INFLUENCE OF ADSORPTION ON THE CHARGE TRANSFER REACTIONS AT THE PYRITE SURFACE. PRELIMINARY STUDY

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Abstract. Electrochemical impedance spectroscopy was used to measure the charge transfer resistance of the reaction: $Fe^{3+} + e^- = Fe^{2+}$ and electrical double layer capacitance on pyrite electrodes of different origin both freshly polished and conditioned in the solutions of several surface active substances which may be used as potential inhibitors of the oxidation of pyrite. The following substances were used for conditioning of the pyrite samples: sodium dodecylsulfate (SDS), sodium oleate (NaOL), n-octanol (n-OA), dodecyltrimethylammonium chloride (CTACl), 2-mercaptobenzthiazole (MBT) and bis(2-etylhexyl) phosphate (D2EHP). The highest degree of adsorption, and the highest increase in the charge transfer resistance was observed for MBT, NaOL and D2EHP. Those compounds can be used as inhibitors of the pyrite oxidation.

1. Introduction

Since the beginning of the 20th century pyrite passed an unusual transformation from the fundamental raw material of the chemical industry to the unwanted and noxious component of the materials processed in mineral industry (Lowson, 1982). Pyrite is the most abundant sulfide mineral accompanying almost all sulfide and many non-sulfide minerals (Craig and Vaughan, 1990). Large quantities of pyrite appear in coal (Twardowska et al., 1978). At the same time pyrite has no application and in flotation process this mineral is directed to tailings. So, flotation tailings may contain as much as 60-70% of pyrite. Pyrite oxidizes relatively easily, and contrary to mono-sulfides, which oxidize to neutral sulfates, pyrite generates sulfuric acid during its oxidation

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \tag{1}$$

in the quantity of one mole of acid per one mole of pyrite. The amount of acid may be lower when pyrite iron oxidizes to trivalent oxidation state:

$$4FeS_2 + 15O_2 + 2H_2O = 2Fe_2(SO_4)_3 + 2H_2SO_4. \tag{2}$$
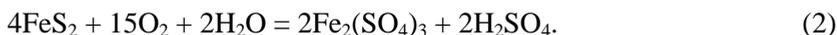
On the other hand, when pH of the surrounding aqueous phase increases above approximately 5.5 ferric sulfate hydrolyses according to the reaction:

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3 H_2SO_4 \tag{3}$$

creating additional amount of sulfuric acid. That sulfuric acid, together with dissolved trivalent iron are the main components of so-called acid mine drainage, i.e. waters flowing from worked-out mines, flotation waste deposits and sometimes from natural rocks containing pyrites (Doyle, 1990; Evangelou, 1995). Neither sulfates nor iron species belong to important environmental contaminants, however the decrease in pH of the water flowing through the wastes and soils causes the dissolution of otherwise insoluble constituents increasing the concentration of metal ions in effluents which leads to the contamination of the environment and sometimes even to catastrophes of buildings (Moore and Luoma, 1990). Pyrites appear also frequently as natural components of soils. Oxidation of those pyrites causes acidification of the soil which has detrimental influence on plants and causes contamination of the environment (Österholm and Åstrom, 2004; Åstrom and Spiro, 2005; Boman et all., 2008).

Weathering of metal sulfides may be considered as a corrosion process and, like in the case of the corrosion of metals it may be prevented by the application of inhibitors (Lipkowski, 1992; Stratmann et al., 1995). Many papers concerning the possible prevention of pyrite oxidation by application of inhibitors have appeared in the literature. Huang and Evangelou (1994) and Nyavor and Egiebor (1995) applied successfully soluble phosphates for that purpose, although Mauric and Lottermoser (2011) reported that application of phosphates in a larger scale led to only limited successes. Belzile et al. (1997) showed the applicability of several compounds (humic acids, lignosulfonates, oxalic acid, sodium silicate and acetyl acetone) in pyrite oxidation inhibition, the best inhibition was observed for the last compound. Cai et al. (2005) showed the inhibitive influence of triethylenetetramine on the oxidation of pyrrhotite. The same was showed by Güler (2005) in the case of dithiophosphinate. Jiang et al. (2000) found oleic acid to be effective as an inhibitor of pyrite oxidation whereas Zhang et al. (2003) and Kargbo et al. (2004) applied successfully lipids for that purpose. Sasaki et al. (1996) applied several organic substances to suppress pyrite oxidation with some success. Pyrite leaching occurs usually with the active participation of bacteria. So, addition of antibacterial agents should depress the oxidation of pyrite. That problem was investigated by Sand et al. (2007) with a partial success.

Most of pyrites appearing in nature show good electrical conductivity (Shuey, 1975; Ennaoui, 1993) and aqueous oxidation of pyrite is an electrochemical process (Holmes and Crundwell; 2000, Rimstidt and Vaughan, 2003), so the electrochemical

methods have been intensively used in the investigations of pyrite. Furthermore, due to specific electronic structure of pyrite surface (Bronold et al., 1994; Nesbitt et al., 2000) charge transfer reactions are facilitated at the surface of pyrite and proceed with low overpotential (Salvator et al., 1991; Mishra and Osseo-Asare, 1992; Nowak and Koziol, 2002). Presence of an adsorbed layer on the surface of pyrite should impede the charge transfer (Lipkowski, 1992). So, measuring the charge transfer resistance of a correctly selected reaction occurring at the surface of a pyrite electrode should give the information on the surface coverage. Such method was previously used by one of the present authors to the investigations of adsorption at the surface of copper sulfides (Nowak and Gucwa, 2008; Nowak, 2010). The reaction of choice is:

$$Fe^{3+} + e^- = Fe^{2+}. \tag{4}$$

It is an outer-sphere charge transfer reaction (Asperger, 2003) so its rate should not depend on the surface properties of the pyrite electrode but it should strongly depend on the presence of an adsorption layer. The charge transfer resistance for that reaction in the equimolar solution of trivalent iron and divalent iron sulfates was measured using electrochemical impedance spectroscopy (EIS) for several pyrite electrodes conditioned in the solutions of potential inhibitors, and compared to the values obtained for the freshly prepared electrodes. Additional information was obtained from the measured specific capacitance of the electrodes.

2. Experimental

2.1. Background of the measurements

The abstraction of a surface active substance from the solution by a sulfide minerals does not necessarily prove that the substance is adsorbed at the surface. There are other processes, like surface precipitation or surfactant decomposition that may lead to the decrease of the concentration without formation of an adsorbed layer. In the case of metallic electrodes adsorption may be conveniently estimated from the measurements of the electrical double layer (EDL) capacitance using the formula:

$$\theta = \frac{C_0 - C}{C_0 - C_{max}}. \tag{5}$$

In that formula C means capacitance of the electrode measured at the coverage θ, C_{max} means the electrode capacitance at full coverage and C_0 means the capacitance of the electrode not covered by the adsorbate. For such electrodes like pyrite electrode C_{max} is difficult to be measured. However for the $C_{max} << C_0$ (which is usually the case) surface coverage may be roughly estimated from the formula:

$$\theta \cong \frac{C_0 - C}{C_0} = 1 - \frac{C}{C_0}. \tag{6}$$

Application of that formula is possible only if the capacitance of EDL on the solid body side of the interface is much higher than the capacitance of EDL on the solution

side. It will be later showed that this condition is fulfilled in the case of pyrite electrodes. Surface coverage may be also estimated from the measurements of the charge transfer resistance of a conveniently selected electrode reaction. When a part of the electrode surface is covered by the layer of adsorbed molecules the charge transfer resistance may be calculated from the formula:

$$\frac{1}{R_T} = \frac{1-\theta}{R_T^0} + \frac{\theta}{R_T^{\max}},$$ (7)

where R_T is the charge transfer resistance at the coverage θ, R_T^0 is the charge transfer resistance at the zero coverage and R_T^{max} is the charge transfer resistance at the full coverage. The latter is difficult to measure but, if $R_T^{max} >> R_T^0$ formula (7) may be simplified to:

$$\theta \cong 1 - \frac{R_t^0}{R_T}.$$ (8)

Although approximate, the formulas (6) and (8) may be used for the sake of comparison between different electrodes and/or different adsorbates.

2.2. Apparatuses, procedures and materials

Five electrodes from pyrites of different origin were used in the measurements (see Table 1). The type of their conductivity was inferred from the thermoelectric force measurements. Pieces of pyrite were hand selected and embedded with epoxy resin at the end of a glass tubing. Electrical connection to the pyrite surface was made with the conducting silver-based glue. Electrodes were polished on emery papers (Struers) of the gradation: 500, 1000, 2400, and finely, 4000 before the measurements. Polishing was performed very gently to avoid heating of the electrode surface (Libowitzky, 1993). After polishing the electrode was dipped in the solution of the selected surface active compound for half an hour, thoroughly washed with distilled water and introduced to the cell. The following compounds were tested as possible pyrite oxidation inhibitors: sodium dodecylsulfate (SDS), sodium oleate (NaOL), n-octanol (n-OA), dodecyltrimethyl ammonium chloride (CTACl), 2-mercaptobenzthiazole (MBT) and bis(2-etylhexyl) phosphate (D2EHP). All compound used were of analytical reagent purity grade. In all cases the concentration of the solution was 10^{-4} mol dm^{-3}. Charge transfer resistance of the reaction (4) was measured in the solution containing: 0.5 mol dm^{-3} Na_2SO_4, 0.01 mol dm^{-3} H_2SO_4, 0.1 mol dm^{-3} $FeSO_4$ and 0.05 mol dm^{-3} $Fe_2(SO_4)_3$. For the sake of comparison the non-treated electrodes were measured too. Measurements were performed in a typical glass cell, in a three electrode configuration, with saturated calomel electrode as the reference electrode and platinum wire as a counter electrode. All measurements were performed at the temperature of 25°C. Doubly distilled water was used to prepare the solutions. Solutions were purged from oxygen by bubbling with 99.999% argon (Linde) before

the electrochemical measurements. XPS instrumentation was described in our previous paper (Nowak et al., 2000).

The impedance spectra were measured in the frequency range of 65535 - 0.125 Hz at the rest potential of the electrode. The measuring system composed of an ECI 1286 potentiostat and a FRA 1250 frequency response analyzer (both Schlumberger – Solartron, Great Britain) was used in the measurements. Charge transfer resistance and the capacitance of the electrical double layer (C_{EDL}) were then calculated from impedance spectra by fitting the proper equivalent electrical circuit (EEC) to the EIS data using the MINUIT program (James and Roos, 1975). More information on the data treatment may be found in our previous paper (Nowak et al., 2000).

Table 1. Origin and conductivity type of the pyrite electrodes used in the measurements

Electrode description	Pyrite origin	Conductivity type
EB	Elbe, Italy	p
RT	Rio Tinto, Spain	n
UR	Ural Mountains, Russia	p
HU	Huenzala, Peru	n
HA	Halemba Mine, Poland	p

3. Results and discussion

3.1. Impedance of the pyrite electrodes in the Fe^{2+} - Fe^{3+} equimolar solution

The rest potential of pyrite electrodes in the equimolar solution containing Fe^{2+} and Fe^{3+} ions of the concentration 0.1 mol·dm^{-3} was many hours stable and equal to the rest potential of a Pt electrode in the same solution, which means that the process occurring at the surface of a pyrite electrode (reaction 4) is well reversible. Figure 1 shows the impedance spectrum of one of the pyrite electrodes in that solution. The impedance plot has the shape of a depressed semicircle in accordance with the assumed EEC. Table 2 shows the results of the measurements performed on freshly polished electrodes which were not conditioned.

For the first three electrodes R_S was almost the same and rather low. It means that the value of R_S was dominated by the resistance of the solution. Both HU and HA showed much higher resistance, which may be ascribed to the low conductivity of the pyrite samples. For all investigated electrodes (except HA) R_T had the value between 13 and 21 Ω cm^2, despite different origin and type of conductivity. The differences may arise from the differences in surface roughness factor. Platinum electrode in the same solution showed similar impedance spectrum and R_T value of 14 Ω cm^2, very close to pyrite electrodes. It means that the exchange current density of reaction 4 at the pyrite electrode surface is very high. So, there is no obstruction to charge transfer at the pyrite surface, in accordance to the theoretical expectations (Bronold et al., 1994; Nesbitt et al., 2000; Salvator et al., 1991; Mishra and Osseo-Asare, 1992).

All electrodes (except HA) showed also similar EDL capacitance. Electrode made of Halemba pyrite showed not only much higher R_S but both also much higher R_T as well as much lower C_{EDL}. That electrode was not considered in adsorption

experiments. Worth mentioning is the high value of EDL capacitance of pyrite electrodes. That value is about twice as much as the electrical double layer capacitance measured in the case of non-stoichiometric copper (I) sulfide electrode and much higher than C_{EDL} measured in the case of metallic Ni electrode (Nowak et all., 2000). That high electrical double layer capacitance may be ascribed to the presence of surface iron (III) hydroxide on the surface of pyrite (Bungs and Tributsch, 1997). That problem will be discussed in our future paper.

Table 2. Parameters of the EEC from Fig. 1 fitted to the impedance data for freshly polished electrodes. R_S - solution resistance, R_T -charge transfer resistance, C_{EDL} – capacitance of the electrical double layer. Each value is a mean from at least 5 measurements

Electrode	R_S / Ωcm^2	R_T /Ωcm^2	C_{EDL} /μF cm^{-2}
EB	7.1±1.3	14.9±3.5	125±22
RT	8.0±0.5	18.6±6.5	97.8±13
UR	10.1±0.5	13.2±2	101.1±11
HU	86.2±6	21.2±5.5	84.4±14
HA	248.0±15.5	50.3±12	9.4±3
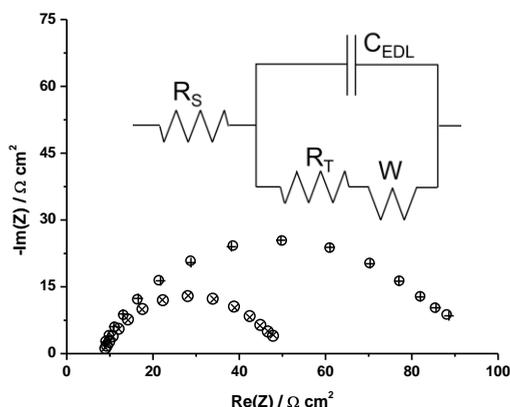
Fig. 1. Impedance spectra (Nyquist plots) of the RT electrode in the solution containing 0.5 mol dm^{-3} Na$_2$SO$_4$, 0.01 mol dm^{-3} H$_2$SO$_4$, 0.1 mol dm^{-3} FeSO$_4$ and 0.05 mol dm^{-3} Fe$_2$(SO$_4$)$_3$ at the rest potential. x – freshly polished electrode, + - the same electrode after 30 minutes of conditioning in 10^{-4} mol dm^{-3} D2EHP solution , o – least-square fitted values of impedance according to the EEC from figure. R_S is the resistance of the solution, pyrite sample and the electrical connections, R_T is the charge transfer resistance, C_{EDL} is the capacitance of the electrical double layer and W is the impedance of the diffusion process (Warburg impedance)

3.2. Influence of the treatment in inhibitor solutions on the electrode impedance

Figure 1 shows the impedance spectrum of one of the pyrite electrodes after the treatment in D2EHP solution. One may see that conditioning in the D2EHP solution did not change the shape of the spectrum but only the diameter of the semicircle which means that the mechanism of the electrode reaction did not change. In the case presented in Fig.1 R_T increased more than twice. Significant decrease in the C_{EDL} was

observed too. Similar behavior was observed in the case of other investigated compounds and other electrodes. The coverage of the electrode by adsorbed layer was estimated both from formula (6) and formula (8). Those data are showed in Figs 2. It must be stated that due to the simplifications made at the derivation of the mentioned formulas those data are very approximate and may be considered only for the sake of comparison. One may see that all four considered electrodes showed similar behavior. The highest decrease in the capacitance and the highest increase in charge transfer resistance was observed in the case of MBT.
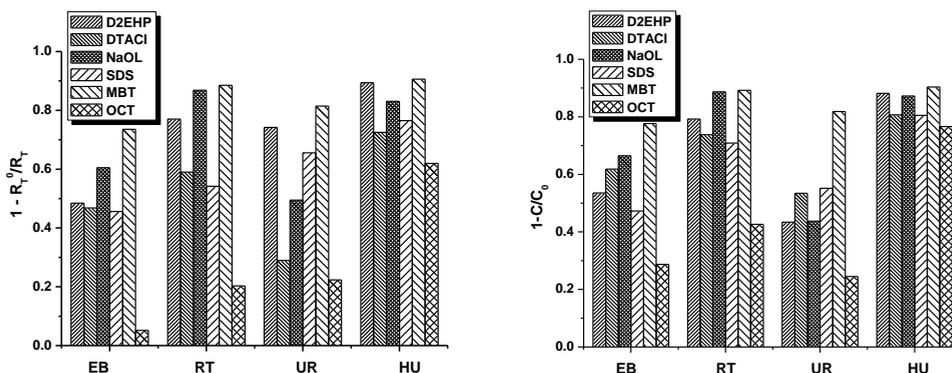
Fig. 2. Surface coverage of pyrite electrodes after 30 min of conditioning in different surfactants, estimated from impedance measurements: left from charge transfer resistance data (formula 8), right from electrical double layer capacitance data (formula 6)

Both D2EHP and NaOL showed similar (but slightly lower than MBT) value of coverage. Note that during the conditioning in a surfactant solution not only adsorption but also oxidation of the surface may occur. The lower is the adsorption the highest oxidation may be expected. Oxidation of pyrite in the mild conditions may lead to appearance of elemental sulfur at the surface and hence to passivation. That effect would obscure the dependence of coverage on adsorption. There are some differences between the electrodes. Those differences reflects probably the differences in surface properties of the pyrite sample. Note, that the biggest differences were obtained for the case of n-octanol which is expected not to adsorb strongly. Oxidation rate depends on the surface properties of the sulfide (impurities, structure faults, non-stoichiometry) and, contrary to charge transfer resistance of the reaction (4), may change from sample to sample. An example of such differences may be seen in Fig. 3, where the degree of oxidation of three different pyrites, after 4 days in air is compared from the XPS data. As can be seen, the differences in the degree of oxidation, expressed as the intensity of the XPS band which may be ascribed to oxidized iron (Fe^{3+}) and oxidized sulfur (SO_4^{2-}) are very high. Very high differences between pyrites of different origin in the corrosion rate was observed by Chmielewski and Nowak (1992).
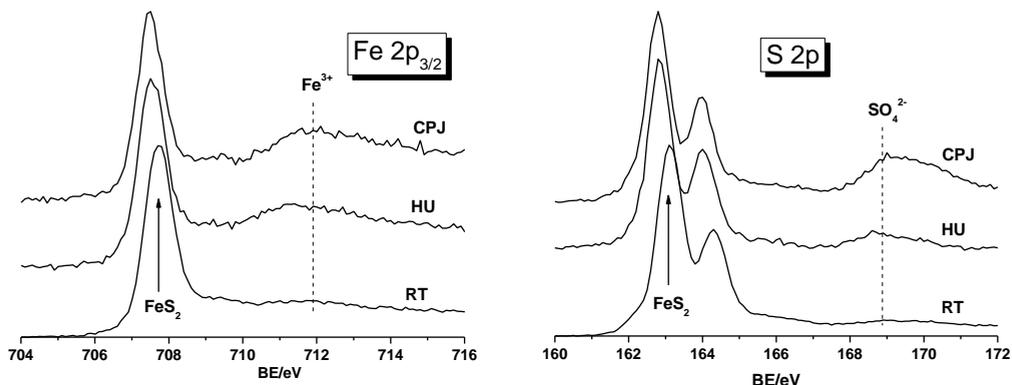
Fig. 3. XPS spectra of three different pyrites: HU, RT and coal pyrite from the Jastrzebie coal mine in Poland (CPJ) after 4 days of the oxidation in air. Surface of the samples was scraped with a steal blade before oxidation

4. Conclusions

Impedance measurements may be conveniently used for the estimation of the adsorption of surfactants at the surface of pyrite. The charge transfer resistance for the reaction $Fe^{3+} + e^- = Fe^{2+}$ as well as the electrical double layer capacitance (measured in the same measurement) do not depend on the origin of pyrite sample (providing that the resistivity of the pyrite sample is low), so this values may give the information on the degree of surface coverage. The highest adsorption was observed for 2-mercaptobenzothiazole, slightly lower, but still high for sodium oleate and bis(2-etylhexyl) phosphate. Those compounds might be used as the inhibitors to suppress the oxidation of pyrite. Note, that during hydrothermal oxidation of metal sulfides in nature the oxidizing agent is usually Fe^{3+} ion. So one of the conjugate reactions which participate in the process of the corrosion of a metal sulfide is just the above mentioned reaction. Surface of pyrite in the solutions containing Fe^{3+} ions is covered by the surface iron(III) hydroxide, which may be inferred from the high value of electrical double layer capacitance.

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