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LEACHING AND PROPERTIES OF MECHANICALLY ACTIVATED CHALOCOPYRITE

The mechanical activation of chalcopyrite was carried out in a vibration mill in different surrounding media (water, methanol). The grinding significantly affects the properties of chalcopyrite (surface, degre of disorder of structure, specific magnetic susceptibility, and resistivity) as well as has influences the course of the oxidative leaching. The rate of reaction of chalcopyrite with hydrogen peroxide depends on the surface of ground particles and on number and quality of the defects generated by grinding.

Introduction

The leaching represents the key stage in the extraction scheme of ore processing. Its course may be affected by selection the kind of leaching agent or by convenient pretreatment of the solid phase. The thermal and mechanical activation are the most important methods of influencing the reactivity of the solid phase.

The thermal activation of sulphidic ores leads to transformation of the poorly soluble minerals into more soluble forms. That enables the better selectivity in transfer of the usable metal into solution, however it appears that some new problems concerning exploitation of the sulphur emissions arise.

The mechanical activation of ores is a physical process wich consists in deformation of the solid phase by the effect of mechanical forces, most frequently by grinding [1-3]. The mechanical activation of sulphidic ores allows for reduction of the temperature of their decomposition or brings about such a degre of deformation of solid that

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the thermal activation may be omitted. The Rebinder effect which manifestates in reduction of the strength of the solid phase due to action of surface active substances (active medium) plays the most significant role in preventing aggregation [4] and is important from the view-point of increased effectiveness of grinding.

Chalcopyrite belongs to the most exploited sulphidic copper ores. The intensification of the leaching of chalcopyrite by mechanical activation has been studied since 1973. The first results proved the favourable effect of vibrational grinding on the rate of leaching [5]. Our own investigation was focused at the influence of mechanical activation on structural sensitivity of chalcopyrite and kinetics of leaching of this mineral in iron (III) sulphate [6-9].

This study was aimed on obtaining information about the changes in surface ,structural, magnetic ,and electric properties of the chalcopyrite mechanically activated by grinding in air or in active methanolic medium and on correlating of these changes with the rate of the oxidizing leaching of chalcopyrite in hydrogen peroxide.

Experimental

The measurements were performed with a sample of chalcopyrite taken from the locality Slovinky (East Slovakia). The sample was crushed in a press and separated under binocular magnifier. The chemical analysis gave the following composition of the mineral : 28.07% Cu, 28.36% Fe, 31.62% S, 0.65% As, 7.47% SiO_2, and 3.80% insoluble rest.

The mechanical activation of samples (50 grams) was performed in a four-chamber vibrational mill (Mining Institute, Slovak Academy of Sciences , Kosice) with variable amplitude and speed of rotation at 75% filling of chamber with steel balls. The material was ground dry or in methanol (100 ml) for 5 to 60 minutes.

The specific surface S_A was determined from the adsorption isotherms of benzene vapour by the BET method [10].

The granulometric surface S_G was calculated from the data of granulometric analysis of particle distribution. The distribution of particles was measured on a sedimentation balance of the type Sartorius (FRG).

The magnetic susceptibility χ was measured with Kappabridge KLY-1 (Institute of Applied Geophysics, Brno).

The electric resistancee of samples R was measured with an apparatus designed at the Institute of Mining (Slovak Academy of Sciences, Kosice) [12]. This equipment allowed to work at a defined overpressure. The resistivity (ρ) was calculated from the measured values according to the equation:

$$R = \rho \frac{l}{S} \qquad (1)$$

where R, is the measured resistance (Ω), l is the length of sample (m), and S stands for the cross section of sample (m^2).

The kinetics of the reaction of chalcopyrite with hydrogen peroxide was investigated in a reactor of the half-through-flow type. The reaction proceeded under the following conditions: 2.5 grams of sample, 200 ml of 4% H_2O_2, Initial temperature of the reaction mixture 293 K, rate of stirring 8.3 revolutions per second. The leaching was accompanied by self-heating of the reaction mixture. The experimental results were processed by using a special form of the Avrami-Jerofejev equation [13].

$$\varepsilon = 1 - e^{-k_{AJ} t} \qquad (2)$$

where ε, k_{AJ} and t are the yield of copper in liquor, apparent rate constant (s^{-1}) and time of leaching (s).

The degre of disorder of the mechanically activated chalcopyrite F was calculated according to Petzak [11]:

$$F = \frac{Y_x}{Y_o}$$

where Y_x-halfwidth of mechanically activated chalcopyrite, Y_o-halfwidth of non-activated chalcopyrite.

The information about the line half-widths of chalcopyrite was obtained on the basis of X-ray diffractometry. The X-ray measurements were carried out with an instrument Dron 2.0 (USSR) by using the following regime : Fe - anode (U=30 kV, I = 12 mA), shift of counting tube $4.2\times10^{-3}s^{-1}$, chart drive $1.6\times10^{-5}ms^{-1}$, sensitivity 1000 impulses per second.

Results and Discusion

The results of ivestigations involving the changes in surface, structural, magnetic, and electric properties of chalcopyrite (1A-1D) and the rate constant of its leachnig with hydrogen peroxide (1E) as functions of the time of mechanical activation are represented in Fig.1. On the basis of the course of these quantities we may state that chalcopyrite is a mineral the properties and reactivity of which are

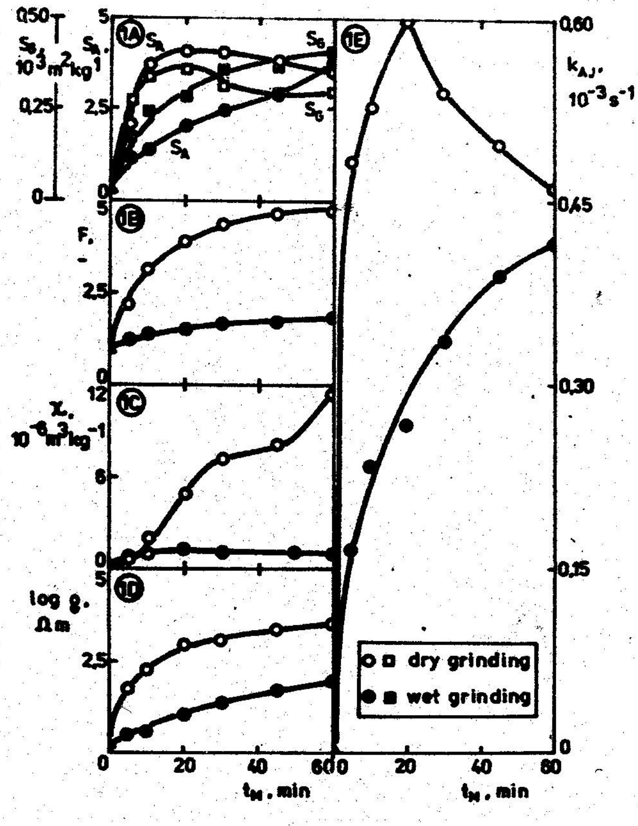

Fig.1. Variation of surface, structural, magnetic, and electric properties (1A-1D) and reactivity (1E) with the time of mechanical activation of chalcopyrite

1A-specific surface $S_A(m^2g^{-1})$ and granulometric surface $S_G(m^2g^{-1})$, 1B-degree of disorder of structure F, 1C-specific magnetic susceptibility $\chi\,(m^3kg^{-1})$, 1D-resistivity ϱ $(\Omega\,m)$, 1E-rate constant of the reaction of chalcopyrite with hydrogen peroxide $k_{AJ}(s^{-1})$

t_M-time of mechanical activation (min) rather sensitive to mechanical strees.

It is known from literature that intensive violation of the crystal structure of minerals is to be achieved by dry grinding while the grinding in liquid medium results in more intensive origination of new surfaces [14.15].

As for dry grinding, the specific surface S_A rapidly increases till the time of grinding equal to 20 minutes. The period corresponding to longer times of grinding is to be characterised by stagnation of the values of S_A. The values of granulometric surface S_G suggest that secondary aggregates start to arise in this region. Moist grinding indicates that methanol plays the part of active medium in the process of origination of new surfaces. In contrast to dry grinding no aggregates arise. The expected effect of more intensive formation of new surfaces when compared with dry grinding can be achieved as late as at t_M=60 minutes (dry grinding S_A = 4.10 m^2g^{-1}, wet grinding S_A = 4.25 m^2g^{-1}).

The dry grinding produces a higher degree of disoroder of the crystal structure of chalcopyrite than the grinding in methanol (Fig.1B). The ratio $F_{air}/F_{methanol}$ is the highest at t_M=20-30 minutes and slightly decreases afterwards. At higher times of grinding, the process of violation of the structure of $CuFeS_2$ is retarded by formation of secondary aggregates.

The dependence of specific magnetic susceptibility on the tme of grinding (Fig.1C) corresponds to the course of surfce characteristics of the mineral only in the region t_M< 20 minutes, i.e. where the amount of supplied energy is proportional to newly formed surfaces. Provided t_M>20 minutes, the value of $\sqrt{\chi}$ continues to increase for dry grinding and remains constant for less intesive wet grinding. We may assume that dry grinding produces high temperatures at the contact of grains and these temperatures are favourable for origination of Fe_2O_3 which is strongly magnetic. The existence of high local temperatures at the contact of grains owing to machanical stress has been experimentally evidenced [1-3].

The resistivity ρ incerases with the time of grinding (Fig.1D). This experimental observation is inconsistent with the results of the measurements performed with the monocrystals of sulphides subjected to static stress by pressure. In general, it is assumed that mechanical stress results in contarction of the forbidden energy gap and in shift towards elecric properties of metals [17]. In our case, we are up against polydisperse material.

We have fonud on the basis of anticipatory measurements that the resistivity of chalcopyrite increases with decreasing size of grains.

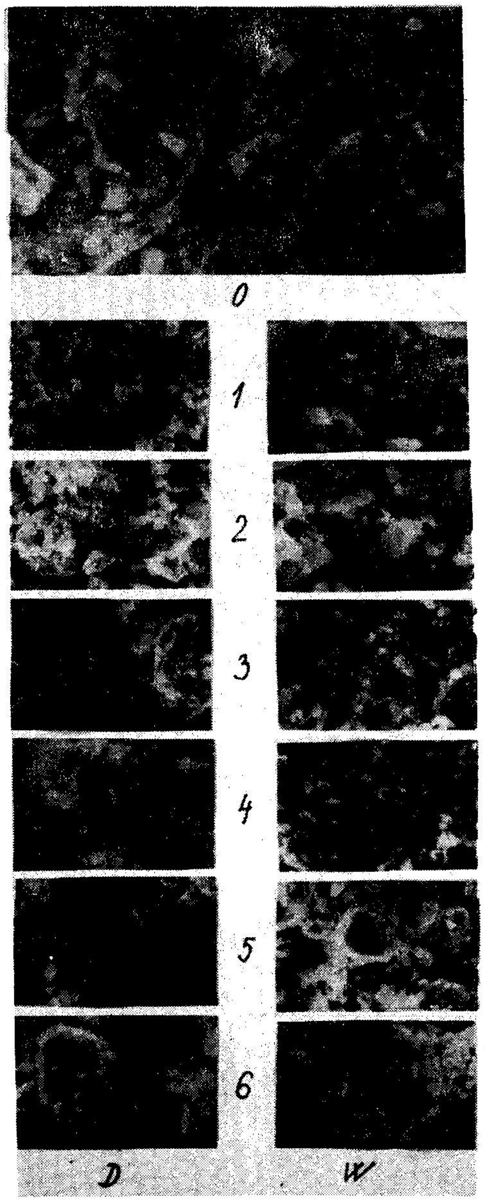

Fig.2. Changes in morphology of particles of the mechanically activated chalcopyrite

D-dry grinding, W-wet grinding

0-non activated $CuFeS_2$

Grinding time : 1-5 min, 2-10 min, 3-20 min, 4-30 min, 5-45 min, 6-60 min.

The existence of transition resistances at the contact of grains is sure to contribute to this effect. Moreover, it may be that the grinding of chalcopyrite is accompanied by some mechano-chemical reactions taking place on its suraface (e.g. desulphurization, oxidation) and the products of these reactions significantly influence the properties of the ground chalcopyrite. The differences in the values of specific susceptibility χ and resistivity ρ due to dry or wet grinding may also be attributed to these effects.

The dependence of the apparent rate constant k_{AJ} on the time of grinding (Fig.1E) indicates a significant influence of mechanical activation on the rate of leaching of chalcopyrite with a solution of hydrogen peroxide. For instance, the reactivity is increased 146 - or 214 times (for wet or dry grinding) with respect to the starting (non-activated) sample. The confrontation of proper ties with reactivity shows clearly (Fig.1) that the rate of the heterogeneous reaction betwen solid phase and liquid is evidently a function of the surface of dispersed particles. Morphology of dispersed particles is represented in Fig.2. As the rates of reactions in heterogeneous systems are often related to both the total surface area and the number and quality of defects, we suppose that the changes in structural, magnetic and electric properties are integral characteristics of these defects the quantitative diagnostics of which will be the topic of our further research.

Conclusions

1. Chalcopyrite $CuFeS_2$ is rather sensitive to mechanical stress resulted from dry and wet grinding.
2. Mechanical activation produces considerable changes in specific surface S_A, granulometric surface S_G, degree of disorder of structure F, specific magnetic susceptibility χ and resistivity ρ of the ground samples.
3. The rate of reaction of chalcopyrite with hydrogen peroxide depends on surface and on number and quality of defects.

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STRESZCZENIE

Balaz P., Briancin J., 1990. Ługowanie i własności mechaniczne aktywowanego chalkopirytu. Fizykochemiczne Problemy Mineralurgii, 22; 193-200.

Chalkopiryt rozdrabiano w młynie wibracyjnym na mokro: w wodzie i metanolu. Stwierdzono, że sposób rozdrabiania znacząco wpływa na takie własności chalkopirytu jak: powierzchnia właściwa, stopień zaburzenia struktury, podatność magnetyczna właściwa, opór właściwy. Sposób rozdrabiania wpływa także na przebieg ługowania utleniającego. Zauważono, że szybkość reakcji z nadtlenkiem wodoru jest zależna od powierzchni ziarn oraz rodzaju i defektów wywoływanych przez rozdrabianie