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Controlled adsorption at the surface of copper sulfide minerals – a way to abate the problem of environment contamination by the copper sulfide oxidation products?

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Abstract. Electrochemical impedance spectroscopy was used to study the adsorption of several surface active substances at the surface of non-stoichiometric copper(I) sulfide. Simultaneously the influence of the treatment of the copper sulfide by the solution of those surface active substances on the leaching rate of the sulfide in oxygenated sulfuric acid solution was investigated and correlated with the type of adsorptive bond formed between the sulfide surface and adsorbed molecules. Both chemisorption and surface precipitation may lead to the formation of a strongly bound product that prevents the dissolution of a mineral. Contrary, physical adsorption is too week to protect the surface from the attack of aggressive medium.

keywords: copper sulfides, adsorption on minerals, corrosion of minerals, prevention of mineral corrosion

1. Introduction

Almost all metals form metal sulfides that appear in the nature as sulfide minerals (Jellinek, 1968, Vaughan and Craig, 1978) and for almost all economically important metals (except iron and aluminum) sulfide minerals are the main ore-forming minerals. Metal sulfides form large ore bodies but they also can accompany other, non-sulfide minerals. Large quantities of pyrite (and other sulfides in much lower concentration) appear in coal (Twardowska et al, 1978). In the case of many metals mining of an ore of the metal concentration much below 1% is still profitable. So, metallurgical industry produces large quantities of wastes containing metal sulfides. For example the Polish copper industry, during fifty years of its activity, left on the depository places approximately 600 million tons of flotation wastes, occupying for that purpose 2300 hectares of ground (Łuszczkiewicz, 2000). So, mining creates a big thread to the environment which led to the appearance of a new field of mineralogy – environmental mineralogy (Vaughan and Wogelius, 2000).

The solubility of metal sulfides is very low. However, when subjected to the attack of an oxidative agent (molecular oxygen, ferric ions) they oxidize to better soluble compounds – oxides, sulfates. So, the presence of sulfides in an ore may cause liberation of the metal ions to the environment at all stages of the ore processing. The wastes from the non-ferrous metal industry are especially dangerous (Helios-Rybicka, 1996, Jambor et al., 2000). The most abundant sulfide mineral is pyrite. Oxidation of pyrite liberates iron species and sulfuric acid, causing so-called acid mine drainage (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. The other reason of the environment acidification which can also lead to the liberation of metal ions is so called acid rain caused by the emission of aggressive gases (SO_2, nitrogen oxides) to the atmosphere.

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. Many papers concerning the possible prevention of pyrite oxidation by application of inhibitors appeared in the literature. Huang and Evangelou (1994) applied soluble phosphates for that purpose, Belzile et al. (1997) showed the applicability of several natural compounds (humic acids for example) in pyrite oxidation inhibition, 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. 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.

It is generally believed, that inhibitors act on metals by forming protective overlayers which decreases the rate of metal dissolution as well as the reduction of oxidizing agents (Lipkowski, 1992). Inhibitors may be attached to the surface of minerals by physical adsorption, chemisorption or surface precipitation. In the present paper authors attempted to test which type of sorption would be most effective in the creation of a good protective layer at the mineral surface, preventing the mineral weathering. Synthetic non-stoichiometric copper (I) sulfide of the composition $Cu_{1.87}S$ was chosen as a model mineral. Using synthetic minerals offers the privilege that large samples of perfectly uniform composition may be prepared. Non-stoichiometric copper (I) sulfide is a very good electrical conductor – its electrical conductivity is comparable to metals (Shuey, 1975). That enabled the application of the electrochemical methods in the investigations. Measurement of the electrical double layer (EDL) capacitance is one of the main methods to study the adsorption of inhibitors at the metal surfaces. The other reason that we used non-stoichiometric copper (I) sulfide as the model mineral is our interest in copper sulfides. Contrary to most world copper ore deposits, where the main copper mineral is chalcopyrite, in Polish copper ores the main copper-bearing constituents are copper sulfides (Large et al., 1995). The synthetic mineral we used is close in composition to the copper sulfides present in Polish copper deposits. Copper sulfides oxidize easily, comparing to other minerals, especially when they form so called galvanic local cells with pyrite (Nowak et al., 1984). So, the rate of their oxidation may be measured relatively easily. No information was found in the literature on the possibility of application of inhibitors to prevent the oxidation of copper sulfides, except the preliminary communications of the present author and coworker (Nowak and Gucwa, 2008, Nowak, 2010).

2. Experimental

Copper sulfide of the composition $Cu_{1.87}S$ was synthesized from high purity copper and sulfur. After synthesis copper sulfide was melted and cast in the form of a grand lump. According to the results of diffraction analysis that sulfide was the mixture of djurleite and low digenite. Part of it was ground and sieved into fractions, part was used to make the electrodes for electrochemical experiments. Electrodes were made from the sulfide by fixing a piece of sulfide in a glass tube with epoxy resin. Electrical contact was made with the use of conducting silver glue. Sieved fraction of the particle diameter of 10 – 15 μm was used in the leaching experiments. More details on the synthesis and the properties of the investigated sulfide as well as preparation of electrodes may be found in our previous publication (Nowak and Pomianowski, 1989). All measurements were performed at the temperature of 25 ^{o}C, More information on the details of the experiments may be found in our previous communications (Nowak and Gucwa, 2008, Nowak, 2010).

Several different possible inhibitors were tested: sodium oleate (NaOL), sodium dodecylsulfate (SDS), dodecyltrimethylammonium chloride (CTACl), N-dodecylpyridinium chloride (NDPCl), n-octanol (n-Oct), potassium ethyl xanthate (EtXK), 2-mercaptobenzothiazole (MBT), (all p.a. purity grade)). Some of them served only as model compounds (n-octanol, for example), some other might become real inhibitors with practical application.

Two types of experiments were performed

(1) Adsorption of investigated compounds at the surface of a non-stoichiometric copper (I) sulfide electrode was investigated by measuring the capacitance of the EDL at the surface of the electrode using electrochemical impedance spectroscopy (EIS) (Nowak, 2010). The surface of the electrode was polished gently on emery papers (Struers) of the grade 500, 1000, 2400 and finally 4000, then it was introduced to the measuring cell containing the solution of the base electrolyte (0.5 mol dm^{-3} Na_2SO_4) and the investigated compound of the predetermined concentration. The measured capacitance was compared to the capacitance of a freshly polished electrode in pure base electrolyte,

(2) The effectiveness of the inhibiting action of investigated compounds was tested in leaching experiments. Weighted portion of the sulfide (usually 1 g) was conditioned in the solution of the inhibitor (30 minutes if not otherwise stated), washed with water then poured to the Erlenmeyer flask containing 50 ml of 0.05 mol dm^{-3} H_2SO_4 solution and vigorously stirred in controlled manner at the free access of air. After the predetermined period of time (usually 24 hours) the solid sample was separated from the solution and the concentration of copper in the solution determined by iodometric titration. Before the conditioning in the surfactant solution the oxidation products were removed from the surface by washing with 0.05 mol dm^{-3} H_2SO_4 solution, from which oxygen was removed by bubbling with argon. The amount of copper released was compared to the amount of copper released from the not-treated sample.

3. Results and discussion

Figure 1 presents the capacitance of the non-stoichiometric copper (I) sulfide electrode in the solutions of several compounds which are known to be surface active agents. The investigated potential range covered practically full potential range of non-stoichiometric copper (I) sulfide thermodynamic stability. Outside that potential range significant currents of either cathodic or anodic dissolution flew. Note that both cationic surfactants (dodecyltrimethylammonium chloride and N-dodecylpyridinium chloride) diminish strongly the capacitance of the EDL. That decrease is due to the adsorption of their molecules at the surface of non-stoichiometric copper (I) sulfide electrode. Adsorption of organic molecules at the surface causes the replacement of water molecules with the organic molecules which leads to significant decrease of the dielectric constant of the surface layer and, consequently, to the decrease of the capacitance of the molecular condenser formed at the surface. Both anionic surfactants did not cause any change in the capacitance of the EDL (within the limit of the accuracy of the measurement).

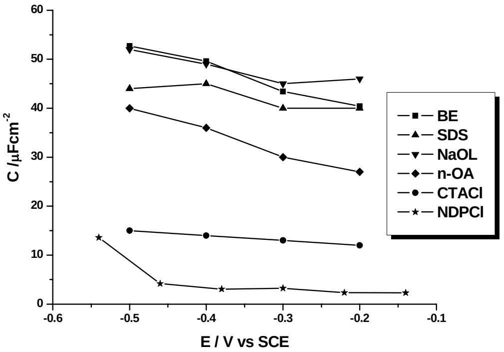

Fig. 1. The dependence of the capacitance of the EDL at the surface of non-stoichiometric copper (I) sulfide electrode in the solution of pure base electrolyte (0.5 mol dm^{-3} Na_2SO_4) (BE) and in the solutions containing, besides base electrolyte, surface active substances: sodium dodecylsulfate (SDS), sodium oleate (NaOL), n-octanol (n-OA), dodecyltrimethylammonium chloride (CTACl) or N-dodecylpyridinium chloride (NDPCl) – all at the concentration of 0.001 mol dm^{-3}

So, no adsorption of those substances at the non-stoichiometric copper (I) sulfide surface has occurred. The nonionic surfactant (n-octanol) caused limited decrease in the capacitance of the EDL and the course of the dependence of capacitance on potential suggests that higher surface coverage occurred at the anodic limit of the investigated potential range.

All those observations may be explained assuming that the potential of zero charge of the electrode lays outside the investigated potential range, on its anodic side. Surfactants molecules adsorb mainly due to the electrostatic interactions. So, cationic surfactants adsorb strongly due to the attraction between the positively charged surfactant ions and negatively charged electrode surface, anionic surfactants do not adsorb due to the repulsion of negative surfactant ions and negatively charged electrode surface and non-ionic surfactant adsorbs better in the range of potentials closer to the potential of zero charge. All above described surfactants (except sodium oleate, see later) decreased the dissolution rate of non-stoichiometric copper (I) sulfide in a very limited manner (see Table 1). Evidently, the electrostatic, physical adsorption is not strong enough to create the protective layer at the surface of the sulfide.

Very strong adsorption was observed in the case of 2-mercaptobenzthiazole (Fig. 2). Similar behavior was observed in the case of potassium ethylxanthate (Nowak, 2010). Note that both compounds form negatively charged ions (anions) in the solution. Both compounds belong to so-called sulfhydryl compounds, strongly adsorbing at the surface of metal sulfides (Woods, 1996). Such compounds form a monolayer of chemisorbed radicals at the surface of a metal sulfide which is compact and impermeable. That monolayer protects the surface against the attack of corroding species effectively. Indeed, very significant decrease of the leaching rate in the case of both compounds was observed (see Table 1). However some desorption of xanthate from the surface was observed when xanthate-covered non-stoichiometric copper (I) sulfide sample was subjected to the desorption in strongly acidic environment. Potasium ethylxanthate is used as a flotation collector. So, one can expect that metal sulfides, present in the flotation wastes, should show relatively low leachability, when xanthate is used as a flotation collector.

A special case, worth to be specially described is sodium oleate. As may be inferred from Figure 1 this compound does not adsorb at the surface of non-stoichiometric copper (I) sulfide. However, when non-stoichiometric copper (I) sulfide was conditioned in the solution of sodium oleate at the free access of air significant decrease in the leaching rate in 0.05 mol dm^{-3} sulfuric acid was observed (Table 1).

Noticeable diminishing of the leaching rate was observed after 1 hour of treatment at so low concentration of sodium oleate as 10^{-6} mol dm^{-3}. Similar decrease of the leaching rate in perchloric acid solutions after treatment in sodium oleate at different conditions was observed in our previous work (Nowak and Gucwa, 2008). It was observed that prolongation of the conditioning leads to even more significant decrease in leaching rate and that the protecting layer, formed on the surface by conditioning in sodium oleate solutions is stable in acidic solutions. The influence of sodium oleate on the surface of non-stoichiometric copper (I) sulfide may be explained in a similar manner like in the case of phosphate influence on pyrite (Huang and Evangelou, 1994). During the oxidation of the non-stoichiometric copper (I) sulfide surface copper ions are liberated. Those ions react with oleate anions forming an overlayer of copper oleate which protects effectively the surface from the attack of the corrosive agents.

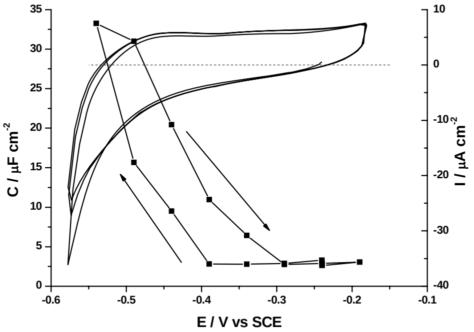

Fig. 2. Cyclic voltammogram (continuous line) of the $Cu_{1.87}S$ electrode in 0.5 mol dm^{-3} Na_2SO_4 solution containing 0.1 mmol dm^{-3} 2- mercaptobenzthiazole and capacitance of the same electrode measured consecutively at different potentials (full squares)

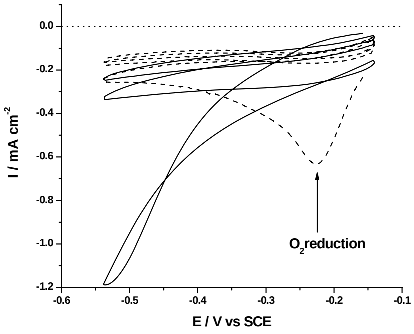

Fig. 3. Cyclic voltammograms in air-saturated 0.5 mol dm^{-3} Na_2SO_4 solution of a freshly polished $Cu_{1.87}S$ electrode (dashed line) and the electrode conditioned 24 hours in 0.001 mol dm^{-3} sodium oleate solution (solid line)

Table 1. The influence of the conditioning of non-stoichiometric copper (I) sulfide in the solutions of surfactants on the amount of copper (II) ions liberated during 24 hours of leaching in air-saturated 0.05 mol dm^{-3} H_2SO_4 solution.

Surfactant	-	SDS	NaOL	NDPCl	DTACl	MBT	EtXK
Concentration, mol sm^{-3}		0.001	0.0001	0.0001	0.0001	0.0001	0.0001
Leached copper, mmol/g	2.16	2.03	0.26	0.61	2.01	0.17	0.43

That may be inferred from Fig. 3, when the voltammogram of a $Cu_{1.87}S$ electrode, conditioned in sodium oleate solution is presented and compared to the voltammogram of a freshly polished electrode. It is to be seen that after the treatment in oleate solution the peak of oxygen reduction on sulfide electrode (marked with an arrow) disappeared, whereas strong cathodic current started to flow at the cathodic limit of the investigated potential range. That current may be ascribed to the reduction of some overlayer formed on the surface during the treatment in oleate solution at the free access of air (presumably copper II oleate). It is worthwhile to mention that similar compound, sodium stearate did not show any positive influence on the corrosion resistance of non-stoichiometric copper (I) sulfide (Nowak and Gucwa, 2008). That may be probably attributed to much lower solubility of sodium stearate in comparison to sodium oleate.

4. Conclusions

Copper sulfides differ from other minerals. Most of the copper sulfide minerals are either diamagnetics or semiconductors, with low free charge carriers concentrations and low capacitance of the space charge layer at the surface. Only very small charge may be stored on the solid side of the mineral/solution interface, so the surface charge is defined by the adsorption of ions and molecules at the surface. In the case of copper sulfides high capacitance of the space charge layer enables accumulation of charge in the surface layer on the solid side of the interface – due to this fact surface charge may be controlled by external polarization. So, the behavior of copper sulfides may be investigated by electrochemical methods. Also in natural conditions the charge of the surface of a copper sulfide mineral may by partly controlled by the charge stored in the space-charge layer formed at the solid side of the interface. That charge may originate from the redox reaction occurring between the sulfide and the oxidative/reductive agent present in the solution.

Physical, electrostatic adsorption does not protect the surface of non-stoichiometric copper (I) sulfide against corrosive attack of the oxidative environment. Either strong chemisorption, or the formation of an overlayer of precipitated salt which is resistive to the action of oxidizing agents is required to protect the surface of a sulfide mineral against oxidative dissolution. The best protective action against the , among the investigated compound, exerted sodium oleate, which does not adsorb at the surface but forms the protective layer by surface precipitation.

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