Physical and Chemical Characteristics of Material Containing Non-Ferrous Metals and Inorganic Aqueous Solutions

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Abstract**—** *Kinetic studies were conducted on the process of the dissolution of non-ferrous metals with the use of sulfur-containing material as a source of leaching agent - sodium thiosulfate. It is shown that with increasing concentrations of sodium hydroxide in solution in the range of 0.1 - 1.0 M, copper recovery is increased from 21.5 to 46.2 %.*

As the temperature increases from 25 to 45 ^{0}C, copper dissolution rate in the initial moment of the time increases, then over time this figure gradually decreases with decreasing the copper content in the initial product. The value of the reaction order is 0.39. The calculated value of the activation energy in the process of leaching copper is 12.01 kJ / mol, which suggests that the analyzed process is proceeds in the diffusion mode.

***Keywords—* complex and low-grade raw materials, the structure of condensed systems, structural-phase transitions, hydrometallurgy.**

I. INTRODUCTION

Based on the analysis of scientific literature, it has been shown that electrochemical dissolution of sulfur-containing minerals, usually and mainly performed in acidic electrolytes, because formed low-soluble compounds, in the first instance iron, are freely soluble in acids. However, the process of leaching of sulfur-containing minerals is also possible in alkaline electrolytes (leaching of refractory ores by cyanide method). There is lack of data on the theoretical foundations of electrochemical leaching processes in alkalinecondition. Especially, there is not enough data on technological application of combined electrochemical reactions converting metals to alkaline solutions. Therefore, studying of electrochemical processes involving various minerals containing sulfide as a source for the extraction of gold and other metals to alkaline solutions is relevant, since the use of toxic solvents in industrial scale is undesirable.

It has been shown that leaching (for example, Cu) accelerates with increasing current density and temperature. A special place in the studies of electrochemical processes is taken by the reactions which transfer metals to solutions having different chemical compositions, and use the electric current - electrochemical leaching. In general, these studies relate to the consideration of the chemical processes that take place under the influence of an electric current of different parameters and different hardware design. For example, alternating current is widely used in dissolution processes[1] and in the processes of metal deposition by electrochemical methods[2, 3]. It can be said that today the possibility of the effective application of an electric current of various parameters as a kind of "chemical agent" has been experimentally demonstrated. It also helps to shift the chemical equilibrium to the desired direction. It is noted that the application of alternating electrical current provides: transmission of energy to impurity atom, facilitates its transportation, increases the rate of diffusion in the crystal, provides a recrystallization of the agent, changes the valence of the impurity atoms; creates a magnetic moment, leading to changes in chemical bonding in solid materials [4].

The study of electrochemical processes involving minerals containing iron sulfides, copper and zinc as a source for the extraction of gold in alkaline electrolytes is relevant since the use of toxic solvents in industrial scale is undesirable. Gold extraction from sulphide ores involves a number of difficulties and possible only after complete degradation of sulfide minerals (pyrite, arsenopyrite, chalcopyrite, etc.), containing of fine gold particles[5, 6]. Sulfide minerals are chemically stable, their degradation is only possible in the presence of a strong oxidizing agent. According to the provisions of the basic theory of sulfide oxidation, the process takes place in the acidic environment, depending on the pH and Eh environments and occurs in the following sequence:

$$S^2 \rightarrow S^0 \rightarrow S_2O_3^{2-} \rightarrow S_xO_y^{2-} \rightarrow SO_4^{2-}$$

Stringent conditions are needed in order to extract noble metals from refractory ores by leaching (high pressure, the temperature, the use of concentrated acid solutions, cyanide-, rodanid- and other complexing agent) [7, 8].

II. METHODOLOGY

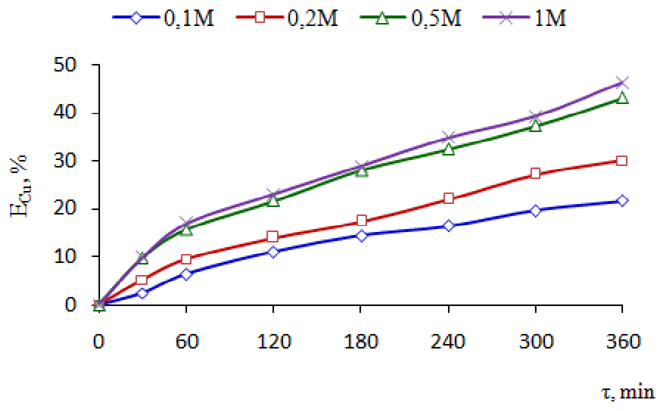
Experiments were conducted on conversion of metals in to the solution of the concentrate, which contained the following amounts of base metals%: Cu - 13,99, Fe - 28,21, Pb - 11,28, Zn - 4.33.

The effect of parameters of elektroleaching process on metal extraction was studied in the presence of carbon disulfide electrode at a current density i - 150 A / m^2, with stirring of 480 rev/min for 6 hours. The concentration of sodium hydroxide solution was 0.1-1.0M 200 ml, t - 25 °C. Sulphur-graphite electrode was used as cathode, and graphite electrode as anode. Metal concentrations were determined by atomic absorption spectrometry «contrAA 300". Parameters of electrochemical experiments were specified by power supply and voltammetry.

III. RESULTS AND DISCUSSION

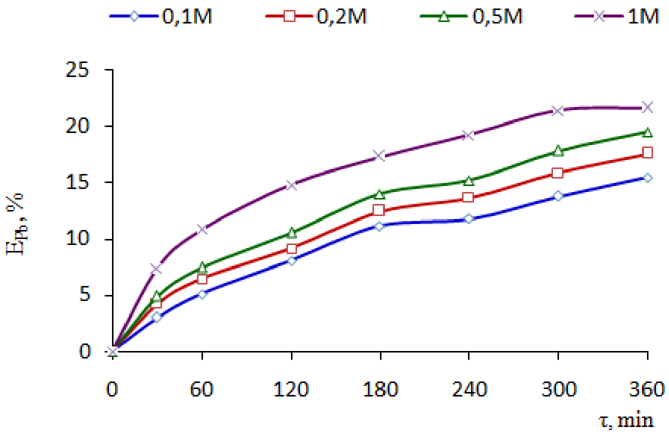
The data associated with the effect of the concentration of sodium hydroxide in the original solution on the leaching process of the concentrate was obtained in order to increase the research material to develop the concept of physico-chemical interactions in multi component systems, typical in hydrometallurgy for nonferrous metals. The represented data of the degree of change in the extraction of copper, lead and zinc into solution was obtained during electrochemical leaching of the concentrate at sodium hydroxide concentration in the initial solution of $C_{NaOH\ -\ 0,1}$ M, 0.2 M, 0.5 M, 1.0 M

The extraction degree of copper during elektroleaching proceeded for 6 hours increases with the concentration of 0.1 M sodium hydroxide to 21.5%, 0.2M to 30.04%, 0.5 M to 43.1%, 1.0M to 46,3% (Figure 1). For lead these figures are, respectively: at a concentration of 0.1 M sodium hydroxide - 15.5%, 0.2 M - 17.6%, 0.5 M - 19.6%, 1.0 M - 21.7 % (Figure 2). These figures for zinc are as follows: at the concentration of sodium hydroxide 0.1 M - 3.7%, 0.2 M - 5.3%, 0.5 M - 8.67%, 1.0 M - 10.88% (Figure 3).



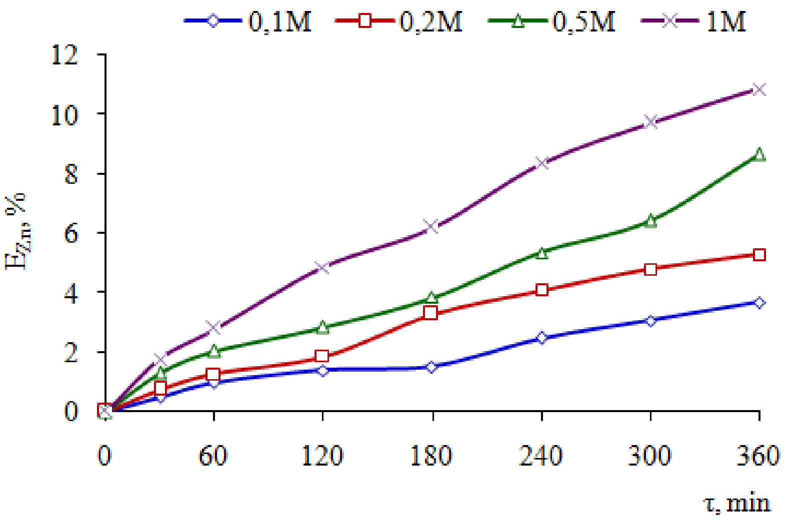
t - 25 °C, i - 100 A/m ^{2,} ω - 480 rev/min, anode - graphite, cathode - sulphur-graphite electrode

FIG. 1 EXTRACTION DEGREE OF COPPER DURING ELEKTROLEACHING OF THE CONCENTRATE, DEPENDING ON THE CONCENTRATION OF SODIUM HYDROXIDE



t - 25 °C, i - 100 A/m ^{2,} ω - 480 rev/min, anode - graphite, cathode - sulphur-graphite electrode

FIG. 2 EXTRACTION DEGREE OF LEAD DURING ELEKTROLEACHING THE CONCENTRATE, DEPENDING ON THE CONCENTRATION OF SODIUM HYDROXIDE

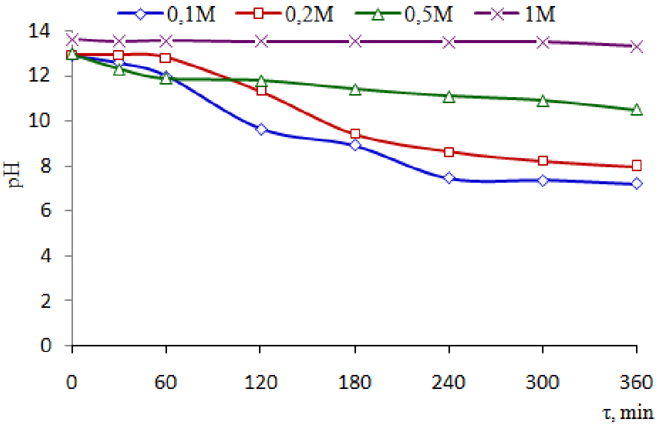


t - 25 °C, i - 100 A/m ^{2,} ω - 480 rev/min, anode - graphite cathode - sulphur-graphite electrode

FIG. 3 EXTRACTION DEGREE OF ZINC DURING ELEKTROLEACHING THE CONCENTRATE, DEPENDING ON THE CONCENTRATION OF SODIUM HYDROXIDE

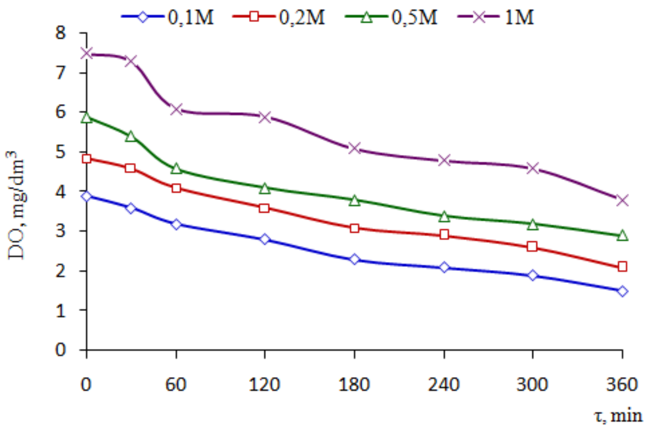
As shown in Figure 4, the pH of the solution at the concentration of 0.5 and 1.0 M during the leaching slightly reduced, but remained at almost the initial value. However, at the alkali concentration of 0.1 M and 0.2 M, pH of the solution decreased from 13.48 to 10.3 and from 8.6 to 12.05, respectively.

Change in oxygen concentration in the solution (Fig. 5) during the leaching process shows that the oxygen concentration decreases monotonically at all possible concentrations of the alkali: at 0.1M oxygen concentration decreases from 3.9 mg/dm^3 to 1.5 mg/dm ^{3,} at 0.2 M oxygen concentration –from 4.85 mg/dm ^{3} to 2.1 mg/dm^3, at 0.5 M the oxygen concentration changes from 5.9 mg/dm^3 to 2.9 mg/dm ^{3}, at 1.0 M oxygen concentration - from 7.5 mg/dm^3 to 3.8 mg/dm^3.



t - 25 °C, i - 100 A/m ^{2,} ω - 480 rev/min, anode – graphite, cathode - sulphur-graphite electrode

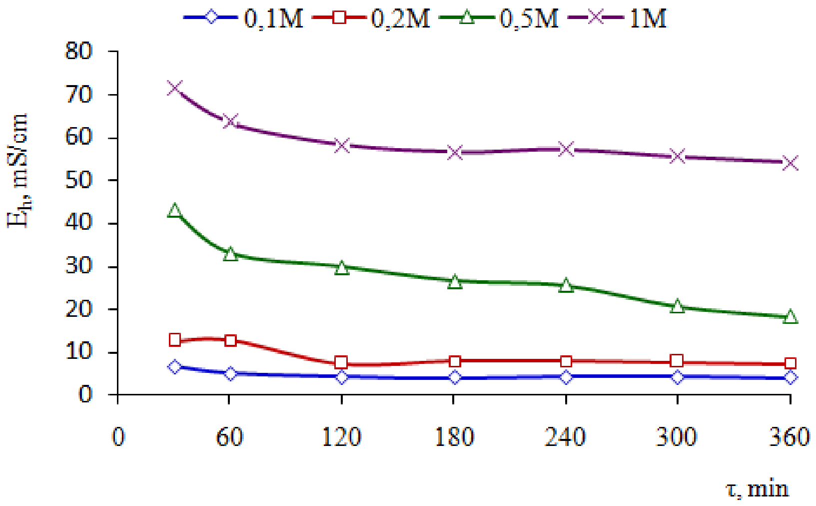
FIG. 4 THE CHANGE IN THE PH OF THE SOLUTIONS DURING CONCENTRATE LEACHING, DEPENDING ON THE CONCENTRATION



t - 25 °C, i - 100 A/m ^{2,} ω - 480 rev/min, anode - graphite, cathode - sulphur-graphite electrode

FIG. 5 THE CHANGE IN THE OXYGEN CONCENTRATION OF SOLUTIONS DURING LEACHING PROCESS OF THE CONCENTRATE, DEPENDING OF THE CONCENTRATION

The electrical conductivity of the solution (Fig. 6) is markedly reducing, and the nature of changes in conductivity does not match to the generally accepted point of view associated with the conductivity mechanism of inorganic aqueous solutions which is with the increase in the concentration of cations and anions, the electrical conductivity of an in organic aqueous solution also increases.



t - 25 C, i - 100 A/m ^{2,} ω - 480 rev/min, anode - graphite, cathode - sulphur-graphite electrode

FIG. 6 CHANGES IN THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS DURING THE LEACHING OF CONCENTRATE, DEPENDING ON THE CONCENTRATION OF NaOH

Thus, during the process of extraction of the elements from the reaction zone, both conductivity and the oxygen content decrease. This is probably due to the high redox properties, which help to increase the rate of dissolution. The nature of the change of the electrode potential of the concentrate revealed that its dissolution in the alkaline thiosulfate solution proceeds phasically.

The order of reaction of the leaching process of non-ferrous metals from concentrateat room temperature was determined.

The order of reaction (n) was determined graphically by the differential method of Van't Hoff:

$$W = kC_0^n$$

By logarithm of the equation, we get:

$$\lg W = \lg k + n\lg C_0$$

Figure 7 represents a dependency graph of $\lg W - \lg C_0$ as a straight line, an angle of slope gives the value of reaction order (n) with respect to the substance, the concentration of which varies.

The value of the reaction order (calculated by copper) during the leaching of concentrate is n = 0,39 (Fig. 7). The fragmentation of values of the reaction order reflects the behavior of the parallel reactions in which the solvent can be spent on the dissolution of the accompanying metals.

The constant of the reaction rate was calculated by applying the equation of Shchukarev - Dolivo - Dobrovolsky:

$$k = \frac{\sigma}{SC^n{}_0} \cdot \frac{C}{\tau},$$

where k – constant of the reaction rate;

C – metal content which passed from the solid phase into solution, mol/dm ^{3};
S - surface area of the initial sample S - 4,5 m ^{2}/g;
n - the order of the chemical reaction at the interface, in this case n = 0,39;
σ - the stoichiometric coefficient indicating the number of moles of the reagent needed to dissolve one mole of solid, σ = 2;
C_0- solvent concentration;
τ - solids contact time with the solvent.

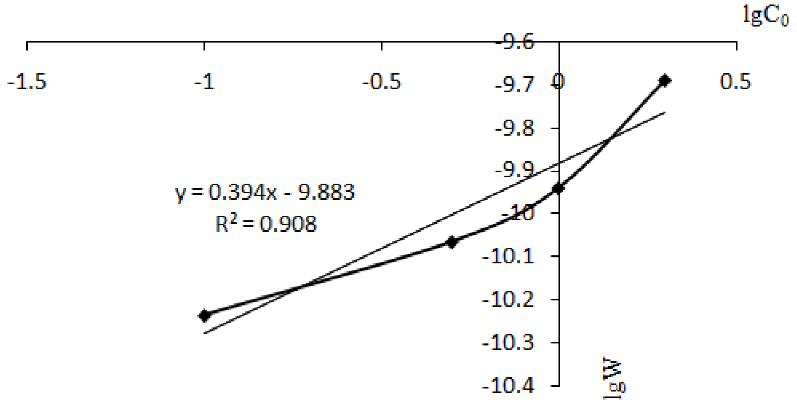


FIG. 7 DEPENDENCY GRAPH OF $lg(W)$ - $lg(C_0)$ OF COPPER DISSOLUTION PROCESS
W - SPECIFIC RATE OF GOLD DISSOLUTION, C_0 - THE CONCENTRATION OF SODIUM HYDROXIDE

It is found that the order of the reaction during electrochemical leaching processes is fractional. This demonstrates the simultaneous dissolution of copper and trace elements.

During the next step, the effect of temperature on dissolution of the non-ferrous metals in the floatation concentrate was studied. Effect of temperature on the rate of dissolution of copper in the floatation concentrate was studied at the temperature range of 25 ^{0}C to 45 ^{0}C with an interval of 10 ^{0}C.The experimental conditions were optimal according to results of the previous studies: the concentration of sodium hydroxide - 0.5 M, the ratio of solid to liquid S: L = 1:10.

Study results showed that at temperature of 25 °C and for 6 hours, the concentration of copper has a value (26.8%), with an increase in the temperature to 45 °C copper recovery increases to 35.7% (Figure 8).

For lead these figures are, respectively: at a current density of 25 °C - 19,57%, 35 °C - 19.6%, 45 °C - 23.5% (Figure 9). For zinc these figures are, respectively: at a current density of 25 °C - 8.67%, 35 °C - 9.48%, 45 °C - 10.49% (Figure 10).

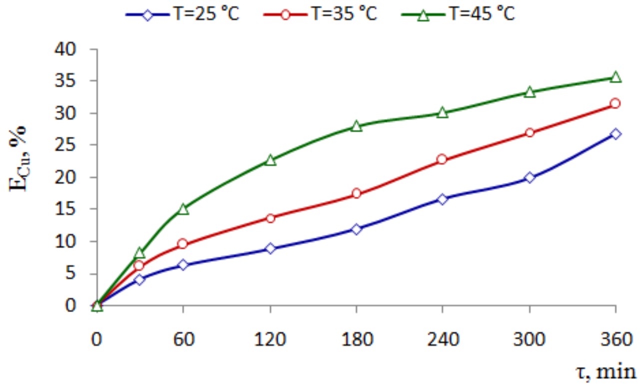


FIG. 8 THE DEGREE OF COPPER EXTRACTION FROM THE CONCENTRATE, DEPENDING ON THE TEMPERATURE

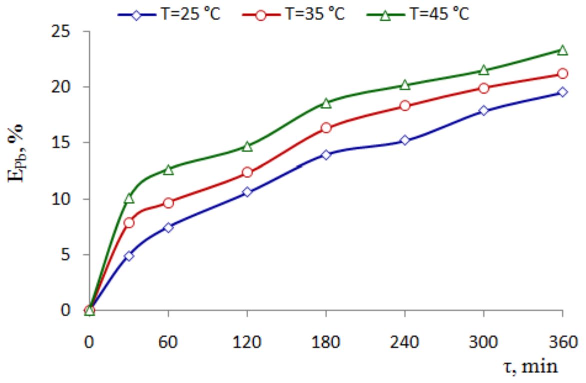


FIG. 9 THE DEGREE OF LEAD EXTRACTION FROM THE CONCENTRATE, DEPENDING ON THE TEMPERATURE

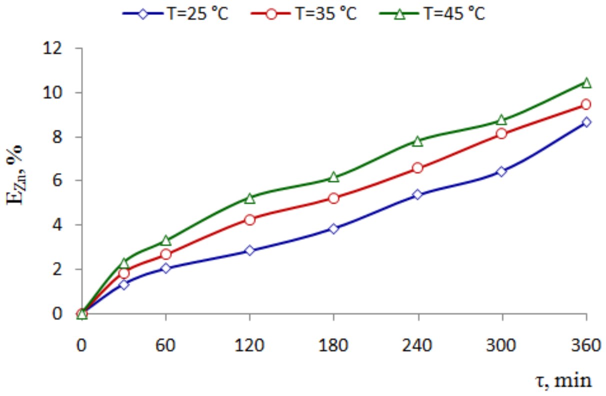


FIG. 10 THE DEGREE OF ZINC EXTRACTION FROM THE CONCENTRATE, DEPENDING ON THE TEMPERATURE

The calculated values of activation energy during the process are -12.01 kJ/mol, suggesting that the process takes place in diffusion mode.

TABLE 1
KINETIC PARAMETERS OF ELECTROCHEMICAL LEACHING OF THE CONCENTRATE

T, K	298	308	318
K	1.61×10^{-06}	3.29×10^{-06}	$3.29 \cdot 10^{-06}$
$E_{act,}$ kJ/mol	12.01		

IV. CONCLUSION

The influence of various physical and chemical factors on the dissolution of non-ferrous metals in the process of cathodic polarization in the presence of sulphur-graphite electrode (SGE) was studied. It is shown that non-ferrous metals proceed into solution during cathodic polarization SGE. It is found that with increasing solvent concentration and temperature, the degree of extraction of metals also increases. This is due to the formation of $S_2O_3^{2-}$ complexes with non-ferrous metals.

During the dissolution process, oxidation and sulphidation of the copper and formation of complex zinc sulfates take place, which prevent further dissolution of metals. Electrolyte concentration and temperature contribute to the increase in the solubility of metals.

Kinetic studies were conducted on the dissolution process of non-ferrous metals with the use of sulfur-containing material as a source of leaching agent - sodium thiosulfate. It is shown that with the increasing concentrations of sodium hydroxide in the solution at the range of 0.1 - 1.0 M, copper recovery increased from 21.5 to 46.2%.

As the temperature increases from 25 to 45 ^{0}C copper dissolution rate in the initial moment of time increases, then over time this figure gradually decreases with decreasing the copper content in the initial product. The value of the order of the reaction is 0.39. The calculated value of the activation energy in the process of leaching copper is 12.01 kJ/mol, which suggests that the process is analyzed in the diffusion mode.

Thus, it is shown that according to conducted research on leaching, dissolution of ferrous metals depends primarily on the nature of the initial content of raw material, metal structure, and products of the leaching process and the nature of the solvent.

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