



# Potential Response of Pyrite Electrode in the Presence of Metal Ions

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## Abstract

Potential response of pyrite in an electrochemically active environment was supposed to shed light on its redox behavior in the presence of  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{Fe}^{+2}$  ions, the commonly existing metal ions in flotation pulps of complex sulfide ores. This study was conducted to elucidate the effect of metal ions on the electrochemical behavior of pyrite. Mineral surface was polarized between pH 3–11 for 30 minutes in open atmosphere condition. Redox potential data revealed that redox reactions ceased almost in a few minutes, and system came to equilibrium. Potential response of pyrite did not vary significantly possibly due to the nobility of mineral. Effect of metal ions both on redox potential and solution pH was measured in free to change condition. Metal ions decreased pH and increased potential. Their effects became more apparent when starting the polarization from alkaline pH.  $\text{Cu}^{+2}$  showed its effect especially on the rest potential. It was thought to adsorb on mineral surface forming Cu-S like species.  $\text{Pb}^{+2}$  could only manipulate redox potential because of the formation of porous Pb-oxides on pyrite when starting the polarization from alkaline pH. Discriminating effect of  $\text{Fe}^{+2}$  was observed at higher dosages due to oxidation of  $\text{Fe}^{+2}$  ions to  $\text{Fe}^{+3}$ -oxyhydroxides. Excess  $\text{H}^+$  ion release during chemical-electrochemical processes caused sharp decrease in solution pH.

Keywords: air pollution, markers, combustion, biomass, fossil fuels, geochemical background

## Introduction

Pyrite ( $\text{FeS}_2$ ) is a widespread and undesired gangue fraction of most complex sulfide ores. It is a semiconductor mineral, and can act as electron source or sink when immersed into an electrochemically active aqueous solution. Electrolytes, present in the sulfide ore pulp, may manipulate the flotation behavior of pyrite depending on their types and concentrations (Chandra and Gerson, 2009; Finkelstein, 1997; Peng et al., 2002). These electrolytes may be metal ions like  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{Fe}^{+2}$  in addition to other possible ions present in the pulp as flotation agents. They are added into flotation pulp as modifying agents to satisfy selectivity, and/or to depress pyrite. They may also present as dissolved species coming from the constituent of ore.

Electrolytes may accidentally activate gangue-pyrite causing concentrate dilution with its recovery in froth. Great interest, then, has focused on the electrochemical interaction of pyrite with electrolytes (Chandra and Gerson, 2009; Ekmekçi, 2000; Finkelstein, 1997; Kocabağ and Güler, 2008). Effects of electrolytes can be assessed measuring the potential response of pyrite or any other conducting material. When come into contact with the aqueous system, oxidation and reduction reactions proceeds complementarily on mineral surface. In this system, pyrite (conductive working electrode) and a surrounding conductive electrolyte are separated by a naturally-occurring Helmholtz double layer. Electron is transferred within this layer between the electrode and

the electrolyte, resulting in a potential difference between them. This potential difference is measured with respect to a reference point, for which a reference electrode is used. The measured value is described as rest potential. It is also known as open circuit potential (OCP), redox potential, mixed potential and electrochemical corrosion potential (Ekmekçi, 2000; Kocabağ and Güler, 2008).

Several electrochemical works have been performed using sulfide mineral electrodes made of highly pure mineral crystals. It has been revealed that interaction of mineral surface with the electrochemically active electrolytes could be measured and controlled (Allison vd., 1972; Ekmekci, 2000; Kocabağ and Güler, 2008; Ruonala vd., 1997). OCP measurement can provide valuable information about possible chemical reactions at pyrite-aqueous interfaces (Kocabağ and Güler, 2008). Since, in a certain aqueous environment, thermodynamically possible reactions, which are expected to proceed on pyrite surface, can become beneficial for process evaluation.  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{Fe}^{+2}$  are commonly observed metal ions in sulfide flotation pulp as modifying agent and/or as dissolved species from ore itself. Their effects on the electrochemical behavior of pyrite are worth mentioning. This work was performed to elucidate the potential response of pyrite electrode in the presence of metal ions.

## Materials and methods

Experiments were made using pyrite crystals from Artvin-Murgul deposit, Turkey. Characterization tests

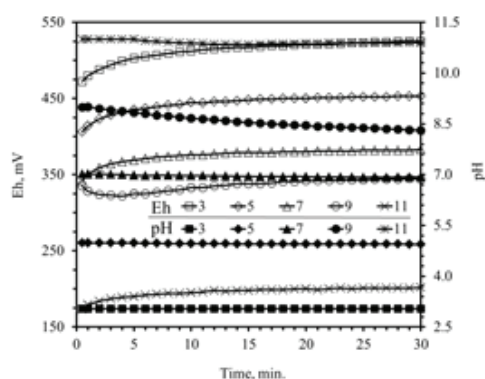


Fig. 1 Effect of open circuit polarization of pyrite on the measured pH and Eh

Fig. 1 Wpływ polaryzacji pirytu na zmierzone wartości pH i Eh

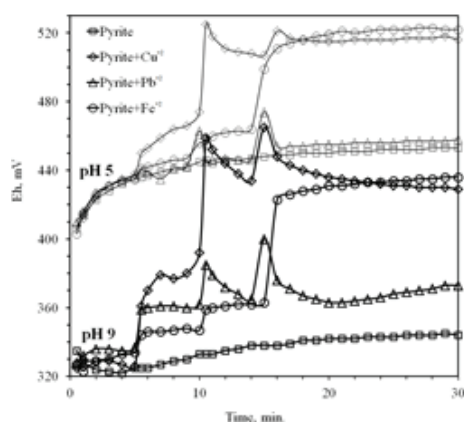


Fig. 2 Effect of metal ions on the potential response of pyrite electrode

Fig. 2 Wpływ jonów metali na odpowiedź elektrody pirytowej

of sample were performed by XRD and XRF, and sample was determined to be highly pure. Working electrode was constructed from pyrite crystal. Electrode preparation can be found elsewhere (Güler, 2005).

Electrochemical measurements were made using a glass cell containing 200 ml distilled water, in which working, reference and pH electrodes were dipped. Redox potential of pyrite electrode was measured with a multimeter using a Ag/AgCl electrode as a reference electrode. Redox potentials were given in the standard hydrogen electrode (SHE) scale by adding 200 mV to the measured values. Surface of working electrode was renewed polishing by 1000-grit SiC paper before each run. Cell was thoroughly washed with chromic acid, and then by distilled water prior to each experiment.

Potential data was taken in open atmosphere cell condition. Solution pH was adjusted at the beginning of experiment, and then left free to change during open circuit polarization work. H<sub>2</sub>SO<sub>4</sub> and NaOH were used as pH modifiers. FeSO<sub>4</sub>·7H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O and Pb(NO<sub>3</sub>)<sub>2</sub> were used as inorganic modifying agents as sources of Fe<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> cations, respectively. Used pH regulators and inorganic modifiers were of analytical grade.

## Results and discussions

Potential response of pyrite was measured in a wide pH range in distilled water (Figure 1). Slight increase in the rest potential of pyrite was observed in the tested pH range. On the other hand, solution pH decreased slightly when initiating the open circuit polarization process at alkaline pHs. In acid medium, the measured pH value did almost not deviate conspicuously from the first measurement.

Potential measurements were made in open atmosphere condition as mentioned above. So, oxygen saturated solution became an oxidizing environment for pyrite. Electrode surface behaved as anode, and oxygen reduction was the cathodic half-cell. When pyrite electrode was immersed into cell, anodic and cathodic half-cell reactions proceed due to over potential between them. Equilibrium potential was reached when redox reactions ceased, which value is named as mixed potential or redox potential (Kocabağ and Güler, 2008).

Anodic oxidation process releases Fe<sup>2+</sup> ions on mineral surface together with elemental sulfur according to reaction 1 (Chander and Briceno, 1987; Tao et al., 2003). Oxidation products of reaction 1 are not stable especially in alkaline condition. Depending on the po-

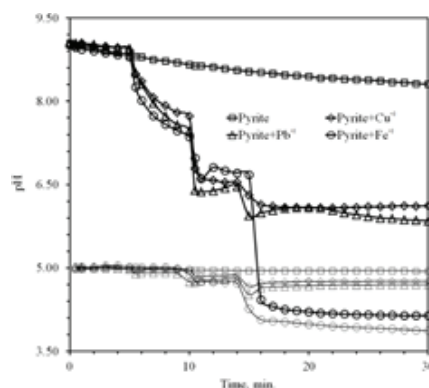
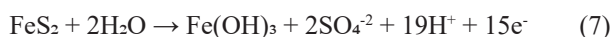
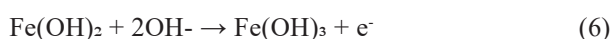
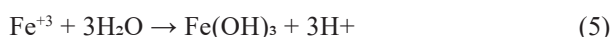
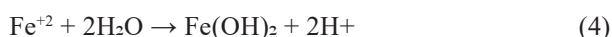


Fig. 3 Effect of metal ions on the pH of solution (Py: pyrite)

Fig. 3. Wpływ jonów metali na pH roztworu (Py – piryt)

larization pH, ferrous ion oxidizes further to form ferric oxyhydroxy species, which is coupled with the cathodic reduction of dissolved oxygen in solution according to reaction 2. This process is strongly pH dependent, and completes with the formation of ferric species above pH 3 (Chartrand and Bunce, 2003; Güler, 2005; Tao et al., 2003). Chemical/electrochemical processes proceed via following reactions. Hydrogen ion is released during the interaction of pyrite electrode surface with solution. Therefore, solution pH decreased slightly in neutral to alkaline conditions. Effect of chemical/electrochemical processes on solution pH could not be discriminated clearly because reacting electrode surface is too small, and reaction rate of the ferric species formation is low (Chander and Briceno, 1987).



Redox potential shows the capability of a solution to oxidize (or reduce) a mineral or any conducting material (Ekmekçi, 2000). Solutions having higher potential oxidize conducting material with lower electrode potential, and vice versa. An electrochemical equilibrium is reached when redox processes cease. Oxidation and reduction reactions proceed at the same speed complementarily, and so, electron balance within the electrochemically active system is established. In such system, cathodic process may be reduction of oxygen

or oxidizing agents while anodic process is the oxidation of mineral or reducing agents (Kocabağ and Güler, 2008).

Metal ions ( $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Fe}^{+2}$ ) were used to manipulate the capability of test solution to oxidize (or reduce) pyrite. They behave as modifying agent in sulfide mineral pulps (Chandra and Gerson, 2009; Finkelstein, 1997; Peng et al., 2002). They react with mineral, and new surface chemical state is established. Ferrous ion was the most active

$$E_{(\text{Fe}^{2+}/\text{Fe}^0)}^\circ = -440\text{mV}$$

tested metal ion whereas cupric ion was the most noble one

$$E_{(\text{Cu}^{2+}/\text{Cu}^0)}^\circ = 337\text{mV}$$

Standard formation potential of lead is between them

$$E_{(\text{Pb}^{2+}/\text{Pb}^0)}^\circ = -126\text{mV}$$

Polarization tests were conducted both in acid and alkaline conditions (Figures 2–3). Pyrite electrode was first conditioned for 5 minutes to reach electrochemically equilibrium condition. Solution of metal ions ( $1 \times 10^{-4}\text{M}$ ) was added into cell at 5th, 10th and 15th minutes of polarization. Metal ions reduced solution pH.  $\text{Cu}^{+2}$  and  $\text{Pb}^{+2}$  ions drew similar curves. Discriminating effect on pH was observed by the addition of  $\text{Fe}^{+2}$  ions: similar variation was observed up to 15 minutes. Then, sharp reduction in pH was observed.

OCP response of pyrite electrode with the addition of metal ions was a bit different from pH response. Metal ions increased rest potential reasonable especially when starting polarization from pH 9. Redox potential lines displayed that OCP value increased with nobility at lower dosages of metal ions. Copper ion – the noblest one used – was found to be more influential on the redox behavior of pyrite. Copper ions adsorb direct-

ly on pyrite surface instead of one-to-one ion exchange with lattice (Chandra and Gerson, 2009; Peng et al., 2012; Weisener and Gerson, 2000). Formed new Cu-S like new surface increased potential response of pyrite electrode behaving as Cu-sulfide mineral. Effect of iron ion on OCP became more apparent by the addition of last dosage (at 15 minutes of immersion). Ferrous ion is not stable in open atmosphere solution condition, and tends to oxidizing further to form ferric species (Chander and Briceno, 1987; Ekmekçi, 2000).

Pb<sup>+2</sup> ions did almost not affect redox potential in acid condition. Its effect on OCP became more apparent in alkaline condition. Pb-activation of pyrite occurs by precipitation of metal oxidation species on mineral surface (Peng et al., 2012). Adsorbed Pb-complexes have porous structure (Nava et al., 2002; Güler, 2012). Therefore, redox reactions proceeded on electrode surface at a reasonable rate. Pyrite oxidation process considerably overshadowed the traces of formation of Pb-complexes in acid condition, and similar potential response was observed except sharp peak formation like a sudden lightning when added. On the other hand, electrochemical response of became more apparent when starting the polarization of the pyrite electrode surface from pH 9.

Metal ions react with mineral surface and aqueous system by chemical/electrochemical processes similar to reactions 1–7 obeying almost similar mechanisms. So, numbers of hydrogen ion released for each case determined pH response. H<sup>+</sup> ion, released from those processes, reduced solution pH. Effect of Cu<sup>+2</sup> ions on pH was seen to be negligible although rapid change oc-

curred in rest potential with its addition because of the formation of activated fake Cu-S like surface (Chandra and Gerson, 2009; Peng et al., 2012; Weisener and Gerson, 2000). Pb<sup>+2</sup> did also exhibit similar results on solution pH. Fe<sup>+2</sup> ions, which were also chemical component of pyrite crystal structure, cause drastic changes both on pH and Eh above 15th minutes. Ferrous species behaved as pH modifier at higher dosages due to instability of ferrous ions and tendency to oxidize further to ferric species in experimental condition (Chander and Briceno, 1987; Peng et al., 2012).

## Conclusions

Effect of metal ions on the electrochemical behavior of pyrite was investigated by open-atmosphere polarization test. Experimental works were conducted in free to change condition in a wide pH range polarizing the pyrite surface for 30 minutes. Polarization did not significantly alter the potential response of pyrite due to its high nobility. Metal ions decreased pH and increased open circuit potential (OCP) due to H<sup>+</sup> ion release during chemical/electrochemical processes proceeding in the system. Cu<sup>+2</sup> ions adsorbed on pyrite as Cu-S like species. Cu<sup>+2</sup> ions significantly increased OCP due to high formation potential of those species although change in pH left at lower rates. Pb<sup>+2</sup> ions adsorbed on pyrite forming a porous layer. Then, effect of Pb<sup>+2</sup> on redox potential and pH could only be apparent when starting the polarization from alkaline pH. Discriminating effect of Fe<sup>+2</sup> ions was observed at higher dosages due to oxidation of Fe<sup>+2</sup> ions to Fe<sup>+3</sup>-oxyhydroxides.

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### *Potencjał elektrody pirytowej w obecności jonów metali*

*Badanie zmiany potencjału pirytu w środowisku aktywnym elektrochemicznie miało na celu określenie zmiany potencjału redoks w obecności jonów  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$  i  $\text{Fe}^{+2}$ , jonów metali powszechnie występujących w zawiesinach flotacyjnych rud siarczkowych. Badania zostały przeprowadzone w celu wyjaśnienia wpływu jonów metali na zachowanie elektrochemiczne pirytu. Powierzchnia mineralna była spolaryzowana przy wartości pH 3-11 przez 30 minut w atmosferze powietrznej. Pomiary potencjału redoks wykazały, że reakcje redoks ustały niemal w ciągu kilku minut, a system osiągnął stan równowagi. Potencjał pirytu nie zmieniał się istotnie. Wpływ jonów metali zarówno na potencjał redoks, jak i pH roztworu zmierzono w warunkach wymiany swobodnej wymiany. Jony metali zmniejszały pH i zwiększały potencjał. Ich efekty stały się bardziej widoczne przy rozpoczęciu polaryzacji przy pH alkalicznym. Jony  $\text{Cu}^{+2}$  wykazywały wpływ na potencjał resztowy. Uważa się, że na powierzchni mineralnych zachodzi adsorpcja Cu-S. Jony  $\text{Pb}^{+2}$  mogą zmieniać potencjał redoks jedynie z powodu tworzenia tlenków Pb na pirycie przy rozpoczynaniu polaryzacji od pH alkalicznego. Obniżający wpływ jonów  $\text{Fe}^{+2}$  wynika z powodu utleniania jonów  $\text{Fe}^{+2}$  do  $\text{Fe}^{+3}$ . Nadmiar jonów  $\text{H}^+$  podczas procesów chemiczno-elektrochemicznych spowodował znaczne obniżenie pH roztworu.*

Słowa kluczowe: zanieczyszczenie powietrza, znaczniki, spalanie, biomasa, paliwa kopalne, tło geochemiczne