

Redox reactions are widely used in the analysis of mineral raw materials. The direct electrochemical determination of mineral decomposition in the phase analysis of mineral raw materials has been investigated. Research in this direction is already taking place: the electroreduction of suspensions is being studied [1] and experimental data have been obtained on the dissolution of mineral powders in controlled current and potential electrolysis [2].

A study of the electrochemical properties of substances used as electrode materials is tied up with the need of obtaining a reproducible surface. This can be achieved by using a combined "substance-carbon" paste electrode which we have developed specially for analytical purposes.*

Adams [3, 4] has suggested the carbon paste electrode to study the polarographic behavior of substances in solutions. Kuwana and French [5] have used a paste containing the investigated substances in the electrooxidation of organic substances.

The combined carbon paste electrode contains various concentrations of the investigated substance which may be a metal, a salt, or a sulfide. Such an electrode has the properties of the substance present in the paste and works in the potential range of the carbon paste electrode. The oxidation or reduction currents of the substance depend on its concentration on the electrode surface and therefore also on its concentration in the paste [2, p. 105].

The paste indicator electrode was a Teflon rod 10 cm long, with a diameter of 1 cm. On one end it had a cavity 5 mm deep, with a diameter of 6 mm which was filled with the paste and the surface smoothed on filter paper. The paste was replaced after every curve taken. The carbon powder for the electrode was prepared from spectral carbon by grinding in a ball mill and calcining at 800°C. α -Bromonaphthalin was added as binder (0.5 ml for each gram of carbon). The mixture was thoroughly homogenized before use.

The reproducibility of the current measurements depends of the uniform distribution of components in the paste and of the treatment of the electrode surface. Small changes in the concentration of the binder already have an effect on the results obtained.

The filter paper used to treat the electrode surface absorbs α -bromonaphthalin. As a result the concentration of the substance on the electrode surface is increased. To avoid this the filter paper must be prewetted with α -bromonaphthalin; if this is not done the reproducibility of the results will be affected.

The particle size of the investigated substance affects the oxidation current. For a quantitative comparison of two substances it is essential to use samples of identical particle size distribution.

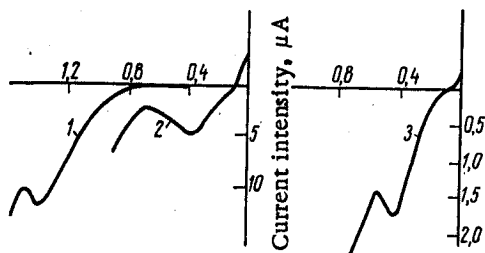


Fig. 1. Voltammetric curves taken on a combined sulfide paste electrode with various supporting electrolytes. 1) 0.1 M KCl, 2) 0.1 M Complexon III, 3) 0.1 M $K_4P_2O_7$.

The polarographic study of electrooxidation of galenite and sphalerite was carried out on monomineral fractions ground to 0.1 mm. All reagents used in this work were of chemical purity grade. The polarograms were obtained on an SGM-8 "Geologorazvedka" polarograph, the potential scanning rate was 0.3 V/min. The cell was thermostated at 25°C and a mercurous iodide electrode was used as the reference electrode ($E = +0.02$ V).

The electrooxidation of the sulfide of a divalent cation generally represents a multistage oxidation of sulfur to

* V. G. Barikov and O. A. Songina, Author's Certificate No. 191209, Byull. Izobr. i Tov. Zn., No. 3 (1967). See also [2, p. 105], paper of V. G. Barikov and O. A. Songina.

TABLE 1. Initial Oxidation Potentials (in V) of Sphalerite, Galenite, and Covellite with Corresponding Supporting Electrolytes

Supp. electr., 0.1 M solns.	ZnS	PdS	CuS
KNO ₃	+0,8	—	+0,4
KCl	+0,8	+0,4	+0,4
NaOH	+0,1	+0,1	0,0
NH ₄ OH	+1,0	+0,3	+0,1
K ₂ C ₂ O ₄	+1,0	+0,2	—
K ₂ CO ₃	+0,2	+0,2	—
Na ₂ HPO ₄	+0,15	+0,4	—
(NH ₄) ₂ MoO ₄	—	+0,2	—
Na ₂ WO ₄	+0,15	+0,3	—
NaF, pH 4—5	+0,6	+0,6	—
NaF, pH-7	+1,0	+0,6	—
K ₄ P ₂ O ₇	+0,1	+0,2	—
Complexon III	+0,15	—	+0,1

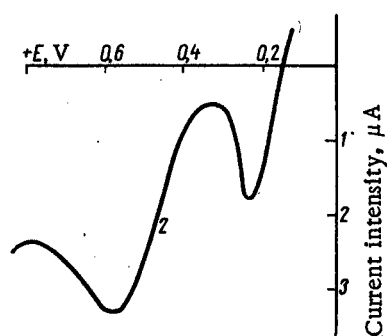


Fig. 3. Voltammetric oxidation curve of a mixture of zinc and lead sulfides (sphalerite and galenite) on the surface of the carbon paste electrode.

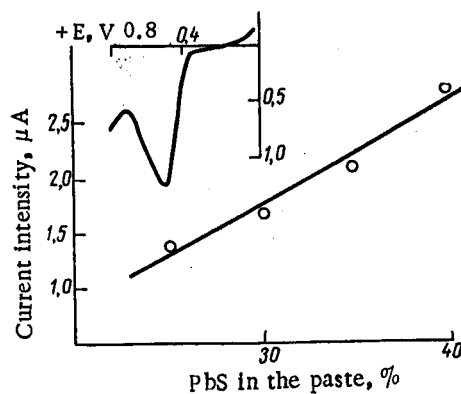


Fig. 2. Peak current of galenite oxidation on the surface of the paste electrode as a function of galenite concentration in the paste.

sulfate which goes through the formation of elemental sulfur and a series of intermediate products. Evidently in the first oxidation stage $\text{MeS} \rightarrow \text{Me}^{2+} + \text{S}^0$ the anion of the supporting electrolyte can affect the course of the anodic reaction by reacting with the sulfide cation which becomes available in the reaction. If, for example, the sulfide cation forms with the supporting electrolyte anion an insoluble compound or a stable complex, this must have an effect on the initial sulfide oxidation potential. The behavior of the supporting electrolyte anion towards the liberated sulfide cation manifests itself on the course of the anodic reaction. The supporting electrolytes used in the polarographic study of sulfide paste electrodes were grouped as follows: 1) electrolytes whose anions formed with the sulfide cation well dissociated soluble compounds; 2) electrolytes which formed complexes with the sulfide cation; and 3) electrolytes whose anions formed with the sulfide cation poorly soluble or insoluble (in water) compounds.

The effect of anions on the polarographic sulfide oxidation curve is shown in Fig. 1 with zinc sulfide. The curve from the paste electrode surface showed a peak and is similar to anodic stripping polarograms [6]. However, in this case the substance is not completely dissolved from the electrode surface and the current drop is usually caused by surface passivation by products of the electrochemical and chemical reactions. Figure 1 shows that in the case of an easily soluble substance (curve 1), the peaks are broadened and shifted along the potential axis towards more positive values. When a very stable complex is formed (curve 2), the potential corresponding to the begin of dissolution is shifted to the negative side. In the formation of a precipitate, i.e., of a stable compound between the sulfide cation and the supporting electrolyte anion (curve 3) the dissolution peaks are sharper and the initial potential of the process is shifted towards negative values. In this case the peak is considerably smaller since the electrode is passivated when a poorly soluble compound is formed.

The same effect of the supporting electrolyte on the shape of the polarographic curves has been observed for all supporting electrolytes and sulfide electrodes investigated. The sulfide oxidation potential depends on the strength of the metal-sulfide bond in the crystal lattice and of the energy of the reaction between the liberated cation and the supporting electrolyte anion. The initial oxidation potentials of the sulfides studied with various supporting electrolytes are given in Table 1.

Since the potential and the position of the sulfide dissolution peak depend on the supporting electrolyte, the possibility is given to find a selective electrolyte for a given sulfide. Experiments have shown that a relationship exists between sulfide concentration in the paste and peak current on the polarogram. The polarogram of galenite oxidation and the curve showing the relationship between peak current and sulfide concentration in the paste are shown in Fig. 2. The curves were taken with 0.1 M ammonium oxalate as supporting electrolyte.

The behavior of a sulfide mixture in the paste electrode is very interesting: the polarography of a mixture of galenite and sphalerite gave either one common peak or two separate peaks, depending on electrolyte composition. For example, with potassium chloride as the supporting electrolyte galenite and sphalerite formed separate anodic peaks while with potassium pyrophosphate one common peak was obtained. With sodium fluoride as the supporting electrolyte and the solution at pH 7, or with ammonia as supporting electrolyte, one peak only was obtained, corresponding to the oxidation of galenite. The oxidation of sphalerite was not observed in these supporting electrolytes. Figure 3 shows the voltammetric curve of the simultaneous oxidation of a galenite and sphalerite mixture (1:1) with 0.1 M sodium hydrogen phosphate as the supporting electrolyte. The first peak represents the oxidation of zinc sulfide, the second peak the oxidation of lead sulfide. Thus, with a carbon paste electrode it is possible to carry out a qualitative and quantitative analysis of sulfide mixtures by selecting the appropriate supporting electrolyte.

LITERATURE CITED

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