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PRELIMINARY STUDIES OF THE KINETICS OF LEAD DISSOLUTION FROM COPPER CONCENTRATE WITH THE AID OF AMMONIUM ACETATE

WSTĘPNE BADANIA KINETYKI ROZTWARZANIA OŁOWIU Z KONCENTRATU MIEDZIOWEGO ZA POMOCĄ OCTANU AMONOWEGO

This paper presents a brief review of methods of leaching copper ores and concentrates with acidic and alkaline reagents, and addresses the nature of the reactions occurring during dissolution of polydispersed material. Based on known studies, a method is proposed to calculate the reaction-rate constants and apparent activation energy for dissolution of lead from copper concentrates. Lead was leached with 10 and 40 percent ammonium acetate solutions at temperatures ranging from 293K to 323K. Based on the experimental results, the apparent activation energy was calculated for dissolution of lead from copper concentrate.

W artykule podano krótki przegląd metod ługowania rud i koncentratów miedzi za pomocą reagentów o charakterze kwaśnym i alkalicznym. Równocześnie zwrócono uwagę na charakter reakcji przebiegających w roztworach w trakcie roztwarzania polidyspersyjnego materiału. W oparciu o znane prace przedstawiono metodę obliczania z zależności stopnia wyługowania od czasu stałych szybkości reakcji i pozornej energii aktywacji reakcji roztwarzania ołowiu z koncentratu miedziowego. Ługowanie ołowiu wykonano za pomocą octanu amonowego o stężeniu 10 i 40% wag., w zakresie temperatur od 293K do 323K. Na podstawie danych doświadczalnych obliczono pozorne energie aktywacji reakcji roztwarzania ołowiu z koncentratu miedziowego.

1. Introduction

In the literature one notes intensified research into hydrometallurgical processing of ores, concentrates and flotation tailings [D u t r i z a c J. E., 1989; Ł ę t o w s k i F., 1974; G u y S., 1983; ibid., 1982; M u k h e r j e e T. K., 1985; H e p e l M., 1973;

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W ó j t o w i c z J., 1971; S a t o T., 1983; M u l a k W., 1995]. Most ores, as well as concentrates, occur in the form of polydispersed systems composed of various minerals. To describe in detail the processes that can occur in such systems, it is necessary to study dissolution of individual mineral components. [H e p e l M, 1976; B i e s z c z a d T., 1975; ibid., 1976; L i n g e H. G., 1976; S u k l a L. B., 1986; D u t r i z a c J. E., 1992; B i e g l e r T., 1976/1977; and others].

In hydrometallurgical processing, either acidic or ammonium solutions can be used for leaching.

The most preferred leaching reagent is sulphuric (VI) acid. Yet as most low-grade ores of non-ferrous metals occur in dolomite deposits, the acid is irreversibly lost to neutralise calcium and magnesium carbonates with no possibility of recovering it, and that is why its use is limited. Diluted acid is an efficient reagent for leaching oxide ores, but it is not sufficient for sulphide ores. In the latter case its action is augmented by adding iron (III) sulphate or by oxygenation of the leaching medium [M u l a k W., 1971; L i n g e h. G., 1976; D u t r i z a c J.E., 1992].

Non-ferrous metals, metal oxides and sulphides are also leached with complexing agents. The use of diketones [S a t o T., 1969], ethylenediamine (EDTA) [D u d a L. L., 1992], and amino-acids was reported in the literature.

Ammonium leaching has been long known and applies mainly to leaching of sulphide ores of copper, nickel, zinc and other metals, and oxide ores. The most often used leaching agents are solutions of ammonium sulphate, carbonate or chloride. The rate of dissolution with these reagents can be increased by the use of oxygen and by elevated temperature.

Dissolution of polydispersed sulphides in ammonium sulphides was studied by H e p e l M., P o m i a n o w s k i A., B i e s z c z a d T., M u l a k W., G u y S., and others, with particular attention being paid to electrochemical nature of the underlying processes. Based on experimental data, the apparent activation energy and the temperature coefficients of the reactions rates were determined [H e p e l M., 1973, ibid. 1976; B i e s z c z a d T., 1975; and others]. The data provided by these authors are in good agreement with results of sulphide solubility obtained by other researchers [G u y S., 1982; ibid., 1976; H a v l i k T., 1995, and others].

As demonstrated by numerous studies, it is possible to determine the region of reactions that copper sulphides undergo ammonium solutions in the presence of oxygen. In these conditions they undergo complex transformations. These include simultaneous, sequential, and most probably, autocatalytic processes. They can be classified as:
- simple dissolution of oxidized surface layers;
- non-stoichiometric transformation during oxidation;
- equilibration between compounds of copper (II) and copper (I) on the surface of the leached materials and in the bulk of the solution;
- oxidation of sulphide sulphur to elemental sulphur, polythionates and thionates, thiosulphates, sulphates (IV) and (VI), and sulphamides;
- decomposition of unstable compounds of oxygen and sulphur re-precipitation of copper sulphides [B i e s z c z a d T., 1981].

In studying dissolution processes, the influence of complexing agents (including ammonium and chloride ions) was also taken into account [B i e s z c z a d T., 1975, B i e s z c z a d T., 1981; G u y S., 1983; M u k h e r j e e T.K., 1985; M u l a k W., 1971].

As can be seen from the cited literature, studies so far have focused mainly on leaching copper from with a view to obtaining it by hydrometallurgical methods. Increased content of lead in copper ores and the lack of effective methods for separating lead from copper in flotation, affect the quality of copper concentrate and its subsequent pyrometallurgical processing. A method that could reduce lead content in the concentrate is selective leaching. A reagent showing high reactivity to lead compounds is ammonium acetate, and that is why we selected this compound for our studies of leaching lead from copper concentrates.

2. Subject of the study

Polydispersed copper sulphide concentrate containing 29.95 percent copper and 1.53 percent lead was used in the experiments. Copper occurs in the concentrate mainly in the form of chalcocite and also, in smaller quantities in the form of bornite, chalcopyrite and covelite, whereas lead occurs in the form of galena and, in small quantities, in oxidized form as lead sulphate.

A representative sample was collected for the sieve analysis, and individual grain classes were analyzed for content of copper and lead. The results of the analysis are shown in Table 1.

TABLE 1

Sieve and chemical analysis of copper concentrate

No	Grain class [mm]	Yield [%]	Copper content [%]	Lead content [%]
1	+0.100	6.42	28.75	0.68
2	0.100–0.071	13.57	35.95	0.90
3	0.071–0.063	5.45	30.05	0.95
4	0.063–0.050	11.51	34.38	1.27
5	0.050–0.045	1.79	33.95	1.32
6	−0.045	61.26	27.80	1.86
	Averaged sample	100.00	29.95	1.53

Obtained values show that the grains less than 0.045 mm dominate in the investigated material (yield 61.3%). The content of copper (27.8%) is the lowest in this class of grains, while the average content of copper in this concentrate is 29.95%.
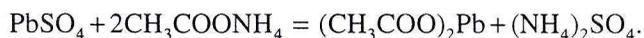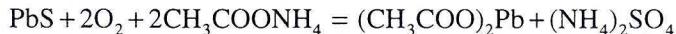
The analysis of the lead content in the samples revealed that the mean concentration of lead increases when the size of grains decrease. The highest concentration of lead (1.86%) was observed for the class of grains less than 0.045 mm, while the average content of lead in the concentrate is 1.53%.

3. Measurement method

The experiments were performed in a beaker placed in a thermostated bath at a temperature that was kept constant with an accuracy of ± 0.2 K. The leaching solution, containing 10 or 40 percent by weight of ammonium acetate was pre-heated to the temperature of the experiment. The leached suspension, containing 10 g of the copper concentrate and 100 cm^3 of the leaching solution, was stirred at a constant rate with an R50D CAT stirrer. The suspension was leached for 60 minutes; during that time 7 samples were taken to determine copper and lead content by ICP or ASA method.

4. Results and interpretation

Lead occurring in the concentrate as PbS and (in the oxidized form) as $PbSO_4$ is dissolved according to the reaction:

$$PbS + 2O_2 + 2CH_3COONH_4 = (CH_3COO)_2Pb + (NH_4)_2SO_4$$

$$PbSO_4 + 2CH_3COONH_4 = (CH_3COO)_2Pb + (NH_4)_2SO_4.$$

These are heterogeneous reactions wherein sparingly soluble lead compounds pass to the solution in the form of easily soluble acetates. One should note that the first reaction occurs only in the presence of an oxidant, which could be atmospheric oxygen dissolved in the leaching solution. These reactions pertain to dissolution in pure model systems; in polymetallic systems, such as concentrates, the process can be affected by both substrates and products of the reaction. During leaching the condition of the solid phase surface and its surface area are changing which in many cases makes it impossible to calculate actual reaction constants. In earlier studies of concentrate leaching in ammonium solutions [Hepel M. et al.; Bieszczad T. et al., 1975; ibid. 1981] a method was proposed to calculate reaction constants and apparent activation energy based on leaching curves. The rate of a heterogenous reaction can be described by the formula:

$$\frac{dx}{dt} = \frac{kP_O}{V} f'(t), \tag{1}$$

where:
x – reduced concentration (degree of leaching),
t – reaction time,

k – reaction constant,

P_O – surface area of the solid phase at $t = 0$,

$f'(t) - (m-1)$th – degree function of time.

The function $f'(t)$ is associated with the time variation of reagent concentrations $c(t)$ and the surface area of the solid phase $s(t) : f'(t) = c(t) \cdot s(t)$.

Integrating equation (1) gives an integral form of the time function $f(t)$:

$$x = \frac{kP_O}{V} f(t). \tag{2}$$

Many experiments indicate that changes in the reduced concentration of reaction products can be described by the general formula:

$$x = a \cdot t^m. \tag{3}$$

Integration of the above equation gives:

$$\frac{dx}{dt} = a \cdot m \cdot t^{-(1-m)}. \tag{4}$$

Comparison of equations (1) and (4) indicates that, if constants a and m and the surface area of the solid phase are known, it is possible to calculate the reaction-rate constant:

$$a \cdot m = \frac{kP_O}{V} \tag{5}$$

Coefficients a and exponents m can be determined experimentally using the logarithmic form of equation (3):

$$\log x = \log a + m \log t. \tag{6}$$

The above equations were used to determine the activation energy for leaching lead from copper concentrate. As the lead content of in the concentrate is almost 20 times lower than that of copper, it is much more difficult to determine its surface area, and that is why we did not determine the reaction-rate constant. We did determine some kinetic constants that are proportional to the reaction-rate constants, which make it possible to determine the activation energy for leaching lead. Fig. 1 shows the dependence of the logarithm of the reduced lead concentration on the logarithm of the leaching time (expressed in minutes). Leaching was performed in a 10% solution of ammonium acetate at temperatures of 293K, 303K, 313K and 323K with a ratio of the liquid to solid phases of 10 : 1 and a stirring rate of 600 r.p.m. Thus obtained straights lines were used to determine a and m, the product of which gives constant K. The dependence of $\log K$ on the reciprocal of the absolute temperature is shown in Fig. 2. From this relationship the slope of the A r r h e n i u s equation was determined:

$$\log K = A' - \frac{B}{T} \tag{7}$$

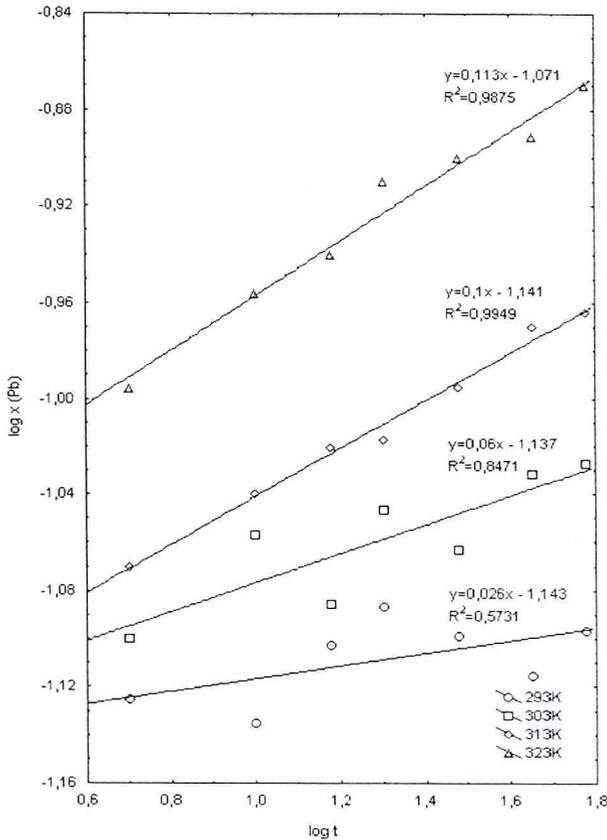and the apparent activation energy was determined from the formula: $E_A = 2.303 \cdot R \cdot B$

Fig. 1. Dependence of the logarithm of the reduced lead concentration on the logarithm of the leaching time. Leaching conditions: concentration of the ammonium acetate solution of 10% by weight; rate of stirring 600 r.p.m.; the ratio of liquid to solid phases is 10:1

The relationship that was found experimentally is: $\log K = 2.99 - \dfrac{2189.8}{T}$

The apparent activation energy calculated from the gradient is 41.9 kJ/mole.

Analogous leaching was conducted in a 40 percent by weight solution of ammonium acetate. The use of more concentrated solution considerably increases the rate of leaching lead from the concentrate. The effect of temperature on the leaching rate was stronger than for the 10% solution of ammonium acetate. The dependence of the logarithm of the reduced lead concentration on the logarithm of the time at various temperatures is shown in Fig. 3. Coefficients a and m determined from the straight lines were used to calculate the constant K. Thus obtained values of constant K for various temperatures were used to plot the dependence of $\log K$ on the reciprocal of the absolute temperature, as shown in Fig. 4. This dependence is linear and can be described by the equation of the straight line: $\log K = 2.17 - \dfrac{1842.12}{T}$.
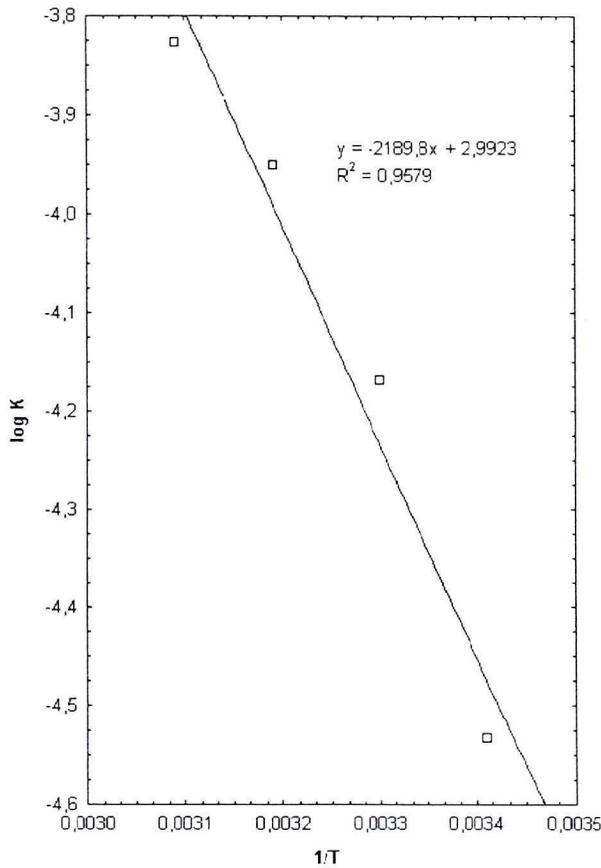
Fig. 2. Dependence of the logarithm of constant K on the reciprocal of the temperature

The apparent energy of activation calculated from the gradient of this line is 35.3 kJ/mole.

The values of apparent energy of activation obtained for leaching with 10% and 40% solutions show a small difference which implies that leaching of lead in this conditions occurs in the mixed region. This mechanism is corroborated by the relatively strong dependence of leaching on the temperature and poor dependence on the rate of mixing of the leached suspension. The results obtained so far justify a supposition that after the conditions of leaching copper concentrate with ammonium acetate are optimised, the lead content in the concentrate can be lowered to levels that are satisfactory for pyrometallurgists and the process will be ecumenically justified.
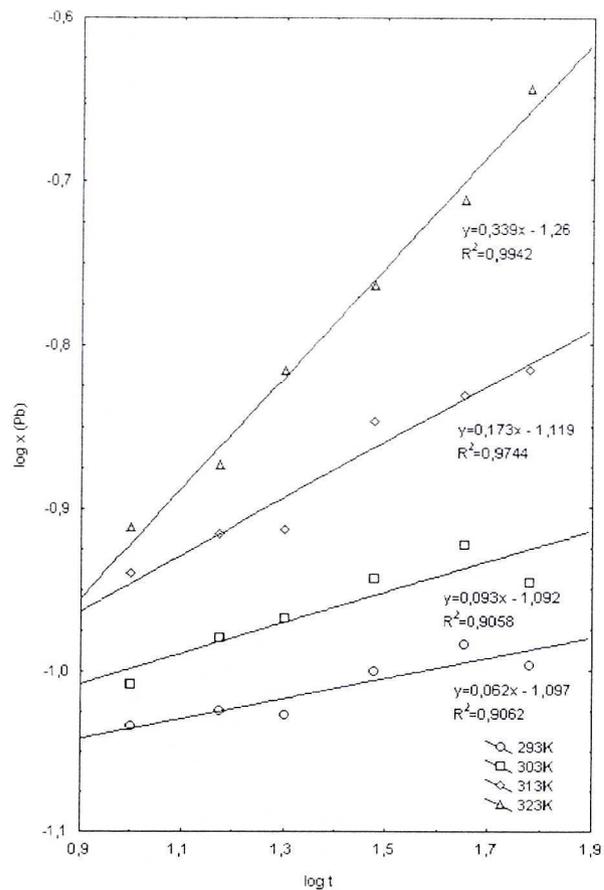
Fig. 3. Dependence of the logarithm of the reduced lead concentration on the logarithm of the leaching time. Leaching conditions: concentration of the ammonium acetate solution of 40% by weight; rate of stirring 600 r.p.m.; the ration of liquid to solid phases is 10 : 1.
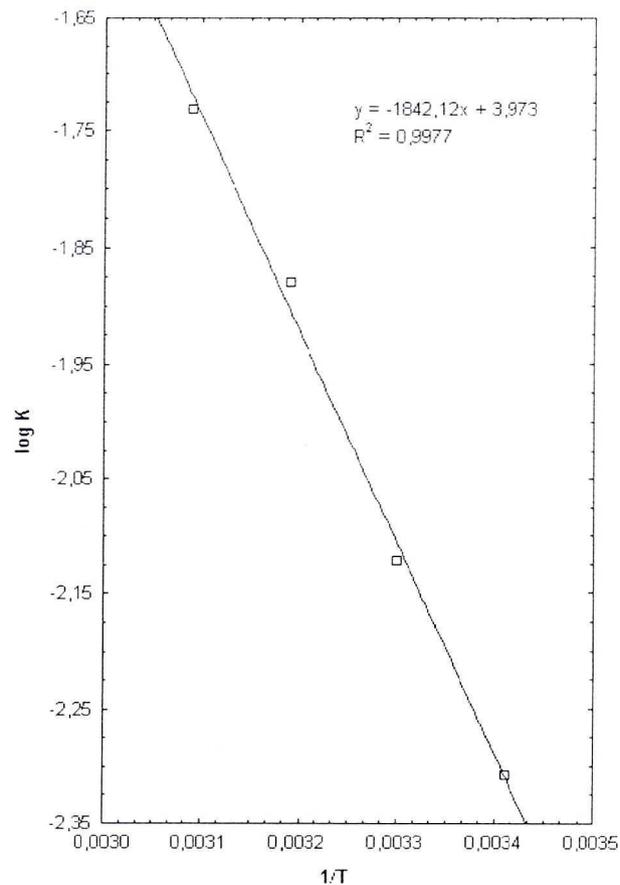

Fig. 4. Dependence of the logarithm of constant K on the reciprocal of the temperature

5. Summary

The leaching of copper concentrate with ammonium acetate occurs in the mixed region.

Increasing the acetate concentration from 10 to 40 percent by weight accelerates the rate at which lead is leached from copper concentrate.

An increase in the leaching rate with temperature was demonstrated for both concentrations as shown in Fig. 1 for ammonium acetate concentration of 10%, and in Fig. 3 for ammonium acetate concentration of 40%.

The calculated activation energy of the sample dissolved in a 10% solution is about 41.9 kJ/mole whereas for the sample dissolved in a 40% solution it is about 35.3 kJ/mole.

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