1 and 10 mL/g for a period of 24 h. On the other hand, it was seen that the precipitates became more extended as the KH_2PO_4 concentration increased from 0.01 to 0.1 M and 0.4 M at a liquid/solid ratio of 100 mL/g.

The coating developed on the surface of pyrite particles treated with H_2O_2 0.1 M, KH_2PO_4 0.4 M, buffered at pH 5.5 with CH_3COONa 0.2 M consists of Fe–K phosphate phases and mixed Fe–K phosphate/Fe^{3+} oxyhydroxide phases, as shown in Fig. 4(a) and (b). This may indicate that during the interaction of pyrite samples with the coating solution, iron phases are firstly formed, followed by an upper layer of phosphate phases. Elsetinow et al. [17] suggested that the phosphate anions bind preferentially and irreversibly to the Fe^{3+}-bearing oxidation phases at a pH ~5, preventing further oxidation of the surface.

4. Conclusions

Based on the results of the batch tests, the following conclusions can be drawn:

Leaching of the pyrite size fractions (−250 + 125), (−125 + 75), and (−75 + 45) μm with H_2O_2 0.1 M buffered with CH_3COONa at pH 5.5 at a liquid to solid ratio of L/S = 100 mL/g resulted in the oxidation of more than 2.3–4.2% of pyrite. The oxidation was significantly impaired after 4 h of testing, attributed to Fe^{3+} precipitation that inhibited its action as oxidizing agent and the coating of pyrite particles by Fe^{3+} oxyhydroxides that prevented H_2O_2 from oxidizing the pyrite surface.

The concentration of hydrogen peroxide and the liquid/solid ratio (mL/g) were critical factors in the solution for the formation of coating. Leaching of the pyrite particles with a solution consisting of H_2O_2 0.1 M, KH_2PO_4 0.4 M, buffered at pH 5.5 with CH_3COONa 0.2 M resulted in a well-developed coating consisting of Fe–K phosphate phases and mixed Fe–K phosphate/Fe^{3+} oxyhydroxide phases.

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