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INFLUENCE OF MECHANICAL ACTIVATION ON THE KINETICS OF NON FERROUS METAL SULPHIDES OXIDATION

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În lucrare sunt prezentate rezultatele cercetărilor experimentale a unui nou concept de oxidare în mediu apos (soluție de carbonat de sodiu) a concentratului sulfuros de cupru, în autoclavă sub presiune de aer, în domeniul de temperatură 100 – 135oC, timp de 5h, presiune parțială de aer 5 atm, în prezența de carbonat de sodiu în exces 30 % față de stoechiometricul necesar oxidării sulfurilor. Determinările s-au făcut în paralel pe concentrat nemăcinat şi concentrat activat mecanic. Pe baza rezultatelor obținute s-a studiat influența activării mecanice asupra cineticii oxidării concentratelor sulfuroase. Prin măcinarea avansată a concentratului de cupru, energia de activare scade de la 118,65 kJ·mol-1 la 25,75 kJ·mol-1.

The paper presents experimental research results on a new concept of oxidation in aqueous medium (solution of sodium carbonate) of copper sulphide concentrate in autoclave under air pressure in the temperature range 100 to 135 ^{o}C for 5 h, partial air pressure 5 atm in the presence of 30% excess of sodium carbonate more then stoichiometrical necessary for oxidation. Determinations were made in parallel on not-milled concentrate and mechanically activated concentrate. Based on the results obtained, the influence of mechanical activation on the kinetics of oxidation of sulphide concentrates was studied. By prolonged milling of copper concentrate, the activation energy decreases from 118.65 $kJ \cdot mol^{-1}$ to 25.75 $kJ \cdot mol^{-1}$.

Keywords: Mechanical activation, milling, pressure oxidation, alkaline media, metal sulphides

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1. Introduction

Currently approx. 70% of world production of copper is obtained by pyrometallurgical methods (melting, refining) which generates SO_2 and volatile dust, with high risk of environmental pollution [1].

Extraction of copper from sulphide concentrates by hydrometallurgical processes has increased tremendously due to less expensive and more environmentally friendly technological processing. Minimizing the emissions or their effects is the ideal direction proposed by the international community as "zero emissions, zero production impact". Methods of oxidation and solubility of copper in different environments were studied before: in concentrated sulfuric acid [2], chlorides [3] and more rarely in ammonia solution in terms of pressure and high temperature autoclave in the presence of oxygen. Effect of mechanical activation on the reactivity of sulphides has been studied for many years. Avvakumov, Kulebakin, and Tkáčová [4] have conducted experiments using arsenopyrite concentrates of Slovak origin (Pezinok).

After milling it was found that mechanical activation change the surface layers and bring defects in its structure. Surface layers have become heterogeneous in terms of morphology and energy. Surface chemical bonds have been broken and this has affected the reactivity of sulphides during leaching.

Mechanical activation, as a method of pretreatment of sulphide mineral, in addition to the effect of increasing the reactive surface has the effect of deformation of the crystalline structure of the mineral. These effects result in accelerated oxidation and leaching [5]. In the end, the increased reactivity of mechanically activated sulphide leads to a decrease of activation energy and accelerates the oxidation of sulphides present in the mineral. This paper concerns the theoretical and experimental study of a new technique of oxidation in alkaline medium of non-ferrous metal sulphides at moderate temperatures and pressures in the presence of air.

2. Materials and methods

2.1. Chemical and mineralogical composition of the investigated copper concentrate

For the experiments regarding the oxidation of sulphides in aqueous medium a copper concentrate from Flotația Baia de Arieş was used. The chemical composition (in wt%) is as follows: 25.0 Cu, 8.15 Zn, 7.16 Pb, 12.73 Fe, 3.50 Bi, 0.063 Sb, 0.052 As, 1.46 Mg, 4.10 Si, 0.31 Ca, 22.5 S.

Mineralogical studies by X-ray diffraction analysis (XRD) and microscopy showed the presence of copper in the concentrate as chalcopyrite - $CuFeS_2$ and bornite - Cu_5FeS_4, of zinc as sphalerite - ZnS, of lead as galena - PbS and of iron as pyrite - FeS_2.

2.2. Experiments of activation and oxidation

Particle size distribution of copper concentrate was about 60% below 44 μm and it was determined by granulometric analyzes with Laser Eye Tech Particle Size and Shape Analyzer.

Mechanical activation of the concentrate was carried out by prolonged grinding in a ball mill, type Attritor, with 3 mm diameter balls in wet media, for 30 minutes, with a ratio balls/concentrate equal to 14:1 and a ratio water/concentrate equal to 2:1.

A copper concentrate was obtained after milling with 100% of the particles below 5 μm, with an increase in specific surface from $0.118 m^2/g$ to $4.872 m^2/g$ and structural changes that positively influenced the reactivity of the material at oxidation.

Experiments of oxidation in aqueous medium (solution of sodium carbonate) were performed in autoclave with classical stirring system on 200 g samples of milled and not-milled concentrate with a ratio of L/S 15:1, at temperatures varying from 100 to $135^{o}C$ for 5h and partial pressure of 5 atm in the presence of air used as oxidizing agent, with an excess of sodium carbonate of 30% more than stoichiometrical necessary for oxidation. Samples were taken at different time intervals during the experiments. They were chemically analyzed by ICP, DCP and FAAS.

3. Results and Discussion

As presented in Fig. 1, an increase in the oxidation temperature results in lower sulfur content for the not-milled concentrate from 22.5% to 8.38% S. The same trend also applies for the milled concentrate, with a reduction from 22.5% to 1.29% S.

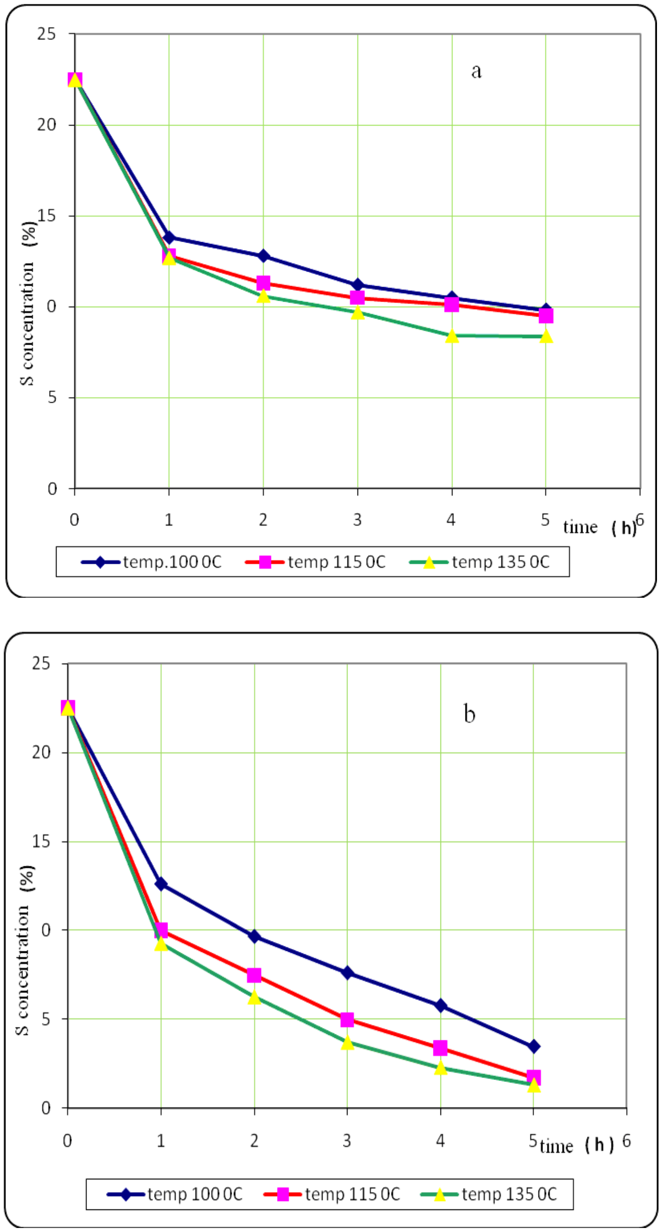

Fig. 1. Variation in time of S concentration of oxidized concentrate versus temperature;
a: not milled, b: milled

3.1. Kinetic study of the oxidation of metal sulphides from concentrate

Based on the results obtained, the influence of mechanical activation on the kinetics of oxidation of sulfide concentrates was studied [6].

To establish the kinetic equation of oxidation of sulphur from solid the following notations are valid:

r - Speed of reaction of the entire process of oxidation of S
c - Concentration of sulfur from concentrate at a given time
t - Time [min]
k - Reaction speed constant
T - Temperature [K]

Assumptions:

- Solid has spherical grains of the same diameter (average diameter is determined from particle size distribution measurements);
- Granules are not porous and the solution does not penetrate the capillaries within them;

The non-reacting-core kinetic model was chosen for kinetic studies, including the following steps:

a. Diffusion of reactants through the liquid phase to the surface of the particle - external diffusion stage

b. Diffusion of reactants through the layer of non-reacting solid surface - internal diffusion stage

c. Chemical reaction at the surface of the solid reactant - phase of kinetics of reaction.

The reaction of oxidation of sulphur in sulfide concentrates will always start in active centers, which are actually points of maximum deformation of the solid network.

Based on the non-reacting-core model the following can be determined: the speed of oxidation, speed of solubility, diffusion of the reactant through the fluid layer adhering on the solid surface, diffusion of reactants through the newly formed product layer and chemical reaction.

The degree of transformation as a function of time was experimentally determined for this purpose, and the values of functions α, $f(\alpha)$ and $g(\alpha)$ versus time were graphically represented, where:

- α is the degree of transformation or reaction degree for the process that is based on a chemical reaction that is limited in terms of kinetics of external diffusion,
- $f(\alpha) = 1-3(1-\alpha)2/3+2(1-\alpha)$, for internal diffusion stage,
- $g(\alpha) = 1-(1-\alpha)1/3$ for chemical kinetics stage.

The calculated values of α and the degree of reaction of the two functions, $f(\alpha)$ and $g(\alpha)$ at different time intervals are plotted in Fig. 2 (a, b, c, d, e and f).

From the analysis of experimental results it was determined that the rate determining stage of the process of oxidation of copper sulphides from the concentrate is described by internal diffusion, in which the layer of solid of reaction products reach the highest value and the kinetic curve corresponds to the function f(α).

The process can be accelerated by increasing the concentration of liquid reactant and by increasing the degree of turbulence (stirring speed)[7]

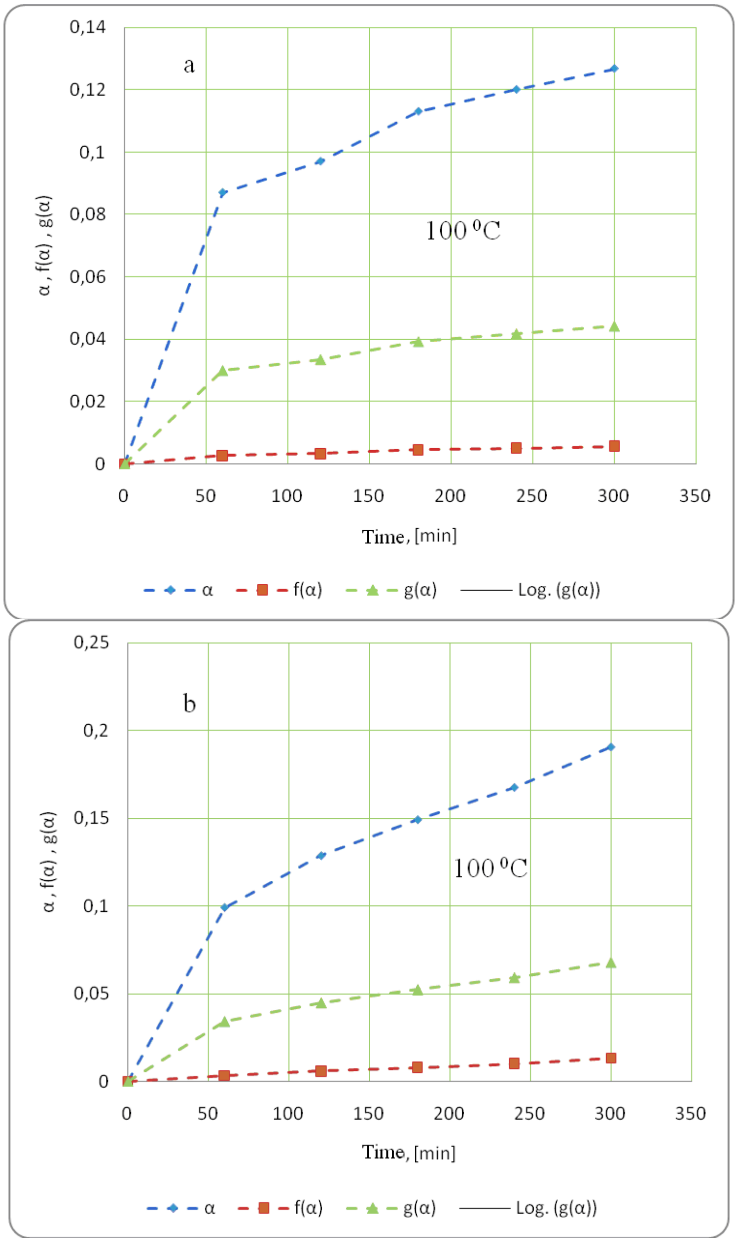

Fig. 2. Kinetic curves: a) not milled, b) milled

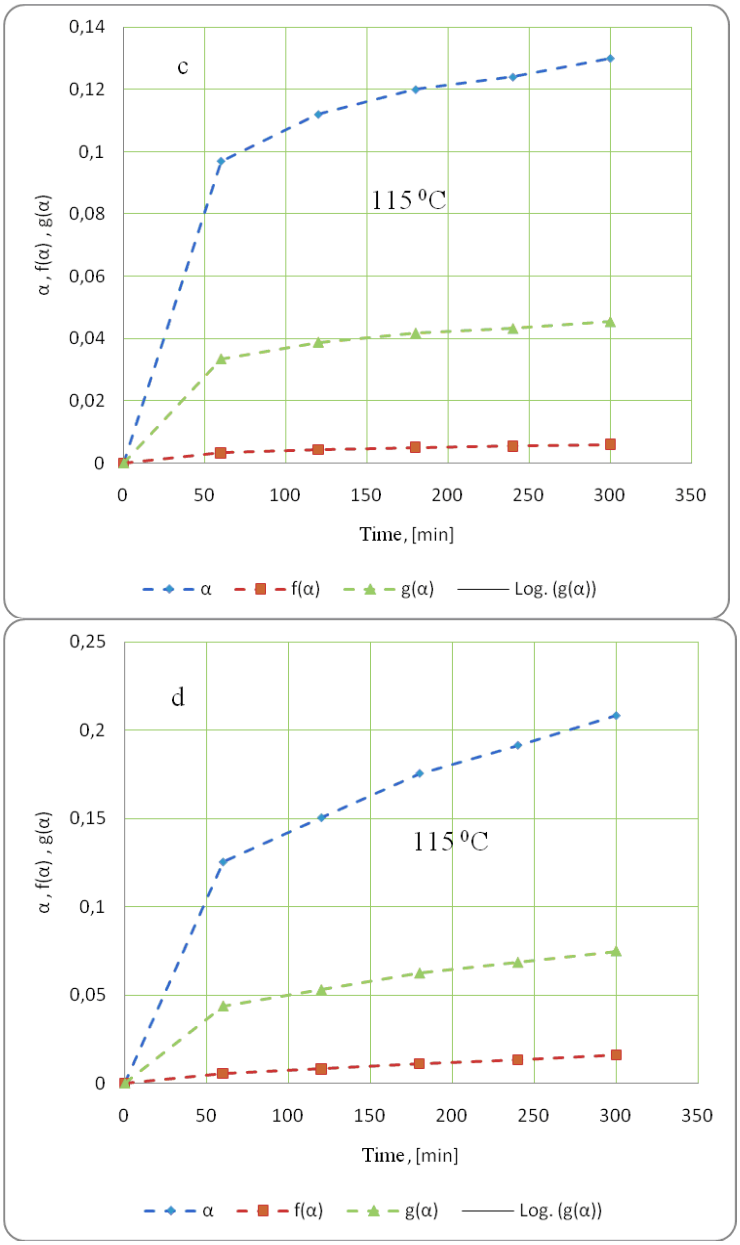

Fig. 2. Kinetic curves: c) not milled, d) milled

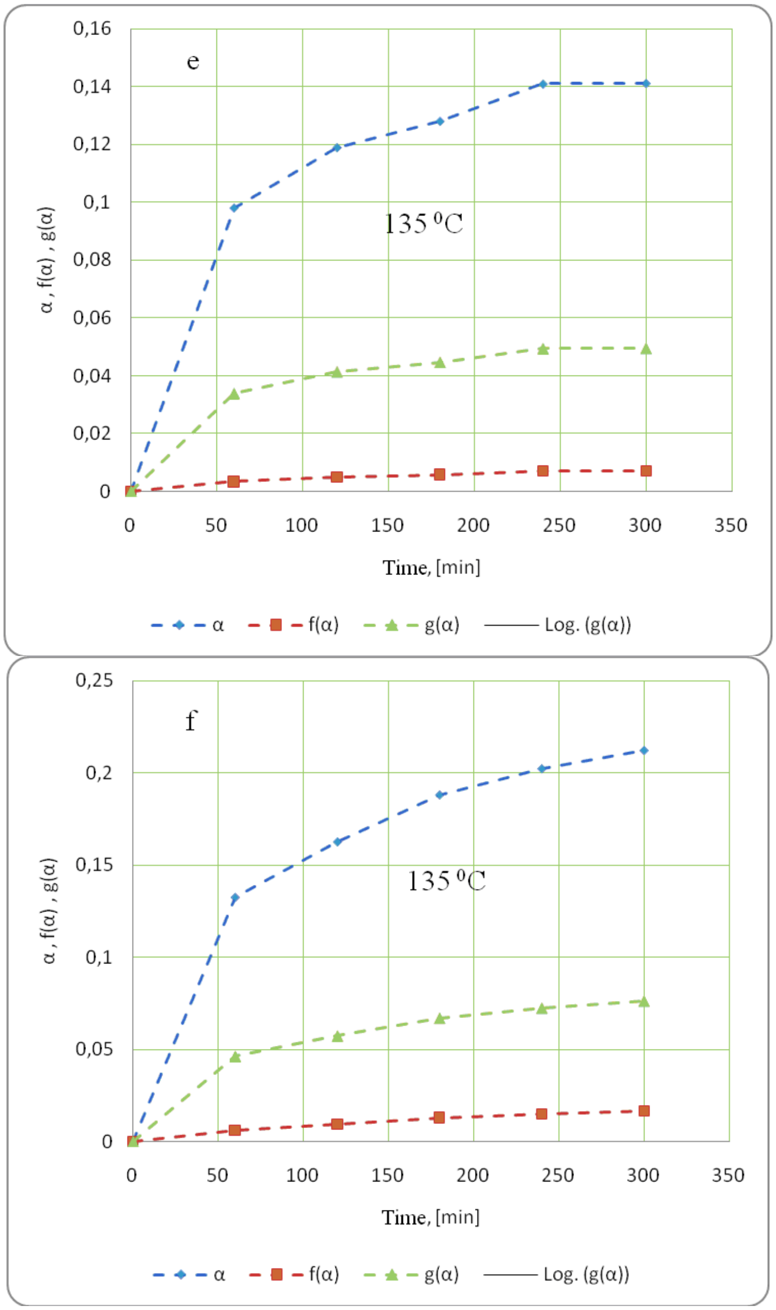

Fig. 2. Kinetic curves: e) not milled, f) milled

Activation energy value was calculated using the slope of the graphic curves log k function of 1/T, obtained experimentally at several temperatures for the milled and not-milled material.

Following values were determined for E_a after:

- 60 minute 0.87 kJ mol^{-1} for un-grinded material and 1.96 kJ mol^{-1} for the grinded material;
- 120 minute 19.44 kJ mol^{-1} for un-grinded material and 6.59 kJ mol^{-1} for the grinded material;
- 180 minute 22.30 kJ mol^{-1} for un-grinded material and 10.42 kJ mol^{-1} for the grinded material;
- 240 minute 37.86 kJ mol^{-1} for un-grinded material and 5.16 kJ mol^{-1} for the grinded material;
- 300 minute 118.65 kJ mol^{-1} for un-grinded material and 25.75 kJ mol^{-1} for the grinded material.

Activation energy variation is shown in Fig.3.

It can be observed that by prolonged grinding of copper concentrate, the activation energy decreases about 7 times, after 4 hours of oxidation of sulphides in the autoclave.

For the two materials tested, the un-grinded and grinded material, no changes were observed while increasing the reaction temperature. However, a significant difference between the values of speed of reaction of the two materials at the same temperature was observed. The speed of reaction after 5 h is doubled, even tripled.

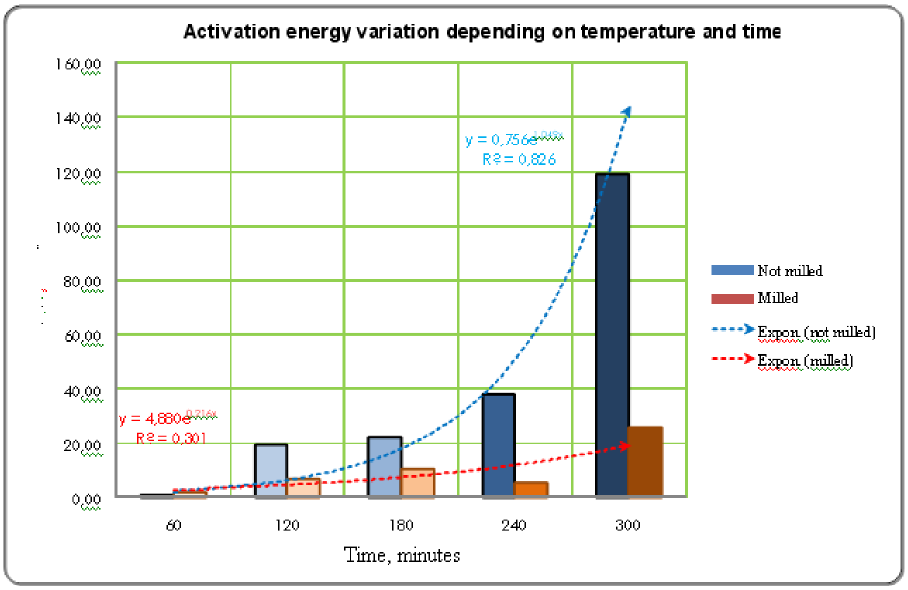

Fig. 3. Activation energy variation depending on temperature and time

4. Conclusions

The analysis of our experimental results found that the rate determining step of the process of oxidation of sulphides from copper concentrate is attributed to internal diffusion, in which the layer of solid reaction products reach the highest value and the kinetic curve corresponds to the function f(α). The process can be accelerated by increasing the concentration of liquid reactants, and by increasing the degree of turbulence (stirring speed).

In practical terms, however excessive reagent over the amount used (approx. 30% over the stoichiometrical necessary) is not recommended. It is recommended to modify the turbulence, by using other stirring systems with higher performances.

With mechanical activation, i.e. by prolonged milling of copper concentrate, the activation energy decreases to about 7 times, after 4 hours of oxidation of sulphides in the autoclave, leading to the possibility of reducing the time of the reaction with implications for productivity growth of the main equipment, i.e. autoclave.

Regarding the influence of temperature used for the experiments on the two materials tested, un-grinded and grinded material, no significant changes were observed by increasing the reaction temperature, but there are important differences between speed of reaction of the original material and the mechanically activated one at the same temperature. After 5 hours the reaction speed doubles or even triples for the grinded material, changes obtained due to the increase in the specific surface and the deformations that may occur in the mineral crystal network.

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