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KINETIC STUDY OF LEACHING STIBNITE IN SODIUM HYDROXIDE SOLUTION

Emília SMINČÁKOVÁ, Ľudmila KOMOROVÁ

Technical University of Košice, Faculty of Metallurgy,
Department of Chemistry, Košice, SLOVACIA

ABSTRACT:
This paper presents the results of the laboratory investigation of alkaline leaching of stibnite (Sb_2S_3) sample, which originated from Pezinok (Slovakia) mine. The leaching media used in this study were aqueous solutions containing sodium hydroxide. Establishing the effect of the following parameters on alkaline leaching: NaOH concentration, temperature of leaching and grain size of solid phase was the focus of this research. The apparent activation energy and apparent order of stibnite reaction with the solution that contained NaOH were determined from experiments as $E_a \approx 50.7$ kJ mol^{-1} and $n \approx 1$, respectively. The rate-determining step, according to experiments, is the reaction at the solid/liquid interface. A simple mathematical model equation was applied to describe the dissolution of antimony during leaching and to summarize the kinetic data.

Key words: stibnite, leaching, apparent activation energy, apparent order of reaction, rate-determining step

1. INTRODUCTION

From environmental aspect a pyrometallurgical processing of sulphide ores during production of non-ferrous metals causes considerable problems because this method results in considerable contamination of air by escaping sulphur dioxide, solid contaminants and other air pollutants. If these pollutants are toxic, which is the case of antimony and arsenic, the possibilities of hydrometallurgical ways of production of non-ferrous metals and the possibilities of processing the secondary materials seem to be superior and less polluting than the pyrometallurgical methods.

Studying kinetic aspects of the leaching process is one of the key elements before establishing the flowsheet for hydrometallurgical method of processing the antimony-bearing ores, minerals or secondary materials. The rate of leaching antimony, which is present in the form of stibnite mineral (Sb_2S_3), may be affected by selecting the appropriate leaching solution or by pre-treating the ore. From thermodynamic aspect for conversion of compounds to solution according to literature [1, 2] it is possible to use acid and also alkaline solutions. The most commonly used from alkaline dissolvent are solutions of sulphides of alkali metals or alkaline earth metal sulphides [3, 4]. Solution Na_2S [5-7] is the most frequently used for leaching of antimony as well as for complex sulphide concentrate with content of Cu, Pb, Zn and precious metals. Application of solution Na_2S offers a high level of selective separation of antimony from the other elements – mercury, tin and arsenic are exceptions [8].

According to the theoretical background of alkaline leaching in hydrometallurgy of antimony, the leaching process proceeds according the following reaction [8]:

$$Sb_2S_3 + 3\,Na_2S = 2\,Na_3SbS_3 \qquad \Delta G^{\circ}_{298} = -\,71.41\ \text{kJ} \qquad (1)$$

A negative value of standard Gibbs energy indicates that this reaction is thermodynamically feasible and spontaneous.

Aqueous solution of sodium hydroxide may react with antimony sulphide thus generating oxothioantimonites and thioantimonites [3, 8]:

$$Sb_2S_3 + 2\,NaOH = NaSbOS + NaSbS_2 + H_2O \qquad (2)$$

Concentration of leaching solution at the reaction interface and the interface area are determining the rate of chemical reaction. A study of kinetics of leaching natural stibnite by using sodium hydroxide solution requires an experimental determination of variation of antimony recovery with the leaching time under different conditions (temperature, concentration of leaching solution, particle size), i.e. determination of X (Sb)-t function. Recovery of antimony was calculated for the formula:

$$X = (m_0 - m)/m_0 \tag{3}$$

where m_0 is the amount of antimony in original sample in time t = 0 s, m is the amount of antimony in time $t \neq 0$ s.

The aim of the research presented in this paper was to study the following:

a) recovery of antimony during agitation leaching of natural stibnite at different:

- Particle size of solid phase
- Temperature
- Leaching time
- NaOH concentration in leaching solution

b) choosing of suitable mathematical model of leaching of natural stibnite (Sb_2S_3) by sodium hydroxide.

2. EXPERIMENTAL

Natural stibnite originating from Pezinok (Slovakia) mine was sampled and subjected to experimental laboratory investigation of leaching process. The chemical composition of the sample in weight percents is summarized in Table 1. Other elements that are not shown in Table 1 are as follows (weight %): 19.15% S, 10.4% Si, 1.81% Ca, 0.37% Mg, 0.115% Cu and traces of Hg, Ti, Mn, As, Sn, Bi, Ag, Ni.

Prior to leaching tests the stibnite sample was crushed, ground and screened to predetermined particle size fractions. Two size fractions, namely 0.25-0.5 mm and 0.18-0.25 mm were used for leaching experiments. The antimony content in different size fraction-chemical composition:

- between 0.25 and 0.50 mm – 34.76wt.%
- between 0.18 and 0.25 mm – 29.70 wt.%. %

Table 1. Chemical analyses of initial antimony concentrate used for experimental investigation

Element	Sb	Zn	Fe	Al	Pb
Weight%	49.3	5.43	0.84	0.65	0.63

Antimony concentrations in the leaching solutions were analyzed by AAS method (VARIAN, model Spectr AA-20 Plus, Australia). The parameters used for analyses were: supply current 10 mA, wavelength 217.5 nm, gap 0.2 nm, range of calibration 0.4-100 μg cm^{-3}. Arsenic and bismuth were analyzed by hydride generation method. Mercury was analyzed by a single-purpose automatic spectrometer TMA 254 (Canada) that is an AAS analyzer controlled by a microprocessor. The range of its sensitivity is 0.2-300 ng Hg [9].

The phase composition of the initial samples of mineral was carried out by X-ray diffraction method on DRON 2.0 with GUR-5 goniometer (Russia) under following conditions: CuK_{α}, 36 kV, 20 mA, the goniometer speed $1°min^{-1}$. The sensitivity of the X-ray diffraction analysis depends on the diffraction capacity of the sample which is typically 1 000 imp s^{-1}.

The range of measurements: from 10 to 100 2θ. Experimental conditions of leaching stibnite in NaOH solutions:

- The volume of leaching solution 200 cm^3
- The sample weight 0.4 g
- The rate of rotation of the stirrer 10 s^{-1}

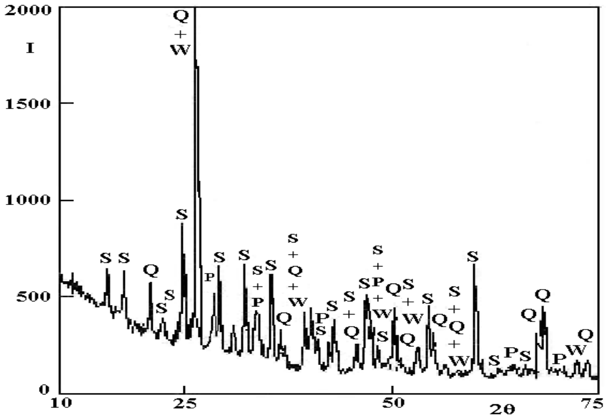

Figure 1. Results of X-ray diffraction analysis of sample with the particle size 0.18-0.25 mm. (S-stibnite, Q-quartz, P-pyrite, W-wurtzite)

The leaching tests were carried out in 250 cm^3 glass containers. Solid and liquid phases were agitated by glass stirrer that rotated at constant speed 10 s^{-1}. Leaching solutions were prepared by dissolving pure NaOH p.a. (Lachema, Brno, Czech Republic) in distilled water. Temperatures at which the leaching tests were performed were maintained at constant level by water thermostat.

3. RESULTS AND DISCUSSION

3.1 Mineralogical composition

The phase analysis revealed that the sample contained stibnite (Sb_2S_3), quartz (SiO_2), pyrite (FeS_2) and wurtzite (ZnS). Other antimony-containing phases were not identified [10].

The X-ray diffraction pattern of the sample with the particle size between 0.18-0.25 mm is plotted in figure 1.

3.2 Effect of particle size

The effect of particle size of natural stibnite on antimony recovery was monitored for two grain classes: 0.18-0.25 mm and 0.25-0.5 mm. Fig. 2 shows the antimony recovery variation with time when leaching was carried out at 298K in 2% NaOH solution. Fig.3 shows the antimony recovery at 323K in 1% NaOH solution. Fig. 2 and 3 indicate positive affect of the decreasing particle size of stibnite on antimony recovery.

3.3 Effect of temperature

Positive effect of increasing temperature of leaching on antimony recovery is shown in Fig.4 where leaching in 1% NaOH solution was carried out on stibnite sample with particle size range between 0.18 and 0.25 mm. Similar situation is depicted in Fig. 5 for stibnite sample particle size range from 0.25 to 0.5 mm.

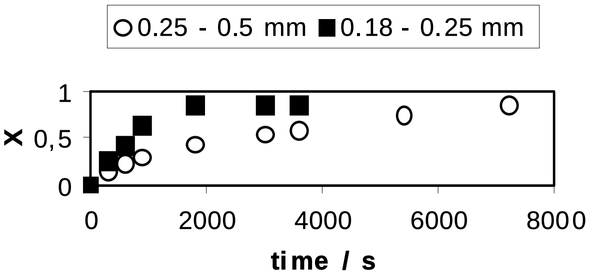

Figure 2. Recovery of antimony versus leaching time of stibnite sample of different size fractions (indicated inside the figure). (Temperature 298 K; 2wt. % NaOH; Stirring rate 10 s^{-1})

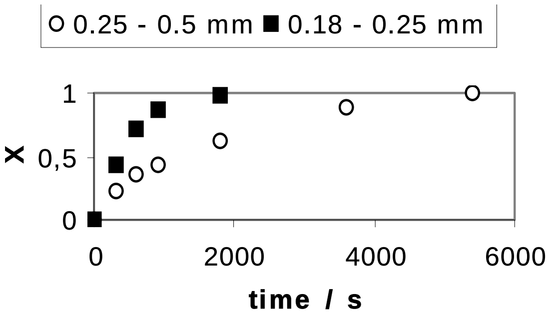

Figure 3. Recovery of antimony versus leaching time of stibnite sample of different size fractions (indicated inside the figure). (Temperature 323 K; 1wt. % NaOH; Stirring rate 10 s^{-1})

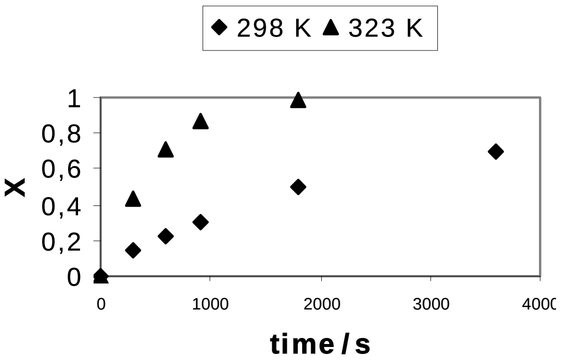

Figure 4. Variation of antimony recovery with leaching time (1wt. % NaOH; Particle size 0.18-0.25 mm; Stirring rate 10 s^{-1})

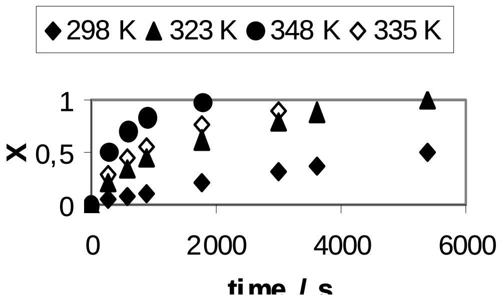

Figure 5. Variation of antimony recovery with leaching time (1wt. % NaOH; Particle size 0.25-0.5 mm; Stirring rate 10 s^{-1})

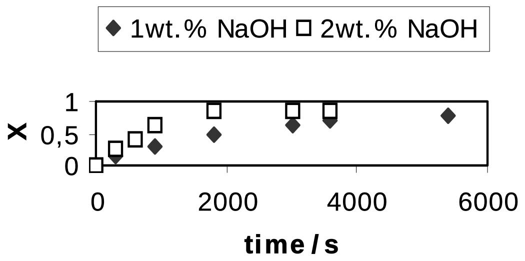

Figure 6. Variation of antimony recovery with leaching time for two different solution concentrations, indicated inside the figure. (Temperature 298 K; Particle size 0.18-0.25 mm; Stirring rate 10 s^{-1})

3.4 Effect of concentration of the leaching solution NaOH

Effect of solution concentration on antimony recovery was evaluated in leaching tests carried out at 298K by using samples of two different size fractions. Leaching test results shown in Fig.6 and Fig.7 correspond to stibnite sample size fractions 0.18 do 0.25 mm and 0.25 do 0.5 mm, respectively.

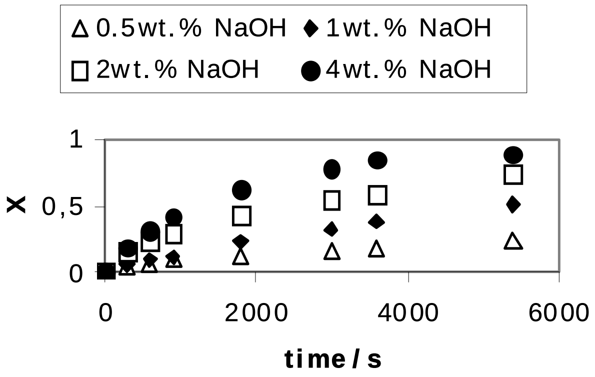

Figure 7. Variation of antimony recovery with leaching time for four different solution concentrations, indicated inside the figure. (Temperature 298 K; Particle size 0.25-0.5 mm; Stirring rate 10 s^{-1})

Apparent activation energy E and apparent order of reaction n were determined by linear regression method from equations 4 and 5 respectively [11]:

$$\ln t_{0.5} = \mathrm{const}_1 + (E/R)T^{-1} \tag{4}$$

$$\ln t_{0.5} = \mathrm{const}_2 - n \ln c_{NaOH} \tag{5}$$

Results are given in Tab. 2, where $t_{0.5}$ is half-time of leaching, i.e. time which is required to obtain 0.5antimony recovery. Hal-time t0.5 (in seconds) determined in each test is presented in Tab.3.

Table 2. Values of the apparent activation energy E and apparent order of reaction n.

Size fraction /mm	E /kJ mol^{-1}	Apparent reaction order n
0.25 – 0.5	50.734	1

Table 3. Experimental conditions of laboratory leaching tests in NaOH solution and half-time of reaction, $t_{0.5}$

Number	NaOH / wt.%	Particle size / mm	Temperature / K	$t_{0.5}$ / s
1	1	0.25-0.5	298	5260
2	1	0.25-0.5	323	1200
3	1	0.25-0.5	348	250
4	2	0.25-0.5	298	2500
5	1	0.18-0.25	298	1950
6	4	0.25-0.5	298	1300
7	1	0.18-0.25	323	350
8	1	0.25-0.5	335	700
9	2	0.18-0.25	298	550

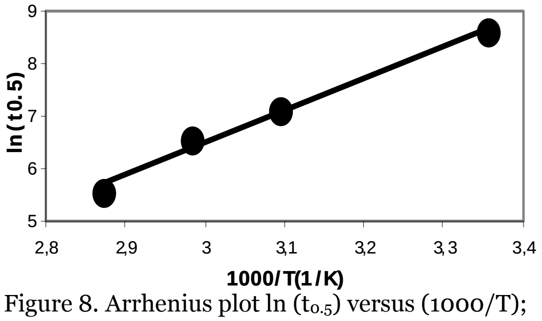

Figure 8. Arrhenius plot ln ($t_{0.5}$) versus (1000/T); correlation coefficient r = 0.9930 (1wt. % NaOH; Particle size 0.25-0.5 mm; Stirring rate 10 s^{-1})

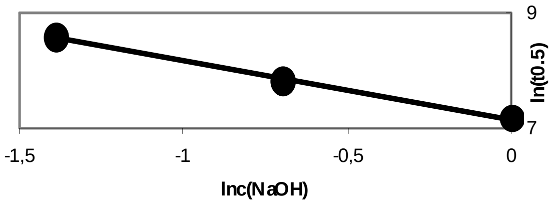

Figure 9. Variation of ln ($t_{0.5}$) with ln c_{NaOH} correlation coefficient r = - 0.9993. (Temperature 298 K; Particle size 0.25-0.5 mm; Stirring rate 10 s^{-1})

Arrhenius plot, i.e. ln $t_{0.5}$ vs. 1000/T and variation of ln $t_{0.5}$ with ln c_{NaOH} are depicted in Fig. 8 and Fig.9 respectively. Correlation coefficients, r, are given in captions.

The value of the apparent activation energy, E = 50.735 kJ mol^{-1} suggests that leaching of stibnite in NaOH solution proceeds in the kinetic region [12, 13] and the variation of ln $t_{0.5}$ with 1000/T depicted in Fig.8 indicates that the mechanism of leaching the natural stibnite remains the same in the entire range of temperatures, i.e. between 298 and 348 K, at which the leaching was carried out.

In order to evaluate how the leaching mechanism is being affected by reaction conditions in the entire range of temperature, solution concentration and particle size, we used the dimensionless equation (6) in accordance with the literature [11]:

$$X = 1 - (1 - 0.2063.\tau)^3 \tag{6}$$

where τ is relative leaching time that is defined by the following equation:

$$\tau = \frac{t}{t_{0.5}} \qquad (7)$$

in which t is the actual leaching time and $t_{0.5}$ is half-time of leaching, i.e. time that is required in order to achieve 0.5 antimony recovery. Fig. 10 depicts variation of antimony recovery with relative time ($t/t_{0.5}$). This variation suggests that the mechanism of leaching remains the same in the entire range of experimental conditions applied in this study, which are summarized in Tab. 3. By comparing results of experiments with results obtained from equation (6) that is depicted by curve in Fig.10 it may be concluded that the agreement between them is satisfactory. However the points depicted in Fig.10 that correspond to experiments in which the antimony recovery was above 0.75 (i.e. $X > 0.75$) do not fit the curve. This disagreement may be a result of: a) reverse precipitation of Sb_2S_3 from the solution and/or b) by rather long half-times of reactions in this range of experimental conditions, the half-times varying between 550 and 5 260 s) see Tab.3).

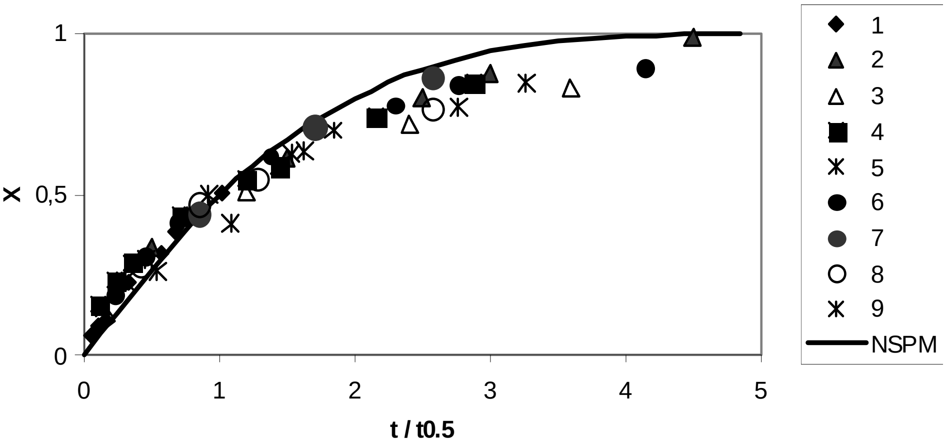

Figure 10. Experimentally determined variation of antimony recovery, X, with relative leaching time ($t/t_{0.5}$)

5. CONCLUSION

While studying the kinetics of leaching stibnite, in which the accompanying minerals are quartz, pyrite and wurtzite the leaching solutions that were applied were aqueous solutions of sodium hydroxide. Results of this experimental study can be summarized as follows:

a) The lower the initial particle size of stibnite the shorter is the leaching time.
b) Within temperature range between 298K and 348K higher temperature had positive effect on rate of antimony transfer into solution. The apparent activation energy $E_a \approx 50.7$ kJ mol^{-1} suggests that the leaching process is taking place within the kinetic region.
c) The apparent order of reaction (2) determined for leaching in sodium hydroxide solutions in the concentration range from 0.125 mol dm^{-3} to 1 mol dm^{-3} is $n \approx 1$.
d) The model dimensionless equation describing the mechanism of leaching stibnite in solutions containing sodium hydroxide is as follows: $X (Sb) = 1 – (1 – 0.2063.\tau)^3$, where τ is the relative leaching time.

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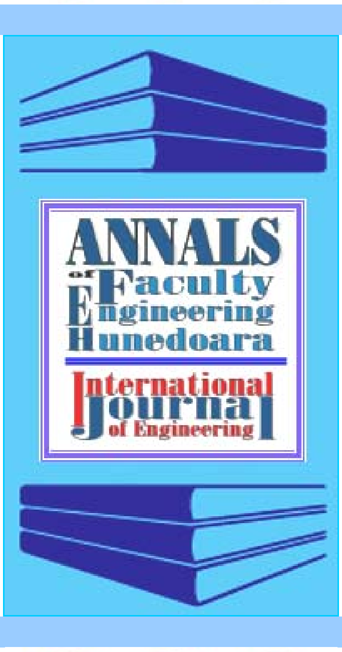

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