

Leaching of Natural Stibnite Using Na₂S and NaOH Solutions

Emília Sminčáková¹, Pavel Raschman²
 Faculty of Metallurgy, Technical University of Košice
 Letná 9, 042 00 Košice, Slovak Republic
¹emilia.smincakova@tuke.sk
²pavel.raschman@tuke.sk

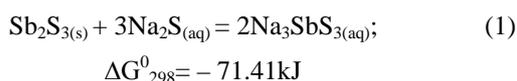
Abstract-First stage of the hydrometallurgical production of antimony is leaching of the raw material that contains antimony-bearing mineral. The raw material can be ore or concentrate. Leaching can be carried out either in alkaline (Na₂S+NaOH; NaOH) or acid (HCl; H₂SO₄; HF) solutions. In order to achieve good antimony recovery it is essential to leach the raw material under optimum conditions. Kinetics of the reaction between particulate stibnite and mixed Na₂S + NaOH solutions were studied. The effects of concentrations of Na₂S 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 Na₂S and NaOH concentration (from 0.5 wt. % to 2.0 wt. %), and temperature (from 292 K to 327 K); b) reached its maximum at Na₂S: NaOH weight ratio equal to 1:1; c) decreased with an increase in particle size (from 40 μm to 500 μm) and L/S ratio (from 10 to 100). The results are presented in terms of the shrinking (nonreacted) core model and shrinking porous-particle model. Apparent activation energy is approximately 44 kJ mol⁻¹ and the apparent reaction order for Na₂S varies from 1.4 to 1.7. Calculated values of the kinetic parameters indicate that the leaching process is controlled by both intrinsic chemical reaction between Sb₂S₃ and Na₂S at the liquid/solid interface, and pore diffusion.

Keywords-Stibnite, Kinetics, Alkaline leaching, Activation energy, Order of reaction

I. 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 Sb₂S₃ dissolves in mixed leaching solutions of Na₂S + NaOH [2]-[6]. Alkaline Na₂S solution acts as a 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 [7, 8].

Leaching of Sb₂S₃ in Na₂S solution can be described by the following chemical reaction [9]:



Negative value of the standard Gibbs energy suggests that reaction (1) is feasible and spontaneous.

The reaction mixture that was formed by chemical dissolution of Sb₂S₃ in Na₂S 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-H₂O and Sb-S-Na-H₂O systems at 298 K as presented in [10]. At pH < 13.6 antimony passes into solution as a complex trivalent anion SbS₃³⁻ [10]. Antimony sulphide and sodium sulphide may combine to form the following species: NaSbS₂, Na₃SbS₃, Na₆Sb₂S₆, Na₄Sb₂S₅, Na₂Sb₂S₄, and Na₂Sb₄S₇ [11].

The solubility of antimony – containing species in water is decreasing in the following order: Na₃SbS₃ > Na₃SbS₄ > NaSbSO > Na₃SbO₃ > NaSbS₂ > Na₃SbO₄.

The solubility in Na₂S solution is decreasing as follows: Na₃SbS₃ > Na₃SbS₄ > NaSbSO > NaSbS₂ > Na₃SbO₃ > Na₃SbO₄.

On the basis of the comparisons of the solubility of antimony-containing species in water and in solutions containing Na₂S it can be said that Na₃SbS₃ is an important final product of leaching both antimony oxides and antimony sulphides in alkaline Na₂S – containing medium [9].

The role of NaOH in mixed Na₂S and NaOH leaching solution is to inhibit hydrolysis of Na₂S [8, 12]. Na₂S hydrolysis is a two-stage process:



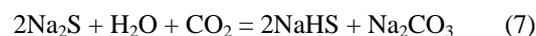
The overall reaction is the sum of reactions (2) and (3):



Under conditions when there is insufficient amount of Na₂S in mixed leaching solution containing Na₂S and NaOH, the role of NaOH may be not only to suppress hydrolysis of Na₂S but act as a leaching agent for Sb leaching [13]-[16] according to Eq. (5):



Sodium sulphide can also react with oxygen and with carbon dioxide present in the surrounding atmosphere according to reactions [9]:



Reactions (6) and (7) are undesirable for leaching of antimonite.

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 (5), or by external mass transfer [17, 18]. 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 [9, 19].

The non-porous shrinking-particle model in the form [18]

$$1 - (1 - \alpha)^{1/3} = k' t \quad (8)$$

was used to analyse 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 mixed Na₂S + NaOH solutions.

II. EXPERIMENTAL

A. 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 I CHEMICAL COMPOSITION OF THE STIBNITE SAMPLE

Element	Sb	S	Si	Zn	Ca	Fe
Weight %	49.35	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 II CHEMICAL COMPOSITION (IN WT.%) OF INDIVIDUAL SIZE FRACTIONS

Particle size (µm)	250–500	180–250	71–90	40–71
Sb (wt.%)	34.76	29.70	47.00	54.75
Si (wt.%)	15.46	20.62	12.66	6.14
Fe (wt.%)	1.12	1.01	1.01	0.90
Zn (wt.%)	1.03	0.86	0.73	0.52

Stibnite (Sb₂S₃) and quartz (SiO₂) were found to be the predominant mineral species according to the results of the X-ray diffraction analysis. Accompanying minerals were identified as pyrite (FeS₂) and wurtzite (ZnS). Other mineral phases were not identified [14].

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.

B. Experimental Procedure and Evaluation of the 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 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 Na₂S + NaOH solution in the reactor had reached the required temperature, 0.4 g of stibnite sample was added. Samples (1 or 2 mL) of the reaction mixture were withdrawn from the reactor at appropriate time intervals, filtered and the filtrates were analyzed using AAS method. pH values of the samples to be analyzed by this method were not modified. The parameters used in analyses of antimony in the samples were as follows: supply current 10 mA, wavelength 217.5 nm, gap 0.2 nm, and range of calibration 0.4–100 µg cm⁻³.

The experiments were carried out under following reaction conditions: temperature from 291 K to 333 K, Na₂S and NaOH concentration from 0.5 wt.% to 2 wt.%, Na₂S:NaOH weight ratio equal to 1:1.

To find the optimum Na₂S to NaOH ratio for leaching the sample with particle size between 250 and 500 µm in mixed leaching solution at 292 K the following solution concentrations were applied: 2 wt.% Na₂S+2 wt.% NaOH, 2 wt.% Na₂S+0.5 wt.% NaOH and 0.5 wt.% Na₂S+2 wt.% NaOH.

In each case of testing a fresh Na₂S+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.% Na₂S+2 wt.% NaOH.

III. RESULTS

A. Effect of Temperature

The temperature dependence of the leaching rate was determined for size fractions 180–250 µm and 250–500 µm, 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.

B. Effect of Na₂S and NaOH Concentration

The effect Na₂S and NaOH concentrations was studied through a series of tests performed at 292 K. The experiments showed that the rate of stibnite dissolution is significantly affected by concentrations of Na₂S and NaOH; an example is presented in Fig. 2.

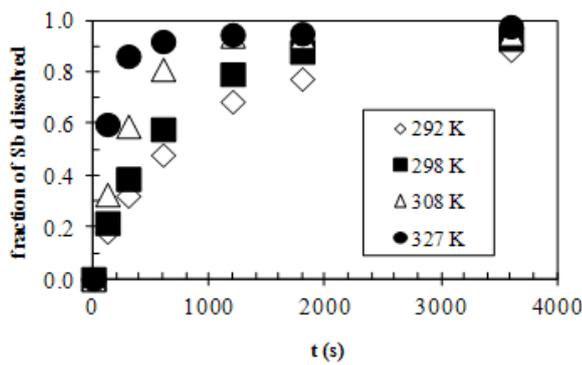


Fig. 1 effect of leaching temperature on fraction of antimony dissolved (reaction conditions: 1wt.% na₂s + 1wt.% naoh; particle size 180–250 μm; agitation rate 10 s⁻¹).

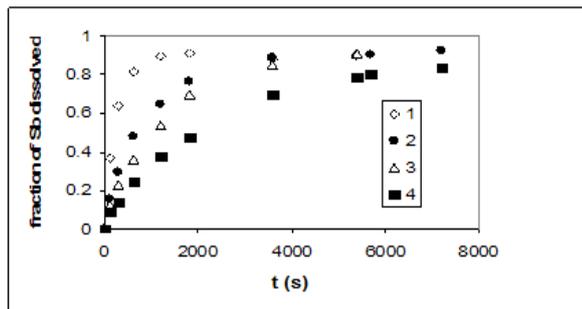


Fig. 2 effect of chemical composition of the leaching solution on fraction of antimony dissolved: 1 – (2wt.% na₂s + 2wt.% naoh); 2 – (1wt.% na₂s + 1wt.% naoh); 3 – (0.75wt.% na₂s + 0.75wt.% naoh); 4 – (0.5wt.% na₂s + 0.5wt.% naoh) (reaction conditionst=292 k;particle size 180–250μm;agitation rate 10s-1)

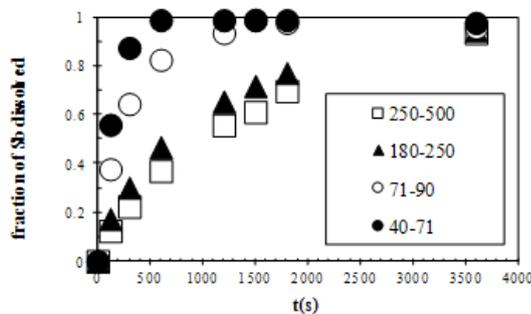


Fig. 3 effect of particle size on fraction of antimony dissolved (particle diameter in micrometers / μm) (reaction conditions: 1wt.% na₂s + 1wt.% naoh;t= 292; agitation rate 10s-1)

C. Effect of Particle Size

The effect of particle size on the leaching behaviour 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.

IV. DISCUSSION

The kinetic experiments were carried out under reaction conditions characterised by a relatively high excess of Na₂S (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, Na₂S: Sb₂S₃ molar ratio ≥ 18.6 was used, and the concentration of Na₂S (and NaOH) in the bulk aqueous phase was maintained constant within >85 % rel. during each run. This means that in the least favourable case (leaching in the solution containing 0.5 wt.% Na₂S + complete antimonite dissolution) almost 15 rel.% of the total amount of Na₂S present in the leaching solution was consumed. Therefore it appears that during leaching the concentration of Na₂S in the leaching solution varies only insignificantly and is evident mainly when leaching in solutions containing higher Na₂S concentration and at lower antimony conversions.

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 Na₂S:NaOH weight 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). The experiments also showed that the rate is significantly affected by the Na₂S:NaOH weight ratio and reaches its maximum at Na₂S:NaOH ≈ 1:1; the situation is represented in Fig. 6.

The kinetic experiments were therefore carried out under the optimum reaction conditions which were as follows: agitation rate = 10 s⁻¹, L:S weight ratio = 500, Na₂S:NaOH weight ratio 1:1. The appropriateness of the non-porous shrinking particle model (NSPM) was evaluated using graphical analysis. The NSPM model (8) in the form

$$\alpha = 1 - (1 - 0.2063 t/t_{0.5})^3 \tag{9}$$

was used to analyse the leaching process [18, 20]. The half reaction time t_{0.5} represents a period of time which is necessary under certain reaction conditions to dissolve one half of the amount of Sb₂S₃ originally present in the sample of stibnite. The values of t_{0.5} for individual experiments are summarized in Table 3. The scatter diagram shown in Fig. 7 reveals that there is a very good correlation between model and experiment for fractions of antimony dissolved up to 0.8. Hence, only α-t kinetic data characterized by α < 0.8 were used to calculate the values of model parameters.

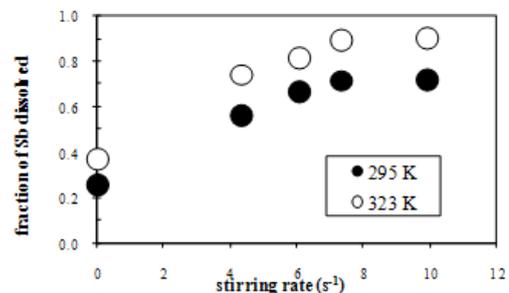


Fig. 4 effect of stirring rate on fraction of antimony dissolved (reaction conditions: 1wt.% na₂s + 1wt.% naoh; temperatures 295 k and 323 k; agitation rate 10s⁻¹).

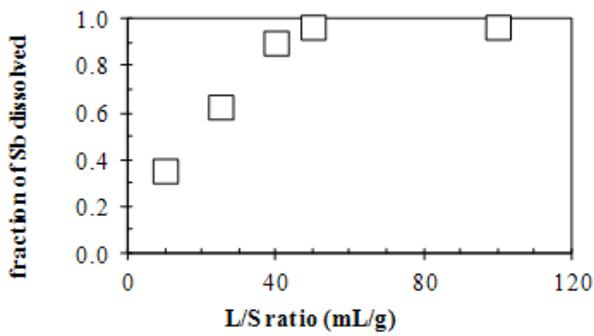


Fig. 5 effect liquid to solid ratio on fraction of antimony dissolved (reaction conditions: 1wt.% na2s + 1wt.% naoh; t= 297 k ; particle size 40-180 μm; leaching time 30 minutes; agitation rate 10s-1).

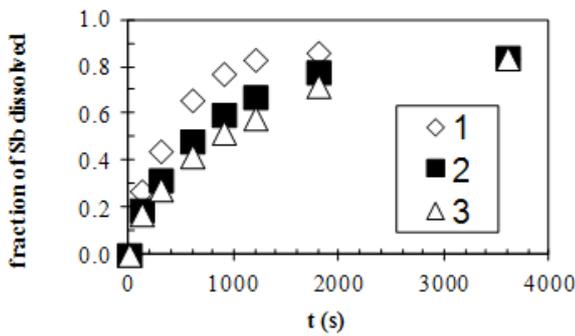


Fig. 6 effect of na2s to naoh weight ratio on fraction of antimony dissolved: 1 – (2wt.% na2s + 2wt.% naoh); 2 – (1wt.% na2s + 0.5wt.% naoh); 3 – (0.5wt.% na2s + 2wt.% naoh) (reaction conditions: t=292k; particle size 250–500μm; agitation rate 10s-1)

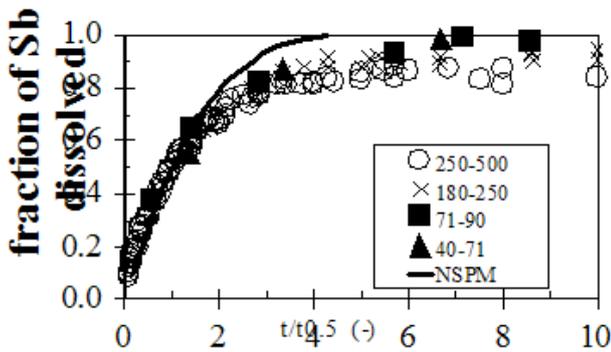


Fig. 7 conversion vs. reduced time relationship for dissolution of stibnite: points –measured data, full line – eq. (9) (reaction conditions: na2s to naoh weight ratio = 1:1; agitation rate 10s-1).

Eliminated effect of agitation rate on the overall rate of the leaching process indicates that the surface chemical reaction (1) and/or (5) might be the rate-determining step. When the rate r of the surface reaction [18, 20, 21] is expressed as a power-law function of the concentration of Na₂S on the particle surface, $c_{Na_2S,w}$, the result is

$$r = k c_{Na_2S,w}^n \tag{10}$$

TABLE III
EXPERIMENTAL CONDITIONS OF THE LEACHING TESTS OF STIBNITE IN ALKALINE SOLUTIONS Na₂S+NAOH AND T_{0.5}

Number	wt.% Na ₂ S	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

TABLE IV
VALUES OF THE APPARENT ACTIVATION ENERGY E AND APPARENT ORDER OF REACTION N

Size fraction (μm)	E (kJ mol ⁻¹)	Apparent reaction order n
250–500	44.1±2.2	1.42±0.14
180–250	44.4±2.1	1.7±0.09

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

$$k_s = k_0 \exp(-E/(RT)) \tag{11}$$

where k_0 is the frequency factor; E the apparent activation energy; R the gas constant. The values of the apparent activation energy E and the apparent order of reaction n were obtained by linear regression using expressions

$$\ln t_{0.5} = \text{const}1 - n \ln c_{Na_2S} \tag{12}$$

and

$$\ln t_{0.5} = \text{const}2 + (E/R)T^{-1} \tag{13}$$

respectively, and are summarized in Table 4. Typical examples of Arrhenius and $\ln t_{0.5}$ vs. $\ln c_{Na_2S}$ plots are shown for illustration in Figs. 8 and 9 respectively. Fractional order of reaction with regard to the initial Na₂S concentration and

relatively high activation energy are indicative of a process controlled by surface reaction.

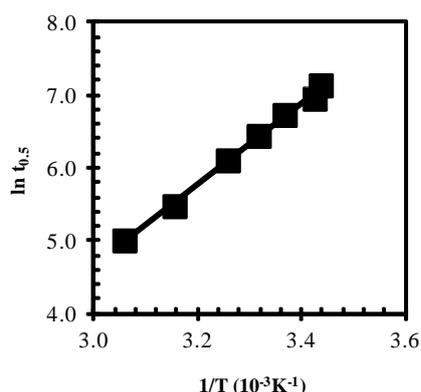


Fig. 8 an example of arrhenius plot (reaction conditions: 1wt.% Na₂S + 1wt.% NaOH; particle size 250–500 μm; agitation rate 10 s⁻¹).

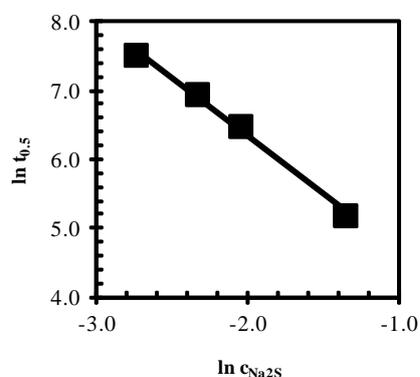


Fig. 9 an example of logarithmic ln t_{0.5} vs. ln C_{Na2S} (reaction conditions: particle size 180–250 μm; t=292k; agitation rate 10 s⁻¹)

V. CONCLUSIONS

This paper brings the measured kinetic data on stibnite alkaline leaching. Kinetics of the dissolution of natural stibnite in mixed Na₂S + NaOH solutions were investigated. Several facts indicate that the dissolution is controlled by the surface chemical reaction of Sb₂S₃ with Na₂S + NaOH solution at the liquid-solid interface:

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

The value of apparent activation energy is relatively high, ≈ 44 kJ mol⁻¹.

It was concluded that the reaction between Sb₂S₃ and Na₂S (Eq. (1)) is much faster than that between Sb₂S₃ and NaOH (Eq. (5)) under the conditions considered in the present work and fractional order of reaction with regard to Na₂S (from 1.4 to 1.7) was obtained.

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