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ON THE INFLUENCE OF THE SOLID STATE PROPERTIES AND TRANSPORT CONDITIONS IN SOLUTION ON THE CHEMICAL AND ELECTROCHEMICAL OXIDATION OF SEMICONDUCTING MINERALS

The solid state properties of semiconducting minerals and their influence on flotation and other hydrometallurgical processes are reviewed, with the special attention to copper sulphides and lead sulphide. The influence of the transport conditions in the solution on the kinetics of leaching processes is considered too.

1. Introduction

There is a wide class of mineral beneficiation processes in which the mineral surface is subjected to influence of aqueous solutions. During the contact of the solid phase with the solution the transfer of mass, electrical charge and energy in both direction may occur which induces the changes in the composition of both phases. Those changes may be inconsiderable, like in the case of physical adsorption of some flotation collectors at the mineral surface, or may lead to complete alteration of the whole volume of the mineral, like in the case of some leaching processes. That is schematically depicted in Fig.1.

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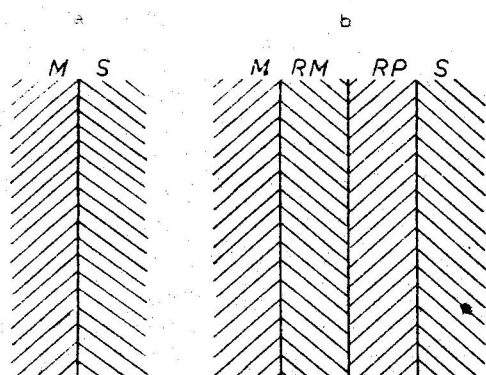


Fig.1 Schematic representation of the interface mineral - solution in the initial period of the process (a) and some time after the beginning (b).
M - mineral, S - solution,
RM - reacted mineral,
RP - reaction product

Depending on the diffusion coefficients of the constituents of the solid phase and its susceptibility to non-stoichiometry significant changes in the composition of the surface layer of the mineral may occur without the formation of an overlayer of the insoluble reaction product (for example leaching of chalcocite) or an overlayer of insoluble reaction product on the unchanged mineral surface may be formed (leaching of galena). In the initial period of the process, when the surface layer of the mineral is altered only slightly and no overlayer of reaction product is present the course of the process is governed mainly by the properties of the interface mineral-solution (Fig.1a). It must be kept in mind however, that like in the case of an adsorption isotherm, where the bulk concentration defines the surface concentration of the adsorbate, the bulk properties of the solid body influence greatly their surface properties. After some time the situation changes to the state depicted in Fig.1b. Transfer through any of the phase boundaries, or through any of the layers may retard the whole process. So, transport properties of all the phases present in the system must be taken into consideration together with the kinetics of the reactions at all phase boundaries.

2. Band structure of the solid body and its reactivity

2.1. Type of bonding in the solid body and non-stoichiometry.

The potential formation at the solid-liquid interface.

The type of bonding in a crystal depends mainly on the difference in electronegativities of the constituents (for the comprehensive discussion of the electronegativity scales, see Mullay (Mullay, 1987)).

When the difference in electronegativities is large the bonding is predominantly ionic. That class of substances forms usually simple crystallographic structures which depends mainly on the ratio of ionic radii. Depending on the mobility of ions forming crystal they are either insulators or ionic conductors. Due to the electroneutrality condition ionic crystals show usually no tendency to non-stoichiometry. When ionic crystal is brought into contact with the solution the potential formation between the solution and the solid proceeds through the exchange of ions between the surface of the solid and liquid phases (van Leeuwen, 1986). Electrodes made of ionic crystals are usually insensitive to redox couples present in solution and due to the pure ionic transport both in the bulk of the solid as well as at both interfaces (crystal-liquid and crystal-metal) form the "second kind" electrodes when the ions constituting the crystal are present in solution. The best example of such substances are silver halides. When the difference in electronegativities of the constituents of the crystal is small the bonding is predominantly covalent. In that case the considered substance is a semiconductor and usually shows some degree of non-stoichiometry. The potential difference at the boundary solid-liquid may be formed both by the exchange of ions as well as by the exchange of free charge carriers at the interface. For such a case the mineral electrode may attain the potential of a redox couple in solution, like a noble metal electrode. When the ions constituting the mineral are present in the solution the potential of the electrode may be calculated from the equation derived by Sato (Sato, 1966):

$$E_{M_1X_j} = E_{M_1X_j}^0 + RT/21j \ln [(a_{M^{j+}})^i (a_X)^j / (a_{X^{i-}})^j (a_{M^{j+}})^i] \quad (1)$$

$$E_{M_1X_j}^0 = (E_{M,M^{j+}}^0 + E_{X^{i-},X}^0)/2 \quad (2)$$

where $E_{M,M^{j+}}^0$ is the standard potential of the metal in the solution of its ions, $E_{X^{i-},X}^0$ is the standard potential of nonmetallic constituent of the binary compound in the solution of its ions and $(a_{M^{j+}})^i$, $(a_X)^j$, $(a_{X^{i-}})^j$ and $(a_{M^{j+}})^i$ are the activities of the metallic and nonmetallic constituents in the solid phase and of metal and nonmetal ions in the solution, respectively. For the four unknown in the brackets in equation (1) there are two additional equations connecting them.

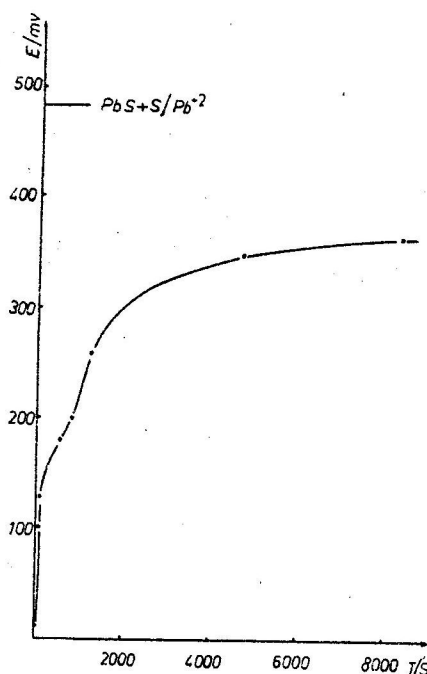
$$(a_{M^{j+}})^i (a_{X^{i-}})^j = K_{sol} \quad (3)$$

$$(a_M)_{M_1X_j}^i (a_X)_{M_1X_j}^j = \exp(-\Delta G^\circ/RT) \quad (4)$$

where K_{sol} is the solubility product of the substance M_1X_j in the solution and ΔG° is the standard free enthalpy of formation of the compound M_1X_j . So, depending on the conditions, equation 1 may be simplified. Equation 1 was derived under the assumption that the range of non-stoichiometry of the compound M_1X_j is so small, that the ΔG° of the substance does not depend on its composition. An example of treating the data of electrode potential measurements in the case of a compound of wide range of non-stoichiometry (djurleite) may be found in the work of Etienne (Etienne, 1972). More exhausting discussion of that problem may be found in the monograph of Vetter (Vetter, 1967). Equation 1 is valid for both ionic and electronic conductors. However in the case of an electronic conductor the electrical equilibrium between the binary compound and the current leads connecting the electrode with the voltmeter may be established by the exchange of electrons. In that case the phase boundary metal-binary compound does not influence the potential of the electrode and the electrode may attain any potential determined by equation 1 which lies between the values for a metal-rich (or pure metal) and nonmetal-rich (or pure nonmetal) electrode in the same solution. In the case of an ionic conductor only ions are allowed to pass the boundary metal-binary compound. So, reversible potential may be obtained only in the case when current leads are made from the metal constituting the binary compound and the binary compound is in equilibrium with the metal. In that case $(a_M)_{M_1X_j}$ is always 1. $(a_X)_{M_1X_j}$ is in accordance with equation (4) and the electrode attains always the potential of the metal-rich electrode. Direct potential measurements are possible only for solids of sufficient electrical conductivity, of course. Probably the sole system in the field of mineral chemistry exhibiting fully the behaviour predicted by equation (1) at room temperature is the system Cu-S (Nowak, 1985, Nowak, 1984, Bärzyk, 1988). The other systems usually deviate from the ideal behaviour due to slow attainment of equilibrium. An example of such behaviour is depicted in Figure 2. The lead sulphide electrode, saturated with lead to the lead-rich limit was introduced to the deoxidized solution of lead ions and potential of that electrode was measured in respect to metallic lead electrode. In the initial period of experiment the potential of the electrode was almost equal to the potential of lead electrode, as is predicted by equation (1). However after some time the potential of the electrode changes in the more anodic direction. That is due to the slow

oxidation of the surface which leads to the removal of lead atoms from the surface. Slow diffusion of lead and sulphur in the crystal lattice of PbS does not equilibrate the surface with the bulk of the electrode. So, the surface becomes more and more "S-rich" and, according to equation (1) its potential changes in anodic direction.

Fig. 2 The changes of the potential of the lead-rich lead sulphide electrode in the 0.01 mol dm⁻³ Pb(NO₃)₂ + 0.1 mol dm⁻³ NaNO₃ solution, measured versus metallic lead electrode. The lead sulphide electrode in the form of thin layer deposited on the surface of gold and equilibrated with the sulphur vapors of proper pressure to obtain metal-rich lead sulphide (unpublished authors' results).



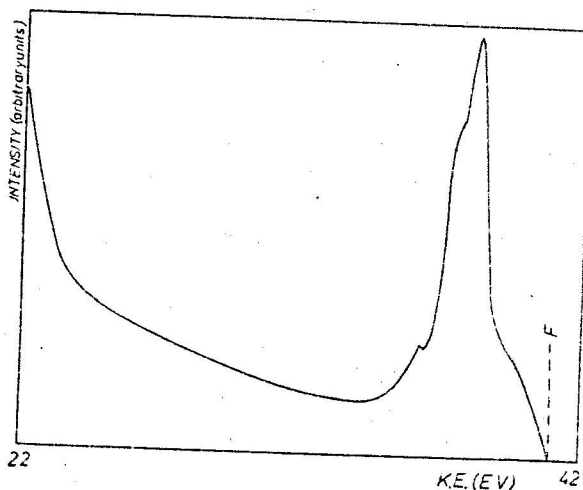
The bonding in minerals and its influence on the properties of minerals is widely discussed in several monographs (Shuey, 1975, Vaughan, 1978, and Berry, 1985). The monograph of Vetter (Vetter, 1967) and Rickert (Rickert, 1982) discuss the problems of potential formation between compound electrodes and ionic environments.

2.2. Band structure of the solid body and the reactions with redox couples in solution.

In gaseous molecule with predominantly covalent bonding a molecular orbital is formed from the outermost atomic orbitals of atoms constituting the molecule. In the solid body the situation is different. The atomic orbitals of the neighbouring atoms mix with each other forming the global bands extending through the whole crystal. For

conductivity depends mainly on the width of band gap (intrinsic semiconductors). The mean free energy of electrons (the electrochemical potential of electrons) is called the Fermi level and in the case discussed above it is located in the middle of the band gap. The location of bands of a compound on energy scale may be calculated using the methods of quantum chemistry (Berry, 1985). The structure of the

Fig. 4 UV - excited photoelectron spectrum of the valence band of non-stoichiometric cuprous sulphide. Note the high density of the electrons at the Fermi level (marked F in figure). Completely filled d band lies below the valence band (un-published authors' results).



bands in the crystal may be investigated using different spectroscopic methods (Berry, 1985) - an example is presented in Fig. 4. There are also simplified methods of calculation of the location of bands on the

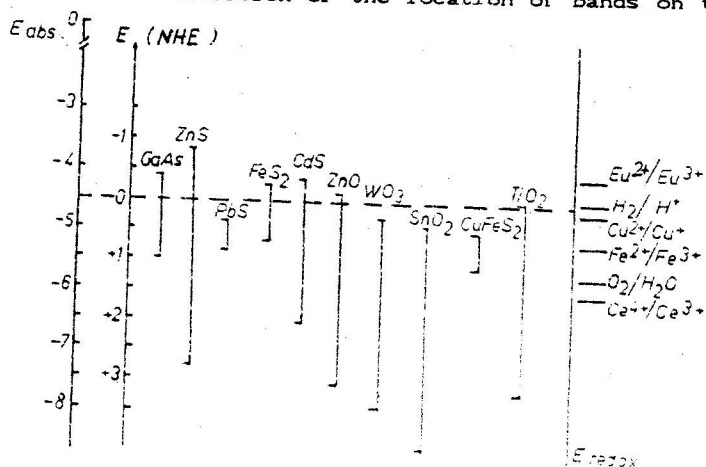
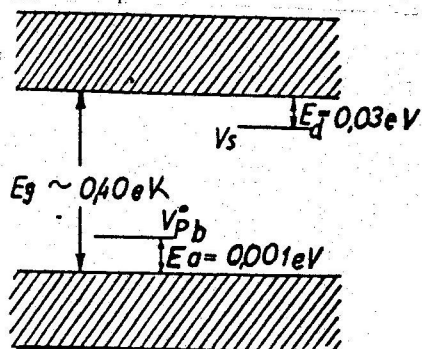


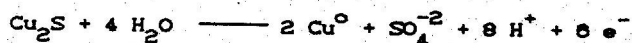
Fig. 5 Simplified band diagrams for some popular semiconducting minerals (Grundwell, 1988, Gerischer, 1978, Pleskov, 1985).

Fig. 6 Simplified band diagram for PbS. Note the very low ionization energies for both lead and sulphur vacancies in comparison with band gap - at room temperature every vacancy should be ionized giving one free charge carrier (Dereń, 1977).



2.3. Reactions of decomposition of semiconducting electrodes as redox processes. Eh - pH diagrams.

Since the appearance of the famous book of Pourbaix (Pourbaix, 1966) the Eh - pH diagrams are widely used in corrosion science and mineral processing to predict the reactions possible in a given system. However they must be used with a great care. At room temperature the reactions between minerals and solutions hardly ever goes to the limits determined by thermodynamic. For example chalcocite in the presence of water should oxidize according to the reaction



but such reaction is never observed - on the contrary choosing the proper conditions we may obtain the oxidized form of copper and elemental sulphur as the product of reactions.

Further restrictions must be taken into consideration in the case of semiconductors. Anodic and cathodic decomposition reactions, like any other redox reactions, may proceed only if the redox potential, calculated for those reactions from thermodynamic data, has proper position on the band diagram. The problem of stability of semiconductor electrodes against anodic and cathodic decomposition is widely described in the literature (Crundwell, 1988, Gerischer, 1968, Gerischer, 1978).

3. Rate equations for reactions of redox couples at the solid body surface.

Charge transfer at the surface of a solid body is governed by the electrical structure of the interface. The charge distribution at the interface is schematically depicted in Figure 7. The main difference between a metal and a semiconductor is the density of free charge carriers. In the case of metal the density of excess charge in surface layer is small in comparison with the density of free electrons (typically one excess electron per 10 conducting electrons). So, the

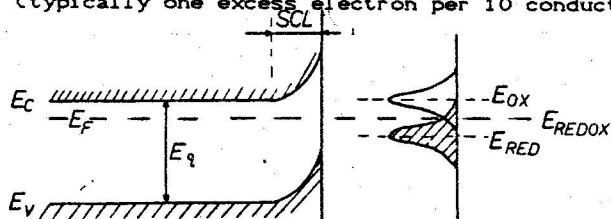


Fig. 7 Band bending at the surface of a semiconductor in contact with the solution (Morrison, 1988).

change is accumulated practically in the first atomic layer. In the case of a semiconductor the density of excess charge may exceed the density of free charge carriers in the bulk of semiconductor many orders of magnitude. So, due to the big difference in concentrations of the free charge carriers the excess charge diffuse into the bulk of the semiconductor and so called space charge layer is created. That space charge layer may be as thick as 1000 nm or more and the Coulombic interactions between the charge of the space charge layer and ions in the solution are much weaker than in the case of a metal. As a consequence the semiconductor electrodes are distinctly less sensitive to adsorption and the substantial part of the potential difference between the electrode and the solution operates through the space charge layer. In the extreme case one assumes that the potential difference through the Helmholtz layer is constants and independent on the potential of electrode, contrary to the metal electrodes where almost whole potential difference is in the Helmholtz layer. The kinetics of an electrode reaction at the surface of metallic electrode is described by Butler-Volmer equation (for 1-electron reaction considering the anodic current as positive).

$$i = i_0 [\exp(\alpha_a \eta F/RT) - \exp(-\alpha_c \eta F/RT)] \quad (5)$$

where i_0 is the exchange current, α_a and α_c - the transfer coefficients for anodic and cathodic reactions respectively and η is overpotential. For the semiconductor electrode the corresponding equation (for the valence band) has the form.

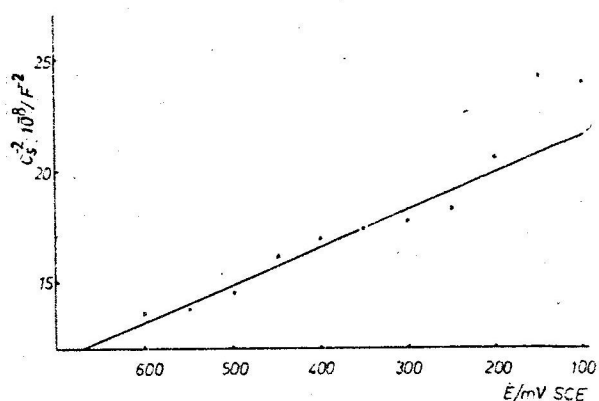
$$i = i_0 [\exp(\eta F/RT) - 1]$$

(8)

For the valence band only the anodic process is influenced by potential-for the conduction band potential influences only cathodic process. The reason of such behaviour is the infinitely large number of electrons in valence band (in comparison with the number of holes) and infinitely large number of empty electronic states in conduction band (in comparison with the number of electrons).

Valuable information about the electrical properties of the semiconductor-electrolyte interface may be obtained from impedance measurements. Such measurements for galena electrodes have been done by Schumann et al (Schumann, 1987). An example of so-called Mott-Schottky plot for a PbS electrode is presented in fig 8. The impedance characteristics of non-stoichiometric cuprous sulphide electrode may be found in the works of Nowak and Pomianowski (Nowak, 1987, Nowak, 1989).

Fig. 8 Mott-Schottky plot for PbS electrode in 0.08 mol dm⁻³ NaF solution. Note linear dependence except most anodic potential and the capacitance values much higher than in the case of wide band gap semiconductors (unpublished authors' results).



4. The concept of surface states. Adsorption at semiconductor surface.

The properties of a semiconductor depend to a great extent on the presence of structural defects, forming isolated electronic states. The surface is very vulnerable to the formation of structural defects. Even the surface itself may be treated as a structural defect (Tamm states). On the other hand the structural defects may migrate to and be collected at the surface. The phenomenon of segregation of foreign atoms at the surface is well documented in the literature. So, the concentration of the surface states may be very large. In such a case the surface states form surface level which may mediate in charge transfer between the proper redox state in the solution and electronic bands in the solid

body. When the concentration of surface states exceeds 10^{13} states \times cm $^{-2}$ (approximately 0.01 monolayer) the Fermi level becomes pinned to the surface band and the semiconductor electrode behaves like a metal one. There is a close connection between surface states and adsorption. The surface states usually play the role of adsorption sites. On the other hand any molecule adsorbed at the surface of a semiconductor electrode automatically gives a surface state. The presence of surface states may completely mask the "bulk" properties of a semiconducting mineral. For example one of the authors (Nowak, 1988) stated that the oxidation of the surface of lead sulphide changes the properties of the sample in such a manner as if it was a p-type sample, despite the initial conductivity type of the sample. It is obviously due to the surface states generated at the PbS surface during oxidation. Those surface states are the lead vacancies created at the surface in the reaction of the oxidation of the surface. The enrichment of the surface in sulphur during oxidation seems to be the phenomenon common to many sulphide minerals and is lastly widely discussed in the literature (Buckley, 1988).

S. Linear, planar and volume defects and their influence on the behaviour of minerals.

The influence of point defects on the behaviour of minerals has already been emphasized in preceding paragraphs. There are however other defects: linear (dislocations), planar (grains boundaries, cracks) and volume (pores, cavities, intrusions, amorphous regions in crystal) which influence also the behaviour of minerals. The solid body in equilibrium with environment contains always some concentration of structural defects. On the curve free energy of formation versus concentration of defects there is a minimum, and this minimum never occurs at the zero concentration of defects. When during the treatment of a mineral (grinding for example) the number of defects exceeding the equilibrium value is introduced the free enthalpy of formation of such a sample of mineral is higher (sometimes much higher) than the free enthalpy of formation of a sample being in equilibrium with environment. That difference in free enthalpy of formation is the additional driving force for any reaction in which the mineral participates and this phenomenon is exploited in the process of so-called mechanical activation. It was showed that intensive grinding accelerates the leaching of chalcopyrite (Tkacova, 1988) due to lower degree of crystallinity of the mineral. Not only the intensive grinding may be the reason of enhanced reactivity.

Goerlich (Goerlich, 1962) has showed that the solubility products of freshly precipitated metal sulphides are higher than in the case of the well crystallized, natural samples. That may be the reason of observed enhanced activity of freshly precipitated lead sulphide in the reactions of oxidation (Eadington, 1969) and adsorption of xanthate (Leppinen, 1986).

6. The role of the transport in the solution and solution composition in leaching processes.

The position of the redox Fermi level of a redox couple on the energy scale is determined by the equation (5). There is the logarithmic dependence of the potential on concentration and the potential shifts by $59/n$ mV (n is the number of electrons exchanged in reaction) on tenfold change in the activity ratio of Ox and Red forms of a given system. Because for a very low concentration the exchange current is very low, the possibilities of changing the redox potential by changing concentration are rather limited. The situation may be changed if the proper complexing agent is present in the solution. Depending on the stability constant of the complex formed the analytical concentration of the oxidizing (or reducing) agent may exceed the activity of the free (not complexed) form of this species by many tenths orders of magnitudes. In that case potential may be shifted even by several volts giving rise in the required changes in the energetic situation at the phase boundary and kinetics of the process. The examples of using complexing agents in leaching processes may be found in the literature (Tomasek, 1982). Any leaching process involves changes in the concentration of the oxidized and reduced forms of the redox couple used, in the leaching reaction. Also the products of dissolution of mineral must be transported away from the interfacial region. So, the transport to and from the surface is of a great importance in leaching processes.

The general equation describing the transport in the solution may be written in the form of generalized Fick's equation

$$\frac{dC_1}{dt} = D_1 \left(\frac{d^2 C_1}{dx^2} \right) - V \left(dC_1/dx \right) + S C_1 \cdot C_j \quad (7)$$

where the first term describes the changes of concentration due to diffusion, the second term the changes of concentration due to

convection and the third term represents the source term connected with the changes of concentration due to chemical reaction and depends not only on C_1 but also on the concentration of all the reacting substances. If the number of substances which must be considered is greater than one the equation (7) must be written separately for every substance -, but they are connected with each other through the source terms (in every equation the source term may have different form but the same concentrations appear in all equations). A set of differential equations is obtained which is usually solved numerically. An excellent review of numerical methods used in solution of such problems may be found in the work of Britz (Britz, 1981). The equation (7) is written in terms of ordinary derivatives and may be applied to the one-dimensional problems. In the case of more complex symmetry of the leaching system the problem must be treated in two or three dimensions and the ordinary derivatives in equation (7) must be replaced by partial derivatives. Further complications arise when the reactions proceeding at the surface are described by nonlinear equations (Butler-Volmer equation for example). In that case only numerical solution of the equation (7) is possible and the computations are usually rather complicated. Examples of such solutions may be found in the literature (Adamczyk, 1987, Wandzilak, 1988).

7. Conclusions.

Most of the "wet" mineral dressing processes have the common point - it is the moment of the first contact of a given mineral grain with the solution. The later course of the process is determined from that moment by the surface properties of the solid body which are closely related to its electronic structure. Depending on the system considered, the surface of mineral changes to some extent to the end of the process. In some processes, like flotation, the changes of the surface are usually limited to first few monolayers. In leaching processes the changes go much further and may involve many different steps. In addition to changes in the composition and structure of the starting state of the surface new reaction products may form and cover the surface (see Fig.1). In the latter case the solid state properties of the mineral itself become less and less important, contrary, the importance of the solid state properties of the overlayer grows up. At the same time the reagents and products of reactions must be transported to and from the surface. So, the conditions of transport in the solution play the very important role too, resulting in a multi-stage complex process.

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Streszczenie

Pomianowski, A., Nowak, P., 1989, Określenie wpływu parametrów fizykochemicznych fazy stałej oraz warunków transportu w roztworze na przebieg chemicznego i elektrochemicznego utleniania minerałów półprzewodnikowych, Fizykochemiczne Problemy Mineralurgii, 21: 79-95.

Przedstawiono przegląd literatury dotyczącej własności fizykochemicznych minerałów półprzewodnikowych i ich wpływu na zachowanie się minerałów półprzewodnikowych we flotacji i procesach hydrometalurgicznych, ze szczególnym uwzględnieniem prac dotyczących siarczków miedzi i siarczku ołowiu. Omówiono również wpływ warunków transportu w roztworze na kinetykę procesów ługowania.

СОДЕРЖАНИЕ

А.Помяновски, П.Новак, 1989. Определение влияния физикохимических параметров твердой фазы, а также условий транспорта в растворе на течение химического и электрохимического окисления полупроводниковых минералов. Физикохимические проблемы обогащения, 21; 79-95.

Представлен обзор литературы, касающейся физикохимических особенностей полупроводниковых минералов и влияния этих особенностей на поведение полупроводниковых минералов во флотации и в гидрометаллургических процессах, с особым вниманием к работам, касающимся сульфида свинца. Обсуждено также влияние условий транспорта в растворе на кинетику процессов выщелачивания.