ACTA TECHNICA CORVINIENSIS – Bulletin of Engineering
Tome V (Year 2012). FASCICULE 1 [January–March]. ISSN 2067-3809

[1.] Emília SMINČÁKOVÁ, Pavel RASCHMAN

LEACHING OF STIBNITE BY MIXED Na_2S AND NaOH SOLUTIONS

[1.] TECHNICAL UNIVERSITY OF KOŠICE, FACULTY OF METALLURGY, LETNÁ 9, 042 00 KOŠICE, SLOVAKIA

ABSTRACT: Kinetics of the reaction between particulate stibnite and mixed Na_2S + NaOH solutions were studied. The effects of concentrations of Na_2S and NaOH, temperature, particle size and liquid-to-solid ratio were investigated. It was observed that the rate of leaching of stibnite: a) increased with an increase in both Na_2S and NaOH concentration (from 0.5 wt. % to 2.0 wt. %), and temperature (from 292 K to 327 K); b) reached its maximum at Na_2S:NaOH molar ratio equal to 1:2; c) decreased with an increase in particle size (from 0.04 mm to 0.5 mm) and L/S ratio (from 10 to 100). The results are presented in terms of the shrinking-particle model. Calculated values of the kinetic parameters indicate that the leaching process is controlled by the chemical reaction between Sb_2S_3 and Na_2S at the liquid/solid interface. Apparent activation energy is approximately 44 kJ mol^{-1} and the apparent reaction order for Na_2S varies from 1.4 to 1.7.
KEYWORDS: stibnite, alkaline leaching, kinetics, apparent activation energy, apparent order of reaction

INTRODUCTION

From the thermodynamic point of view dissolution of antimony compounds (oxides, sulphides) can take place both in acidic and alkaline solutions, which stems from the amphoteric properties of antimony [1]. In industrial applications Sb_2S_3 dissolves in mixed leaching solutions of Na_2S + NaOH [2-10]. Alkaline Na_2S solution acts as an universal solvent for the majority of antimony compounds. On the other hand, most other metals exhibit low solubility in this solution. Exceptions to this rule would include arsenic, tin and mercury [11, 12]. Leaching of Sb_2S_3 in Na_2S solution can be described by the following chemical reaction:

$$Sb_2S_{3(s)} + 3Na_2S_{(aq)} = 2Na_3SbS_{3(aq)}$$
$$\Delta G^0_{298} = -71.41 kJ \qquad (1)$$

Negative value of the standard Gibbs energy suggests that reaction (1) is feasible and spontaneous. In case that mixed leaching solution (Na_2S + NaOH) is used, sodium hydroxide reacts with Sb_2S_3 according to the reaction:

$$Sb_2S_3 + 6NaOH = Na_3SbS_3 + Na_3SbO_3 + 3H_2O \qquad (2)$$

Reactions (1) and (2) describe the process of Sb_2S_3 leaching in alkaline solutions [13]. The resulting leaching solution is a complex system containing various species (Sb, S, Na), which upon reaction with water create a series of complex ions. These ions can be identified using the equilibrium pH – potential diagrams of the Sb-S-H_2O and Sb-S-Na-H_2O systems at 298 K as presented in [14]. At pH<13.6 antimony passes into solution as a complex trivalent anion SbS_3^{3-}

For non-porous stibnite particles, the dissolution of antimony during the initial stage of the process may be controlled by the surface chemical reactions (1) and/or (2), or by external mass transfer [15]. When the surface chemical reaction is a rate-determining step, high values of apparent activation energy (from 40 kJ mol^{-1} to 300 kJ mol^{-1}) are observed [16]. The non-porous shrinking-particle model in the form [17]

$$1 - (1 - \alpha)^{1/3} = k' t \qquad (3)$$

was used to analyze the leaching process. α is the fraction of antimony dissolved, t is the reaction time and k´ is the rate parameter.

This article presents the results of the experimental determination of the effect of temperature, composition of the leaching solution, speed of agitation, liquid/solid ratio and particle size on the leaching rate of stibnite in Na_2S + NaOH solutions.

EXPERIMENTAL - MATERIALS

Natural stibnite from Pezinok (Slovak Republic) was used in the present study. Table 1 summarizes the chemical composition of the sample (in wt.%). Minor elements present in the sample (wt.%) were: 0.65% Al, 0.63% Pb, 0.37% Mg and traces of Ti, Mn, As, Sn, Bi, Hg and Ag.

Table 1. Chemical composition of the stibnite sample

Element	Sb	S	Si	Zn	Ca	Fe
Weight%	49.3	19.15	10.4	5.43	1.81	0.84

Size fractions were obtained by crushing, dry-grinding and dry-screening. The contents of antimony, silicon, iron and zinc (in wt.%) in different size fractions are shown in table 2.

Table 2. Chemical composition (in wt.%) of individual size fractions

Particle size (mm)	0.5-0.25	0.25-0.18	0.09-0.071	0.071-0.04
Sb	34.76	29.70	47.00	54.75
Si	15.46	20.62	12.66	6.14
Fe	1.12	1.01	1.01	0.90
Zn	1.03	0.86	0.73	0.52

Stibnite (Sb_2S_3) and quartz (SiO_2) were found to be the predominant mineral phases according to the results of the X–ray diffraction analysis. Accompanying minerals were identified as pyrite (FeS_2) and wurtzite (ZnS). Other mineral phases were not identified [10].

Analytical reagent grade chemicals and distilled water were used in all experiments. In each of the experiments at least three runs were made for a given set of reaction conditions.

EXPERIMENTAL PROCEDURE & EVALUATION OF KINETIC DATA

Leaching of the samples of stibnite was carried out in a 0.2 L mixed glass batch reactor at constant temperature. Constant agitation rate (equal to 10 s^{-1}) was used in all experiments. The temperature was maintained to within 1 K by a heating glass coil connected to a thermostat.

When the Na_2S + NaOH solution in the reactor had reached the required temperature, 0.4 g of stibnite sample was added. Samples (about 2 mL) of the reaction mixture were withdrawn from the reactor at appropriate time intervals, filtered and the filtrates were analyzed using AAS method.

The experiments were carried out under reaction conditions as follows: temperature from 291 K to 333 K, concentrations of Na_2S and NaOH from 0.5 wt. % to 2 wt. %, Na_2S : NaOH molar ratio equal to 1:2.

In each case of testing a fresh Na_2S+NaOH leaching solution was prepared in order to avoid its possible coagulation. In one case, however, the coagulation process appeared and was noticed visually after twelve hours in the solution containing 2 wt.% Na_2S+2 wt.% NaOH.

RESULTS AND DISCUSSION - EFFECT OF TEMPERATURE

The temperature dependence of the leaching rate was determined for size fractions 0.18–0.25 mm and 0.25–0.5 mm, at solution temperatures in the range 291 K to 327 K. A typical situation is shown in Fig. 1. It can be seen that the rate of stibnite dissolution is very sensitive to the temperature.

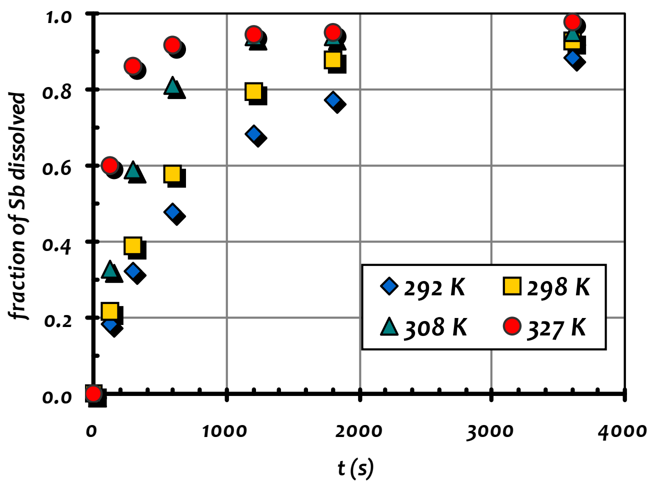

Figure 1. Effect of leaching temperature on fraction of antimony dissolved (reaction conditions: 1wt.% Na_2S + 1wt.% NaOH; particle size 0.18–0.25 mm; agitation rate 10 s^{-1}).

EFFECT OF Na_2S AND NaOH CONCENTRATIONS

The effect of Na_2S and NaOH concentrations was studied in a series of tests performed at 292 K. The experiments showed that the rate of stibnite dissolution is significantly affected by concentrations of Na_2S and NaOH. An example is shown in Fig. 2.

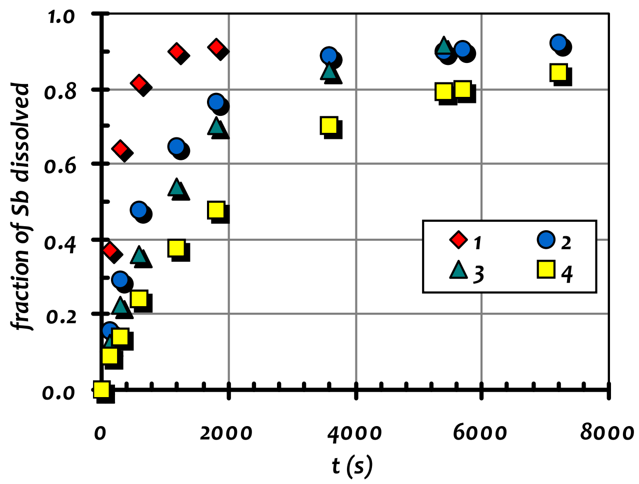

Figure 2. Effect of chemical composition of the leaching solution on fraction of antimony dissolved:
1 – (2wt.% Na_2S + 2wt.% NaOH); 2 – (1wt.% Na_2S + 1wt.% NaOH); 3 – (0.75wt.% Na_2S + 0.75wt.% NaOH); 4 – (0.5wt.% Na_2S + 0.5wt.% NaOH); (reaction conditions: T = 292 K; particle size 0.18–0.25 mm; agitation rate 10 s^{-1}).

EFFECT OF PARTICLE SIZE

The effect of particle size on the leaching behavior of stibnite at 292 K is shown in Fig. 3. It is evident that the rate of chemical dissolution of the antimony increases as the particle size decreases.

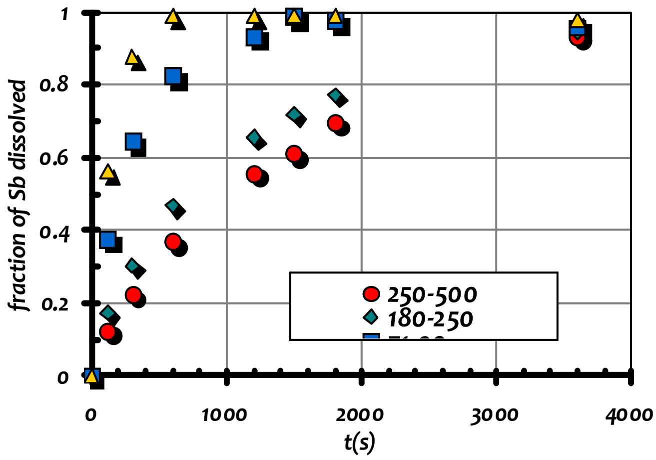

Figure 3. Effect of particle size on fraction of antimony dissolved (particle diameter in micrometers / μm) (reaction conditions: 1wt.% Na_2S + 1wt.% NaOH; T=292 K; agitation rate 10 s^{-1}).

DISCUSSION - EXPERIMENTAL METHOD

The kinetic experiments were carried out under reaction conditions characterized by a relatively high excess of Na_2S (and NaOH) in the solution, in order to eliminate possible effects of the changes in lixiviant composition during individual runs on the rate of leaching.

In this study, Na_2S : Sb_2S_3 molar ratio ≥ 18.6 was used, and the concentration of Na_2S (and NaOH) in the bulk aqueous phase was maintained constant within >85 % rel. during each run.

Some preliminary experiments were carried out with the objective to find the optimum reaction conditions for the actual kinetic measurements. The effects of the rate of agitation, liquid-to-solid ratio and the Na_2S:NaOH molar ratio were investigated; the results are shown in Figs. 4, 5 and 6, respectively. No noticeably significant effect of the first two process parameters on the rate of leaching of the original sample of stibnite (crushed and dry-milled) has been observed for the rate of agitation ≥ 8 s^{-1} (Fig. 4) and L:S ratio ≥ 50 (Fig. 5).

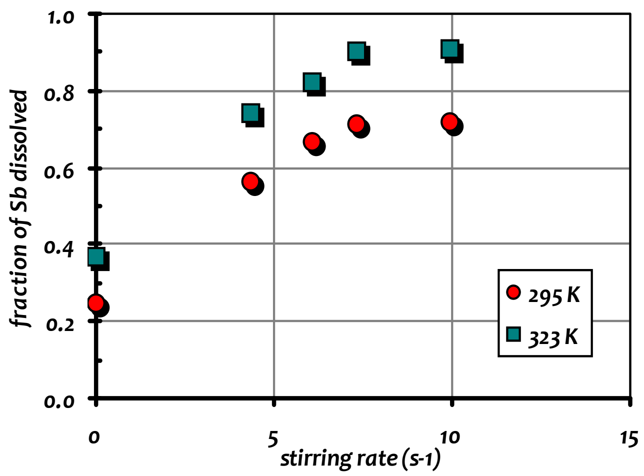

Figure 4. Effect of stirring rate on fraction of antimony dissolved (reaction conditions:1wt.% Na_2S + 1wt.% NaOH; leaching time 5 min; temperatures 295 K and 323 K).

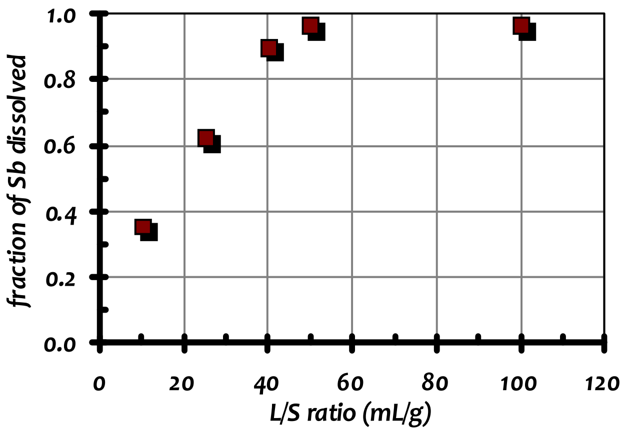

Figure 5. Effect liquid to solid ratio on fraction of antimony dissolved (reaction conditions: T=297 K; agitation rate 10 s^{-1}; particle size 40–180 μm; 1wt.% Na_2S + 1wt.% NaOH; leaching time 30 minutes).

The experiments also showed that the rate is significantly affected by the Na_2S : NaOH molar ratio and reaches its maximum at Na_2S:NaOH ≈½; the situation is represented in Fig. 6. The kinetic experiments were therefore carried out under the reaction conditions which were as follows: agitation rate = 10 s^{-1}, L:S weight ratio =50, Na_2S:NaOH molar ratio 1:2.

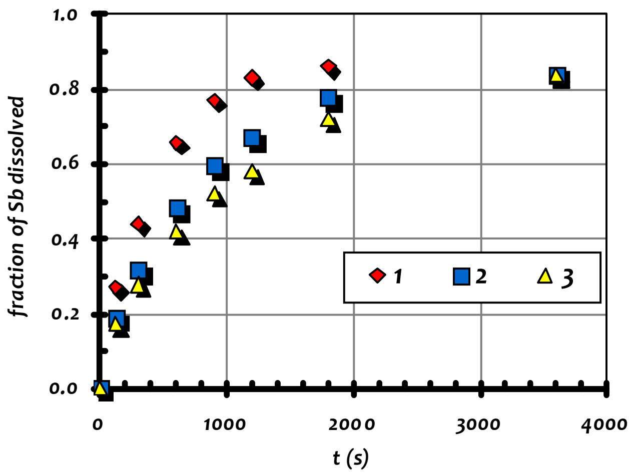

Figure 6. Effect of Na_2S to NaOH molar ratio on fraction of antimony dissolved: 1 – (2wt.% Na_2S + 2wt.% NaOH); 2 – (2wt.% Na_2S + 0.5% NaOH); 3 – (0.5wt.% Na_2S + 2wt.% NaOH); (reaction conditions: T=292 K; agitation rate 10 s^{-1}; particle size 250–500 μm).

MECHANISM OF LEACHING

The applicability of the non-porous shrinking particle model (NSPM) was evaluated by graphical analysis. The NSPM model (3) in the form

$$\alpha = 1 - (1 - 0.2063\, t/t_{0.5})^3 \qquad (4)$$

was used to analyse the leaching process. The reaction half-time $t_{0.5}$ represents a period of time, which is necessary under certain reaction conditions to dissolve one half of the amount of Sb_2S_3 initially present in the sample of stibnite. The values of $t_{0.5}$ for individual experiments are summarized in Table 3.

Table 3. Half-times of stibnite leaching in Na_2S+NaOH solutions

Experiment	wt. % Na_2S	wt. % NaOH	Particle size (μm)	T(K)	$t_{0.5}$(s)
1	0.5	0.5	180–250	292	1860
2	0.75	0.75	180–250	292	1050
3	1	1	180–250	292	660
4	2	2	180–250	292	180
5	1	1	180–250	298	420
6	1	1	180–250	308	210
7	1	1	180–250	327	90
8	0.75	0.75	250–500	292	1320
9	1	1	250–500	292	1050
10	1.25	1.25	250–500	292	810
11	2	2	250–500	292	360
12	1	1	250–500	291	1260
13	1	1	250–500	297	840
14	1	1	250–500	301.5	630
15	1	1	250–500	307	450
16	1	1	250–500	317	240
17	1	1	250–500	327	150
18	1	1	71–90	292	210
19	1	1	40–71	292	90
20	2	0.5	250–500	292	630
21	0.5	2	250–500	292	840

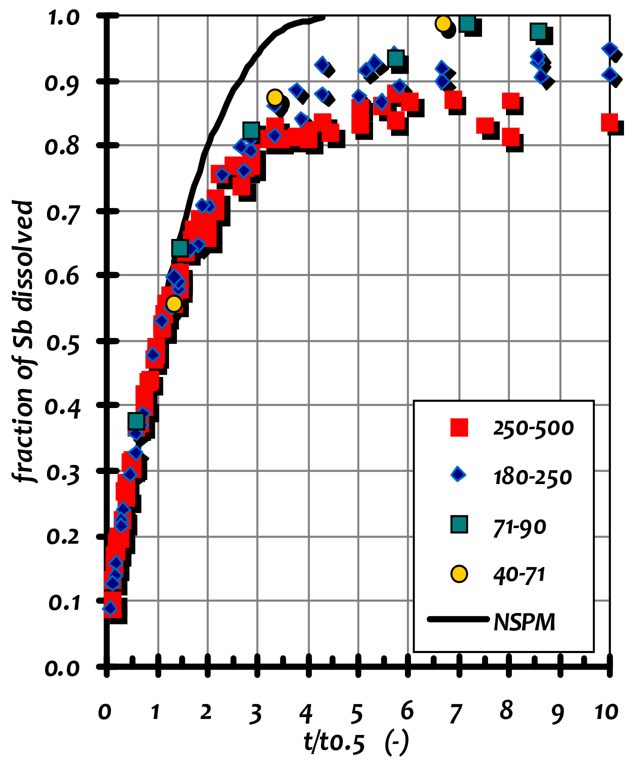

Figure 7. Conversion vs. reduced time relationship for dissolution of stibnite: points – measured data, full line – Eq. (4) (reaction conditions: Na_2S to NaOH molar ratio = 1/2; agitation rate 10 s^{-1}).

The diagram depicting the results of experiments as scattered points shown in Fig. 7 reveals that there is a very good correlation between model and experiments for a portion of antimony dissolved in the solution up to 0.8. Therefore only α–t kinetic data characterized by α < 0.8 were used to calculate the values of model parameters.

Eliminated effect of agitation rate on the overall rate of the leaching process indicates that the surface chemical reaction (1) and/or (2) might be the rate-determining step. The difference between the last two values of $t_{0.5}$ in Table 3 indicates that the reaction (1) is much faster under the conditions considered in the present work. When the rate r of the surface reaction is expressed as a power-law function of the concentration of Na_2S at the particle surface, $c_{Na2S,w}$, the result is

$$r = k\, c^{n}_{Na2S\ w}. \qquad (5)$$

The coefficient k is the apparent reaction-rate constant and n is the apparent order of the overall surface chemical reaction. Temperature dependence of k can be expressed using the Arrhenius expression

$$k = k_o \exp\left(\ E/(RT)\right), \qquad (6)$$

where k_o is the frequency factor; E the apparent activation energy; R the gas constant. Both the apparent activation energy E and the apparent reaction order for Na_2S n were obtained by multiple linear regression using the expression

$$\ln t_{0.5} = \text{const} + (E/R)T^{-1} - n \ln c_{Na2S} \qquad (7)$$

and are summarized in Table 4.

Table 4. Apparent activation energy E and apparent order of reaction n fitted by experiments

Size fraction (μm)	E (kJ mol^{-1})	Apparent reaction order n	r_c^2
250–500	44.1±2.2	1.42±0.14	0.985
180–250	44.4±2.1	1.70±0.09	0.996

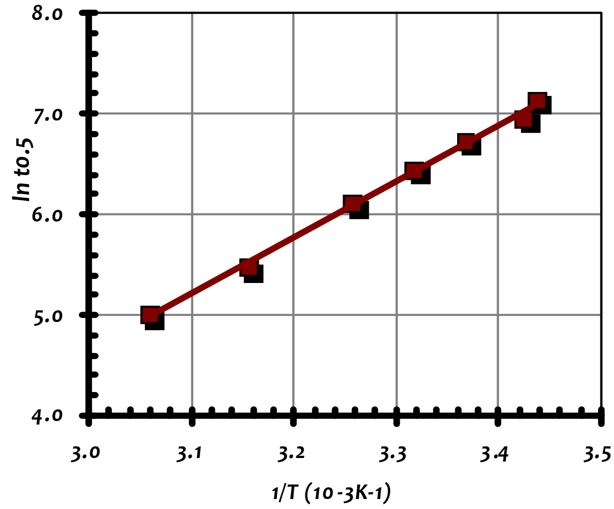

Figure 8. An example of Arrhenius plot (reaction conditions: particle size 250–500 μm; 1wt.% Na_2S + 1wt.% NaOH; agitation rate 10 s^{-1}).

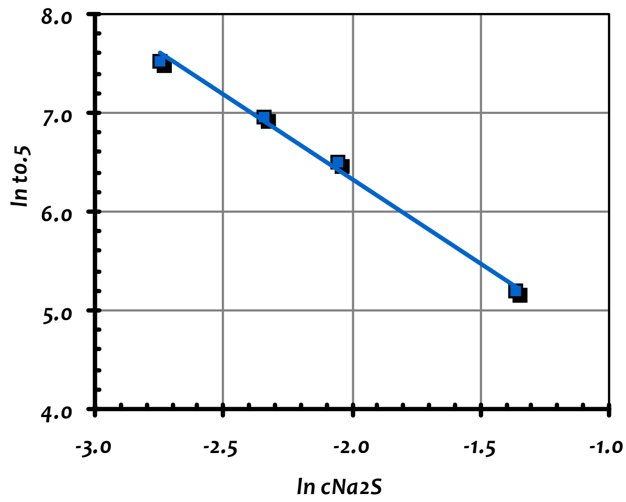

Figure 9. An example of logarithmic ln $t_{0.5}$ vs. ln c_{Na2S} (reaction conditions:particle size 180–250 μm; T=292 K; agitation rate 10 s^{-1}).

Typical examples of Arrhenius plot and ln $t_{0.5}$ vs. ln c_{Na2S} plot are shown for illustration in Figs. 8 and 9, respectively. Fractional order of reaction with regard to Na_2S and relatively high activation energy are indicative of a process controlled by the surface reaction.

CONCLUSIONS

This paper brings the measured kinetic data on stibnite alkaline leaching. Kinetics of the dissolution of natural stibnite in mixed Na_2S + NaOH solutions were investigated.

Several facts indicate that the dissolution is controlled by the surface chemical reaction of Sb_2S_3 with Na_2S + NaOH solution at the liquid-solid interface:

a) The effect of agitation speed on the rate of leaching was eliminated using high agitation rates.

b) The value of apparent activation energy is relatively high, ≈ 44 kJ mol^{-1}.

It was concluded that the reaction between Sb_2S_3 and Na_2S (Eq. (1)) is much faster than that between Sb_2S_3 and NaOH (Eq. (2)) under the conditions considered in the present work and fractional order of reaction with regard to Na_2S (from 1.4 to 1.7) was obtained.

ACKNOWLEDGEMENT

This research was supported by the Slovak Grant Agency for Science (Grant 1/0267/09).

NOTATION

c_{Na_2S} bulk concentration of Na_2S in the leaching solution, mol L^{-1}

$c_{Na_2S\,w}$ concentration of Na_2S at the particle surface, mol L^{-1}

E apparent activation energy, J mol^{-1}

k apparent reaction-rate constant, mol m^{-2} s^{-1}

k_o frequency factor, mol m^{-2} s^{-1}

n apparent reaction order for Na_2S; -

r dissolution rate of Sb_2S_3, mol m^{-2} s^{-1}

r_c coefficient of correlation, -

R gas constant (8.314), J mol^{-1} K^{-1}

t time of leaching, s

$t_{0.5}$ half- time of reaction for Sb_2S_3, s

T temperature, K

α fraction of antimony dissolved, -

REFERENCES

[1.] M. POURBAIX, Atlas d´Equilibres Electrochimiques, Paris–Vilars, 1963.

[2.] J.B. ACKERMAN, C.G. ANDERSON, S.M. NORDWICK, L.E. KRYS, Hydrometallurgy at the Sunshine Mine Metallurgical Complex, in: Proc. SME–AIME Meeting Hydrometallurgy-Fundamentals, Technology and Innovations, Littleton, 1993, pp. 477– 498.

[3.] S.M. NORDWICK, C.G. ANDERSON, Advances in antimony electrowinning at the Sunshine mine, in: Proc. SME–AIME Meeting Hydrometallurgy–Fundamentals, Technology and Innovations, Littleton, 1993, pp. 1107–1128.

[4.] Y. SONGQING, G. BINGKUN, J. HANYING, Experimental and fundamentals studies on sulfide minerals in China, in: Hydrometallurgy, ICH´92, vol.1, Changsha, China, 1992, pp. 163–168.

[5.] P. BALÁŽ, M. ACHIMOVIČOVÁ, Y. BASTL, T. OHTANI, M. SÁNCHEZ, Influence of mechanical activation on the alkaline leaching of enargite concentrate, Hydrometallurgy 54 (2000) 205– 216.

[6.] P. BALÁŽ, M. ACHIMOVIČOVÁ, Mechano–chemical leaching in hydrometallurgy of complex sulphides, Hydrometallurgy 84 (2006) 60– 68.

[7.] O. CELEP, I. ALP, H. DEVECI, Improved gold and silver extraction from refractory antimony ore by alkaline sulphide leach, Hydrometallurgy 105,3-4, (2011) 234–239.

[8.] I. ALP, O. CELEP, H. DEVECI, Alkaline sulphide pre-treatment of on antimonial refractory Au-Ag ore for improved cyanidation, JOM, Vol. 62, No. 11, (2010), 41-44

[9.] O. CELEP, I. ALP, D.PAKTUNC, Y. THIBAULT, Implementation of sodium hydroxide pre-treatment for refractory antimonial gold and silver ores, Hydrometallurgy, vol.108, 1-2, (2011), 109-114

[10.] E. SMINČÁKOVÁ, Leaching of natural stibnite using sodium hydroxide solution, JOM, Vol. 61, No. 10, (2009) 32-35

[11.] C.G. ANDERSON, L.E. KRYS, Leaching of antimony from a refractory precious metals concentrate, in: Proc. SME–AIME Meeting Hydrometallurgy-Fundamentals, Technology and Innovations, Littleton, 1993, pp. 341–365.

[12.] S. UBALDINI, F. VEGLIO, P. FORNARI, C. ABBRUZZESE, Process flow–sheet for gold antimony recovery from stibnite, Hydrometallurgy 57 (2000) 187– 199.

[13.] Z. TIANCONG, The Metallurgy of Antimony, Central South University of Technology Press, Changsa, The People´s Republic of China, 1988.

[14.] T. MOTANG, Z. TIANCONG, A thermodynamic study on the basic and negative potential fields of the systems of Sb–S–H_2O and Sb–Na–S–H_2O, Journal for central-south institute of mining and metallurgy, 1988, pp. 35–43.

[15.] F. HABASHI, Principles of extractive metallurgy, Vol. 1, Gordon and Breach, New York, 1970.

[16.] A.H. ZELIKMAN, G.M. VOLDMAN, L.V. BELJAJEVSKAYA, Theory of Hydrometallurgical processes, Russian edition, Metallurgia, Moscow, 1983.

[17.] H.Y. SOHN, M.E. WADSWORTH, Rate Processes of Extractive Metallurgy, Plenum Press, New York, 1979.

ACTA TECHNICA CORVINIENSIS – BULLETIN of ENGINEERING

ISSN: 2067-3809 [CD-Rom, online]