



LEACHING OF STIBNITE IN NaOH SOLUTIONS

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ABSTRACT:

The objective of the research study presented in this paper was to determine, under laboratory conditions, antimony recoveries in alkaline leaching of the stibnite (Sb_2S_3) sample originated from Pezinok (Slovakia) mine. The leaching media used were aqueous solutions containing NaOH or $Na_2S+NaOH$. Establishing the effect of the following parameters on alkaline leaching: NaOH and $Na_2S+NaOH$ concentration in the leaching solution, temperature of leaching and grain size of the solid phase were the focus of this research. The experiments were carried out in order to elucidate the role of NaOH in alkaline leaching and its effect on leaching in mixed $Na_2S + NaOH$ solution.

KEYWORDS:

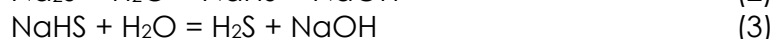
antimony, alkaline leaching, stibnite, recovery

1. INTRODUCTION

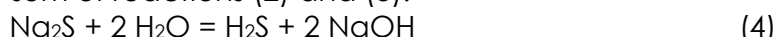
At the first stage of hydrometallurgical processing of stibnite (Sb_2S_3), i. e. its leaching, the following acidic leaching media are commonly applied: mixture of hydrochloric and tartaric acids, mixture of nitric and tartaric acids and hot concentrated sulphuric acid [1]. In alkaline leaching, on the other hand, the aqueous solutions of alkali metal sulphides or alkaline earth metal sulphides are considered to be the best leaching agents [1, 2, 3]. Alkaline Na_2S solution is the universal solvent for antimony compounds. The solubility of the majority of other metals is, however, very low except for As, Hg and Sn [4, 5, 6]. It is believed that the alkaline leaching of antimony sulphide proceeds in accordance with the following reaction [7, 8]:



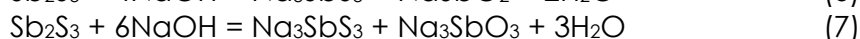
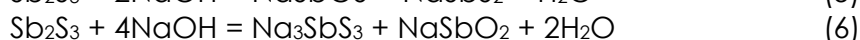
The role of NaOH in alkaline leaching is to inhibit hydrolysis of Na_2S [1, 8]. Na_2S hydrolysis is a two-stage process:



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



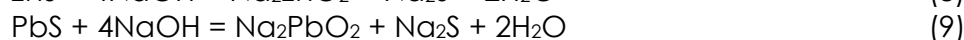
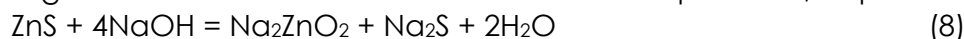
Aqueous solution of NaOH may react with antimony sulphide according to reactions [1, 9, 10]:



The reactions (1), (5), (6) and (7) suggest that stibnite dissolution in alkaline solution results in formation of different antimony species that are water-soluble such as antimonites, thioantimonites, oxothioantimonites, etc. Natural stibnite is always

accompanied by other minerals such as quartz, pyrite, wurtzite and other minor mineral constituents.

Lead and zinc sulphides that accompany stibnite may be dissolved in NaOH leaching medium in the form of soluble zincate and plumbite, respectively [8]:



Iron (II) sulphide reacts with sodium hydroxide according to the following reaction:



Reactions (8), (9) a (10) result in formation of Na_2S , which, on the other hand is the reactant in reaction (1).

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

- a) Antimony extraction during agitation leaching of natural stibnite at different:
 - NaOH concentration in leaching solution
 - leaching time
 - temperature
 - particle size of solid phase
- b) Behaviour of accompanying metals (Fe, Pb, Zn) during alkaline leaching of stibnite
- c) The role of NaOH in mixed leaching solution ($\text{Na}_2\text{S} + \text{NaOH}$) and its effect on Sb recovery.

2. EXPERIMENTAL

Laboratory experiments were carried out using stibnite that originated from Pezinok Mine (Slovak Republic). The chemical composition expressed in weight percents is summarized in Table 1. Other minor elements that are not shown in Table 1 are as follows (weight %): 1.81% Ca, 0.65% Al, 0.37% Mg, 0.115% Cu, 0.015% Hg, 0.0018% Ni and traces of Ti, Mn, As, Sn, Bi, Ag.

Prior to leaching tests the stibnite sample was crushed, ground and screened to predetermined particle size fractions. Two size fractions, namely 0.25 - 0.5mm and 0.18 - 0.25mm were used for leaching experiments. The respective compositions of the above size fractions are presented in Table 2.

Table 1. Chemical analyses of the initial antimony material

Element	Sb	S	Si	Zn	Fe	Pb
Weight %	49.3	19.15	10.4	5.43	0.84	0.63

Table 2. Chemical composition of size fractions

Particle size/mm	Chemical analysis/wt.%			
	Sb	SiO ₂	Fe	Zn
0.25 – 0.5	34.76	33.13	1.12	1.03
0.18 – 0.25	29.70	44.18	1.01	0.86

All leaching experiments were carried out on 0.4 g of sample that was added to 200 cm³ of solution in glass reactor with the total volume of 250 cm³. Solid and liquid phases were agitated by a glass stirrer that rotated at constant speed 10 s⁻¹. The experimental temperatures: 298 K, 323 K, 348 K were maintained constant by water thermostat. The maximum duration of leaching was 180 min.

Prior to leaching experiments at 298 K the NaOH solutions applied for leaching were characterized by the following theoretically calculated parameters: ionic strength I, mean activity coefficient γ_{\pm} and pH. Results are summarized in Table 3.

Table 3. Characteristics of NaOH leaching solutions: I, γ_{\pm} and pH

NaOH/wt.%	I/mol dm ⁻³	γ_{\pm}	pH
0.5	0.125	0.6655	12.9
1	0.25	0.5623	13.1
2	0.5	0.3535	13.3
4	1	0.3162	13.5

Ionic strength of solutions according to Debye – Hückel theory [11] is expressed by equation:

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (11)$$

where

c_i is concentration of the i th ion,

z_i is its charge (positive for cations and negative for anions)

The mean-activity coefficient at 298K for a solution with anion charge z_- and cation charge z_+ is expressed by:

$$-\log \gamma_{\pm} = |z_+ z_-| 0.5 \sqrt{I} \quad (12)$$

Activity of hydroxyl anion, pOH and pH are calculated from:

$$a_{OH^-} = c_{OH^-} \gamma_{OH^-}; pOH = -\log a_{OH^-}; pH = 14 - pOH.$$

It was assumed that leaching of antimony proceeds via reaction (5). In all experiments an excess amount of leaching solution was applied, keeping the molar ratio of NaOH to Sb higher than 21.

Antimony, zinc, iron, and lead concentrations in the leaching solutions were analyzed by AAS method (VARIAN, model Spectr AA-20 Plus, Australia). The parameters used for analyses are summarized in the Table 4.

Table 4. AAS parameters of analysis

Element	Supply current /mA	Wavelength/nm	Gap/nm	Range of calibration/ $\mu\text{g cm}^{-3}$
Sb	10	217.6	0.2	0.4 – 100
Fe	5	372	0.2	1 – 100
Pb	10	216.7	0.7	0.1 – 5
Zn	5	213.9	1	0.01 – 2

The phase composition of the initial samples was determined by X-ray diffraction method on DRON 2.0 with GUR-5 goniometer (Russia) under following conditions: $\text{CuK}\alpha$, 36 kV, 20 mA, the goniometer speed 1° min^{-1} . The detectability of the X-ray diffraction analysis depends on the diffraction capacity of the sample which is typically $1\ 000 \text{ imp s}^{-1}$. The range of measurements: from 10 to $100\ 2\theta$. Leaching solutions were prepared by dissolving pure NaOH and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, p.a. (Lachema, Brno, Czech Republic) in distilled water.

3. RESULTS AND DISCUSSION

The phase analysis was carried out in order to identify the mineralogical composition of sample. Identified minerals were: stibnite (Sb_2S_3), quartz (SiO_2), pyrite (FeS_2) and wurtzite (ZnS). Other antimony-containing phases were below the determination limit [12, 13].

3.1 Stibnite leaching in NaOH solution

Effect of NaOH concentration in leaching solution on leaching solid sample fraction 0.25mm - 0.5 mm was studied at 298 K. The duration of leaching was 0 – 180 min. Samples of leaching solution taken at regular intervals were analysed for Sb. Results of chemical analyses were then used for calculating antimony recoveries at

particular time. Variation of antimony recovery with time is presented in Fig.1. Results are presented in Figure 1. The changing position of curves depicted in Figure 1 clearly suggests the positive effect of increasing NaOH concentration in leaching solution, i. e. pH of the solution on antimony recovery at constant temperature. For example, maximum Sb recovery in 1wt.% NaOH (pH= 13.1) solution was 50.8 %, whereas in 2 wt.% NaOH (pH=13.3) solution it was much higher, reaching 74.2% after 90 minutes of leaching which is a 24% increase of recovery in comparison with 1wt.% NaOH solution. Leaching experiment with 4 wt.% NaOH solution was interrupted after 90 min as further agitation of solid/liquid suspension did not bring about any addition transfer of antimony into the aqueous phase as can be seen from the trends of other three curves (0.5wt.% NaOH, 1wt.% NaOH and 2wt.%) that level off after 90 min. Leaching solutions seem to reach the equilibrium Sb concentration that is maintained at constant level.

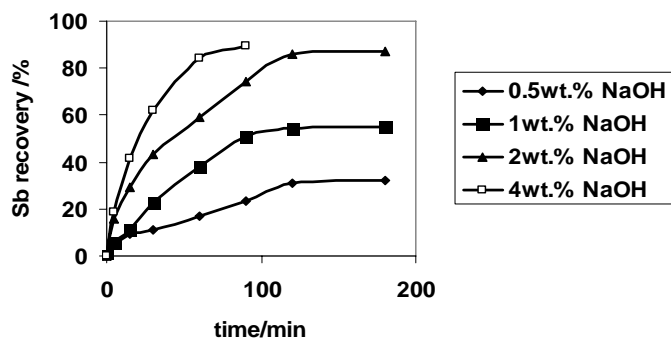


Figure 1. Effect of NaOH concentration in leaching solution on variation of antimony recovery versus time (Temperature 298 K; Particle size 0.25 – 0.5 mm; Stirring rate $10s^{-1}$)

The beneficial effect of temperature on antimony recovery in leaching in 1wt.% NaOH solution is documented in Figure 2. Increasing temperature from 298 K to 323 K resulted in the corresponding enhancement of antimony recovery from 38 to 87 % after 60 min leaching time.

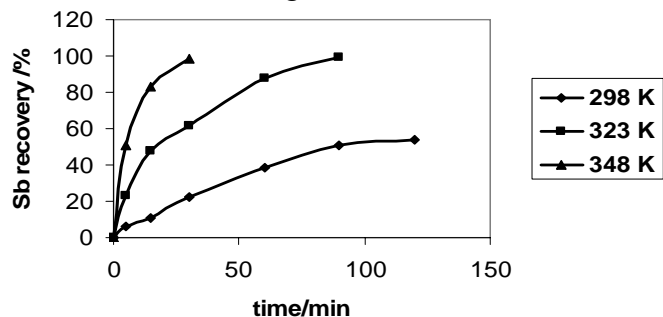


Figure 2. Antimony recovery versus time at different temperatures (1wt.% NaOH; Particle size 0.25 – 0.5mm; Stirring rate $10s^{-1}$)

Figure 3 shows the rate of Sb leaching in 1 wt.% NaOH solution at 298 K. The relative location of leaching curves suggests that antimony passes into leaching solution faster from the particles size fraction 0.18 – 0.25 mm than from 0.25 – 0.5 mm size fraction and higher recoveries are reached at all time intervals. This means that the lower the initial grain size of the solid phase the higher the antimony recovery.

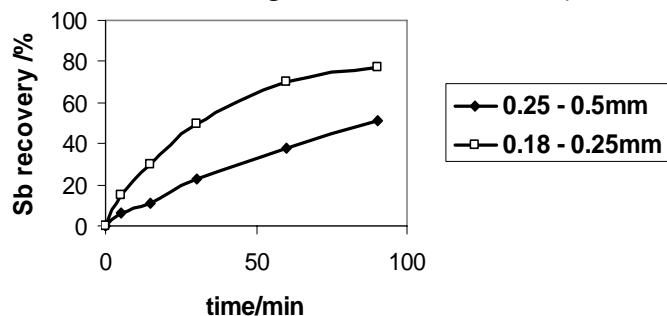


Figure 3. Antimony recovery from two size fractions versus leaching time (1wt.% NaOH; T= 298 K; Stirring rate $10s^{-1}$)

3.2 Behaviour of accompanying metals in NaOH leaching solution

Effect of temperature on recoveries of Fe, Pb and Zn in leaching with 1 wt.% NaOH solution is summarized in Table 5.

Table 5. Effect of temperature on Fe, Pb and Zn recoveries in leaching with 1 wt.% NaOH solution

Temperature/ K	Recovery/%		
	Fe	Pb	Zn
298 (90min)	1.74	0.49	0.82
323 (90min)	2.01	0.59	0.91
348 (60min)	2.34	0.49	0.90

The data shown in Table 5 for Pb and Zn recoveries are below 1%. Temperature increase resulted only in higher recoveries of Fe; at 348 K after 60 min leaching the recovery of Fe reached 2.34%. The data in Table 5 provide sufficient evidence that the reactions (8), (9), (10) proceed simultaneously with reactions (5), (6) and (7). Moreover, the product of reactions (8), (9) and (10) is Na_2S , which, being the reactant of reaction (1) shifts its equilibrium to the right.

Concentration of NaOH solution has favourable effect on leaching Fe while other parameters of leaching (time, temperature) are maintained at constant level, as can be seen in Table 6.

Table 6. Iron recoveries in leaching by NaOH solutions of different concentration (temperature 298K, leaching time 90 min)

NaOH /wt.%	0.5	1	2	4
Fe recovery /%	1.44	1.74	3.4	6.9

3.3 Stibnite leaching in mixed aqueous solution ($\text{Na}_2\text{S} + \text{NaOH}$)

In this series of experiments leaching was carried out in solution containing Na_2S and NaOH. The effect of Na_2S to NaOH concentration ratio on Sb recovery from stibnite sample size fraction 0.25mm - 0.5mm was investigated at 298K. Results obtained in this type of experiments are depicted in Figure 4. Results indicate that:

- Leaching in aqueous solution consisting of 2wt.% $\text{Na}_2\text{S} + 2\text{wt.}\%$ NaOH yielded the highest Sb recovery that is in agreement with its highest ionic strength shown in Table 8. Maximum Sb recovery 86% was obtained after 30 minutes leaching. Longer leaching time did not result in higher Sb recoveries.
- Leaching in aqueous solution containing 2wt.% $\text{Na}_2\text{S} + 0.5\text{wt.}\%$ NaOH (curve No. 3) resulted initially in higher Sb recoveries in comparison with leaching in solution 0.5wt.% $\text{Na}_2\text{S} + 2\text{wt.}\%$ NaOH (curve No.2) but after 60 minutes of leaching the Sb recoveries in both solutions were identical, approximately 84%.

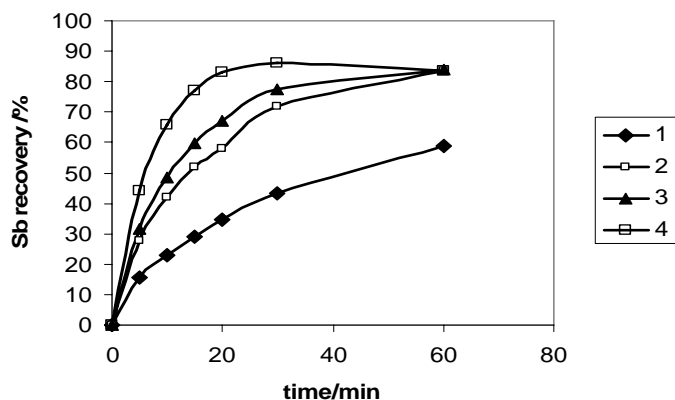


Figure 4. Effect of Na_2S to NaOH concentration in mixed leaching solution on Sb recovery. 1 - 2wt.% NaOH; 2 – (0.5wt.% $\text{Na}_2\text{S} + 2\text{wt.}\%$ NaOH), 3 – (2wt.% $\text{Na}_2\text{S} + 0.5\text{wt.}\%$ NaOH), 4 – (2wt.% $\text{Na}_2\text{S} + 2\text{wt.}\%$ NaOH) (Experimental conditions: $T = 298\text{ K}$; Particle size 0.25-0.5mm; Stirring rate 10s^{-1})

- c. When leaching was carried out in mixed solution containing 0.5wt.% Na₂S + 2wt.% NaOH the role of NaOH is not only to suppress hydrolysis of Na₂S but it is an active leaching agent for Sb leaching under conditions when there is insufficient amount of Na₂S in leaching solution.
- d. Leaching in mixed aqueous solution (see curves No.2, 3 and 4 in Figure 4) brings about higher Sb recoveries than leaching in solution that contains only NaOH (see curve No.1 in Figure 4) which agrees well with the corresponding ionic strengths of individual solution presented in Table 8.
- e. It therefore seems that the optimum molar ratio of Na₂S to NaOH concentration in mixed (Na₂S + NaOH) leaching solution is ½.

In order to calculate the ionic strength of the mixed solution it is necessary to take into consideration the ionic strength of both NaOH solution (see Table 3) and Na₂S solution (see Table 7).

Table 7. Na₂S concentration in solution, ionic strength and mean activity coefficients

Na ₂ S/wt.%	Na ₂ S/mol dm ⁻³	I/ mol dm ⁻³	γ±
0.5	0.0639	0.191	0.3647
1	0.1279	0.3837	0.2402
2	0.2558	0.7674	0.133

The ionic strengths of mixed (Na₂S + NaOH) solutions summarized in Table 8 were calculated on the basis of data presented in Tables 3 and 7.

Table 8. Calculated data of ionic strength of alkaline solutions applied in leaching experiments

Solution composition	I(Na ₂ S) + I(NaOH)
2wt.% Na ₂ S + 2wt.% NaOH	1.2674
2wt.% Na ₂ S + 0.5wt.% NaOH	0.8924
0.5wt.% Na ₂ S + 2wt.% NaOH	0.691
2wt.% NaOH	0.5

Leaching in solution containing 1wt.% Na₂S + 1wt.% NaOH resulted in higher Sb recoveries than leaching in solution that contained only 1wt.% NaOH as follows from Figure 5. Similar comparisons of antimony recoveries between leaching in mixed solutions and solutions containing only NaOH were summarised in previous publication by authors of this paper [12].

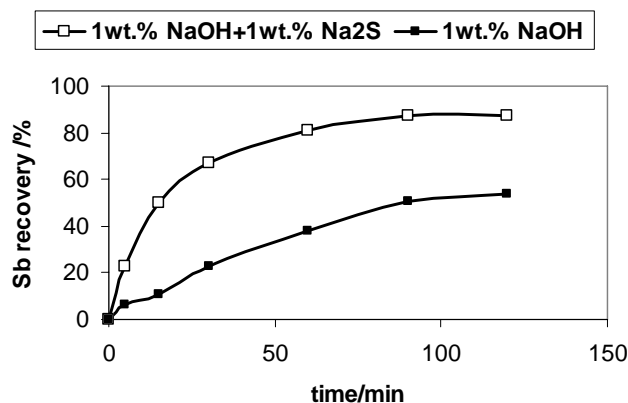


Figure 5. Variation of antimony recovery with time obtained in leaching experiments in solution containing 1wt.% Na₂S+1wt.% NaOH and in solution with 1wt.% NaOH (Particle size 0.25 – 0.5mm; T= 298 K; Stirring rate 10s⁻¹)

4. CONCLUSIONS

Leaching experiments under laboratory conditions focused on detail study of behaviour of antimony during leaching of stibnite in NaOH aqueous solutions as well as in solutions containing Na₂S+ NaOH. Concentration of leaching solution, temperature and particle size of the solid phase were the parameters whose effect on Sb recovery as well as recoveries of accompanying minor constituents, i.e iron, zinc and lead were the objective of this experimental research. The test results can be summarised as follows:

1. The sample used for leaching consisted of mineral phases: stibnite, quartz, pyrite and wurtzite as determined by X-ray diffraction analysis.
2. The beneficial effect of increasing NaOH concentration in leaching solution was observed at time interval 0 to 90 min. Longer leaching times did not result in higher Sb recoveries.
3. Temperature and leaching time favourably affected Sb leaching in aqueous solution containing 1wt.% NaOH. After 60 min leaching Sb recovery increased from 38% to 87% as a result of temperature increase from 298 to 323 K.
4. Lower particle size of the solid phase brings about the same Sb recovery levels within shorter leaching times.
5. Leaching in NaOH solution resulted in partial transfer of iron, zinc and lead into solution alongside antimony.
6. The optimum molar ratio of Na₂S to NaOH in mixed solution was determined as 1/2.
7. Application of mixed (Na₂S+NaOH) resulted in higher Sb recoveries in comparison with leaching in solution containing only NaOH. The role of NaOH in this case is to suppress Na₂S hydrolysis and as a principal leaching agent in case that there is insufficient amount of Na₂S in leaching solution.

The experimental investigation carried out in the laboratory environment suggests that the shorter leaching times in alkaline leaching of stibnite can be achieved by increasing alkalinity (pH) of the solution, at higher temperature and smaller particle size of the solid phase.

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