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EXCHANGE CURRENT DENSITY FOR THE REACTION OF EXCHANGE OF METAL IONS BETWEEN METAL SULFIDES AND SOLUTION AS THE MEASURE OF SUSCEPTIBILITY OF SULFIDE MINERALS TO OXIDATION

The exchange current densities (ECDs) for the reaction of the exchange of metal ions between the surface of several most important metal sulfides and the 0.1 mol/dm^3 solutions of the ions of the metal constituting the sulfide were measured. The measured ECDs correlate well with the known susceptibilities of sulfide minerals to oxidation.

1. INTRODUCTION

It is now commonly accepted (Buckley and Walker, 1988) that the first step in the aqueous oxidation of sulfide minerals is the transfer of metal ions from the crystal lattice of the mineral to the solution. For a sulfide with the ideal stoichiometry MeS_m, this reaction may be written as follows:

$$Me_{1+y}S_m \rightarrow Me_{1+y-x}S_m + xMe^{+n} + xne \qquad (1)$$
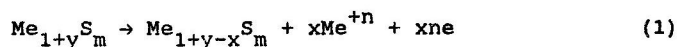
where the formula $Me_{1+y}S$ reflects the fact that sulfide may be originally non-stoichiometric (with either $y>0$ or $y<0$). When x becomes greater than y the formation of the layer of sulfur-rich (or metal-depleted) sulfide on the surface starts to grow. Such a layer of non-stoichiometric sulfide is a hydrophobic entity and its formation is considered as one of the possible reasons for the collectorless flotability of sulfide minerals (Heyes and Trahar, 1977).

In many cases the process of the sorption of a collector at the mineral surface may proceed in an analogous way:

$$Me_{1+y}S_m + nxX^- \rightarrow Me_{1+y-x}S_m + xMeX_n + xne \qquad (2)$$
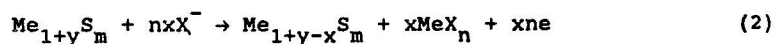
with the formation of the layer of non-stoichiometric sulfide, too. Note that reaction (2) is also the reaction of the transfer of metal ions from the crystal lattice of the mineral to the solution.

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Unfortunately, there is practically no quantitative data on the kinetics of the reaction (1) in the literature. The main difficulty in studying the kinetics of reaction (1) is the dependence of the reaction rate on the stoichiometry of the surface. When the reaction (1) proceeds from left to right, the surface becomes more and more depleted in metal and the reaction rate diminishes.

In the present work, an attempt was undertaken to estimate the rate of the reaction of transfer of metal ions from the crystal lattice of a sulfide mineral to the solution for the case of several most important sulfide minerals (galena, pyrite, non-stoichiometric chalcocite, chalcopyrite). To avoid the above mentioned difficulty the measurements were performed in the following way. The metal sulfide electrode was placed in the solution containing rather high concentration of ions of the metal constituting the sulfide. In such a case the reaction (1) and the reaction opposite to reaction (1) proceed at the equal rate, which may be expressed as the reaction:

$$Me_{lat}^{n+} \; <---> \; Me_{aq}^{n+} \tag{3}$$

The current flowing in both directions is called the exchange current. The electrode was then polarized with low-amplitude sinusoidal potential difference symmetrical versus the rest potential of the electrode and the current response was measured simultaneously. Such a method is frequently used in the case of metal electrodes for the measurements of the exchange current density (ECD) of electrochemical reactions at metal electrodes (Sluyters-Rehbach and Sluyters, 1970, Macdonald, 1987). In the case of sulfide electrodes it was used only by the present author (Nowak and Pomianowski, 1985).

The reaction rate may be easily calculated from the measured ECD, dividing ECD by Faraday constant and the number of electrons exchanged in the reaction. Of course, the measured current also contains the capacitive component (due to charging and discharging of the electrical double layer), and only a part of the imposed potential difference operates through the interface (due to the ohmic resistance of the solution, for example). So, the measurement at one frequency of sinusoidal current is not enough to calculate ECD. Usually a series of measurements at different frequencies is performed and the equivalent electrical circuit (EEC) is chosen on the basis of the analysis of the dependence of measured interfacial impedance on frequency.

The aim of this work was to test the applicability of the method to the estimation of the ECD for metal sulfides' electrodes in solutions of

respective metal ions and to check whether this value may be used to characterize the susceptibility of a metal sulfide to oxidation in aqueous environment.

2. EXPERIMENTAL

The following minerals were used in the experiments: pyrite from Huenzala deposits in Peru, chalcopyrite from Messina (Transvall) in South Africa and galena from Brushy Creek deposits (Missouri, USA), all supplied by Wards Natural Science Establishment (Rochester, New York), and non-stoichiometric synthetic chalcocite of the composition $Cu_{1.87}S$ synthesized in the author's laboratory (Nowak and Pomianowski, 1989). Mineral samples were cut with a diamond saw to the shape of a cylinder and embedded in a glass tube with epoxy resin. The electrical contact to the mineral was made with silver containing conducting epoxy resin. The working surface of the electrode was gently polished on emery paper grade 800 and next on filtering paper before introducing to the solution. The solutions were made from analytical reagent grade metal sulfates and sulfuric acid, except galena for which solution containing lead nitrate and sodium nitrate was used. In all cases the solutions containing 0.1 mol/dm^3 of metal ion and 1 mol/dm^3 of base electrolyte were used. The impedance spectra were measured with a system consisting of Frequency Response Analyzer 1250 and Electrochemical Interface 1286 (Schlumberger - Solartron) and a Hewlett-Packard computer. The three-electrode configuration with either saturated calomel electrode (SCE) or mercury - mercurous sulfate - 1 n H_2SO_4 electrode (MMSE) as a reference electrode was used. The EEC presented in Figure 1 was used to describe the frequency dependence of measured impedance. The equation describing the dependence of the EEC impedance on frequency was least-squares fitted to impedance data using the MINUIT program (CERN Computer Program Library). More information on the sample preparation and handling as well as data treatment may be found in previous works (Nowak and Pomianowski, 1989; Nowak, 1991; Chmielewski and Nowak, 1992).

3. RESULTS

Figure 2 presents an example of the fit of the equation, describing the impedance of the EEC from Figure 1, to experimental results in the case of pyrite electrode. A depressed semicircle, characteristic of a Faradaic reaction, changing at some frequency to a straight line, characteristic of diffusion (the so-called Warburg impedance)is clearly visible. From the diameter of the semicircle one may calculate
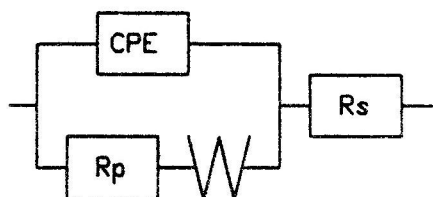
Figure 1. The equivalent electrical circuit used in the analysis of experimental data. Rp - resistivity of the Faradaic reaction, Rs - resistivity of the solution, W - diffusional (Warburg) impedance, CPE - constant phase element, used to describe the frequency-dependent double layer capacitance
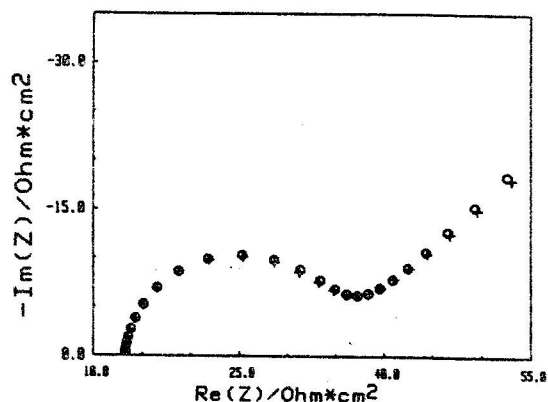
Figure 2. The imaginary part versus real part of the impedance of pyrite electrode in the 0.1 mol/dm^3 FeSO$_4$ solution, + - measured points, O - least squares fitted points

the ECD for the ion exchange reaction (reaction 3) - from the Warburg constant the diffusion coefficient may be calculated, too. The estimated values of the exchange current density for the investigated sulfides in 0.1 mol/dm^3 solutions of the respective metal ions are given in Table 1. One general comment should be made before the discussion of the results of experiments performed in particular systems. The exchange current density, like a rate constant of the chemical reaction, is a kinetic, not thermodynamic quantity and strongly depends on the state of the sample surface. So, the values presented should not be considered as "absolute" values, but rather as related to particular experimental conditions. Further, it must be stated that due to unavoidable irreproducibility of the procedure of the preparation of the sample surface some scatter of the results was observed. So, the values given in Table 1 are the mean values from at least 5 measurements.

3.1. Pyrite/Fe^{2+} system

There are no doubts that iron in pyrite occurs as divalent ion (Shuey, 1975). So, the reaction of the transfer of an iron ion from the crystal lattice of pyrite to the solution may be described by the reaction:

$$Fe^{2+}_{lat} \longleftrightarrow Fe^{2+}_{aq} \tag{4}$$

Table 1. The exchange current densities (ECD) for the reaction of the exchange of metal ions between the surface of a sulfide and the 0.1 mol/dm^3 solution of metal ions (1 mol/dm^3 base electrolyte)

Sulfide	Solution	Electrolyte	ECD (mA/cm^2)
Pyrite	$FeSO_4$	H_2SO_4	0.67
$Cu_{1.87}S$	$CuSO_4$	H_2SO_4	20.6
$CuFeS_2$	$FeSO_4$	H_2SO_4	$8.3 \cdot 10^{-3}$
$CuFeS_2$	$CuSO_4$	H_2SO_4	$1.1 \cdot 10^{-3}$
PbS	$Pb(NO_3)$	$NaNO_3$	$4.3 \cdot 10^{-3}$

Rather high ECD for that reaction was measured (see Table 1). The reproducibility of the measured ECD was quite good (keeping in mind the above expressed remarks). In five independent measurements (the electrode surface repolished in each case) the following values of ECD were measured: 1.09, 0.41, 0.67, 0.63 and 0.57 mA/cm^2. Similar reproducibility was observed in the case of other sulfides investigated. Much better repeatability was observed for a series of measurements performed on the same electrode kept in the solution for some time. For example, three consecutive measurements performed after 10, 1010 and 2010 s after introduction of the electrode to the solution gave the ECD values of 1.09, 1.06 and 1.16 mA/cm^2, respectively. The constancy of the ECD value means that the pyrite electrode is stable in the Fe_{aq}^{2+} solution - neither oxidation nor reduction of the surface takes place.

3.2. Non-stoichiometric chalcocite/Cu^{2+} system

In all copper sulfides, copper occurs as monovalent, despite of the sulfide stoichiometry (Shuey, 1975). Unfortunately, the copper (I) salts are practically insoluble in water. It was shown (Nowak and Pomianowski, 1985) that the reaction:

$$Cu_{lat}^+ \longleftrightarrow Cu_{aq}^{2+} + e \qquad (5)$$

proceeds in two steps, with the Cu_{aq}^+ ion as an intermediate product. For a complex reaction, composed of two consecutive steps, the overall reaction rate must be lower than the rate of the slower step. So, at least the lower limit for the possible value of the reaction rate for the reaction

$$Cu_{lat}^+ \longleftrightarrow Cu_{aq}^+ \qquad (6)$$

may be estimated from the measurements of the ECD in the solution of Cu(II) salt. It is to be seen from Table 1 that the ECD for the reaction (5) is very high (much higher than the ECD for metallic copper in the same solution). For the reaction (6) ECD must be even higher.

3.3. Chalcopyrite/Fe^{2+} and chalcopyrite/Cu^{2+} systems

As in pyrite, the formal oxidation state of iron in chalcopyrite is +2. However, the ECD for chalcopyrite in the 0.1 mol/dm^3 Fe^{2+} ions solution is almost two orders of magnitudes lower than in the case of pyrite! Even lower ECD was observed in the case of chalcopyrite in copper (II) ions solution (see Table 1). Note, that this result is in good agreement with the observation that chalcopyrite in the initial steps of oxidation preferentially loses iron from the surface.

3.4. Galena/Pb^{2+} system

Also in this system the ECD was very low (see Table 1), as in the case of chalcopyrite. This system was the most difficult to study – the repeatability of the measurements was much lower than in the case of the other systems. It is not surprising because the diffusion coefficients of both sulfur and lead in lead sulfide at room temperature are known to be very low. So, any accidental, uncontrolled oxidation of the surface leads to significant changes in the surface stoichiometry, which, in turn, changes the rate of reaction 3 proceeding at the surface.

4. CONCLUSIONS

The most striking observation resulting from this work is the big difference between the ECDs measured for different sulfides. The highest measured ECD is more than four orders of magnitudes higher than the lowest one. The observed differences in ECD for the reaction of exchange of metal ions between the solution and the surface layer of sulfide correlate very well with the differences in their susceptibility to oxidation. Both chalcocite and pyrite are known to oxidize fast – both chalcopyrite and galena oxidize much slower. Of course, the measurement of ECD for reaction 3 exaggerates the differences – when the reaction (1) proceeds from left to right, the surface becomes more and more depleted in metal and this process is faster for the sulfide for which the ECD is higher. So, when the oxidation proceeds, the difference in oxidation rate should diminish. The other factor is the difference of

the oxidation of sulfidic sulfur - fast in the case of pyrite, extremely slow in the case of chalcocite.

REFERENCES

Buckley, A.N., and Walker, G.W., (1988), *Proceedings of the XVI Intern. Mineral Processing Congress*, Elsevier, Amsterdam, p. 589.

Chmielewski T., and Nowak P.,(1992), *Fizykochemiczne Problemy Mineralurgii*, 25, 59.

Heyes, G.W., Trahar W.J., (1987), *Int. J. Mineral Process.*, 1977, 4, 317

Macdonald J.R., Impedance Spectroscopy, New York,J. Wiley & Sons.Nowak

P., Pomianowski A., (1985), *Anal. Chem. Symp. Ser.* 22, 591.

Nowak P. Pomianowski A.,(1989), *Colloids and Surfaces*, 41, 15.

Nowak P.,(1991), *Fizykochemiczne Problemy Mineralurgii*, 24, 127.

Shuey R.T., (1975), *Semiconducting Ore Minerals*, Elsevier, New York.

Nowak P., (1993), Gęstość prądu wymiany reakcji wymiany jonów metalu pomiędzy siarczkiem metalu a roztworem jako miara podatności minerałów siarczkowych na utlenianie, *Fizykochemiczne Problemy Mineralurgii*, 27, 37-43   (English text)

Zmierzono gęstości prądu wymiany dla reakcji wymiany jonów metalu pomiędzy warstwą powierzchniową siarczku a 0,1 mol/dm^3 roztworem jonów metalu dla kilku najpopularniejszych siarczków metali. Wykazano istnienie zależności pomiędzy zmierzoną wartości prądu wymiany a podatnością siarczku na utlenianie.