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BEHAVIOUR OF STIBNITE IN ALKALINE LEACHING

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ABSTRACT:
Stibnite (Sb_2S_3) occurs in nature accompanied by quartz (SiO_2), pyrite (FeS_2) and wurtzite (ZnS). This paper describes the behavior of antimony and some minor accompanying elements (Hg, Fe, Zn, Cu, Ni) during leaching of sample of natural stibnite in the solution consisting of 1wt.% Na_2S+1wt.% NaOH at temperatures ranging from 294 K to 341 K. Laboratory test results showed that temperature and leaching time favorable affect antimony removal into alkaline solution. The maximum antimony recovery (85.3%) was obtained after 15 minutes of leaching at 341 K. The beneficial effect of temperature and leaching time on recovery was not detected in case of minor constituents. After 15 minutes of leaching at 341 K the following metal recoveries were determined: 2.79% Hg, 0.83% Fe and 0.049% Zn. Copper and nickel were not present in the leaching solution. Low recoveries of the minor constituents (Zn, Cu and Ni) suggest that only Hg and Fe should be analyzed in the leaching solution. Agitation leaching test results revealed that the best condition for antimony dissolution was solid to liquid ratio of 1 (g) to 50 (cm^3). At this s:l antimony recovery was 96.8%.
KEYWORDS:
stibnite, leaching, antimony, recovery

1. INTRODUCTION

Hydrometallurgical method of extracting metals from sulphide concentrates is an alternative way to pyrometallurgical technologies that is more environmentally friendly. In this method there is no air pollution by sulphur oxide, volatile antimony oxides or flying solid dust. Leaching of natural stibnite (Sb_2S_3) that occurs together with other minerals such as quartz (SiO_2), pyrite (FeS_2) and wurtzite (ZnS) is a very important unit operation in which antimony passes into the leaching solution. Leaching is controlled by thermodynamic and kinetic aspects. From the thermodynamic point of view either acidic or alkaline leaching solutions can be applied for recovering antimony [1, 2].

Alkaline metal sulphide solutions or alkaline earth metal solutions are frequently applied for this purpose [3, 4]. Sodium sulphide (Na_2S) solution has been successfully applied in leaching the complex sulphide concentrates containing copper, lead and zinc sulphides accompanied by precious metals [5-8]. Leaching in sodium sulphide solution is highly selective with regard to antimony and good separation of antimony from other accompanying metals such as mercury, tin and arsenic can be achieved [9]. Antimony, tin and arsenic sulphides react with Na_2S-NaOH aqueous solution according to the following reactions [9]:

$$Sb_2S_3 + 3Na_2S = 2Na_3SbS_3 \quad (1)$$

$$Sb_2S_3 + 4NaOH = Na_3SbS_3 + NaSbO_2 + 2H_2O \quad (2)$$

$SnS_2 + 2Na_2S = Na_4SnS_4$ (3)
$3SnS_2 + 6NaOH = 2Na_2SnS_3 + Na_2SnO_3 + 3H_2O$ (4)
$As_2S_3 + 2Na_2S = NaAsS_2 + Na_3AsS_3$ (5)
$As_2S_3 + 2NaOH = NaAsS_2 + NaAsS(OH)_2$ (6)

The product of the reaction of aqueous solution of sodium sulphide with mercury sulphide is the water-soluble sodium thiomercurate as per following reaction [10]:

$HgS + Na_2S = Na_2HgS_2$ (7)

Ferrous sulphide and zinc sulphide react with NaOH solution according to the following reactions [11]:

$FeS + 2NaOH = Fe(OH)_2 + Na_2S$ (8)
$ZnS + 4NaOH = Na_2ZnO_2 + Na_2S + 2H_2O$ (9)

Both reactions generate Na_2S that is dissolved in the leaching solution thus changing its composition.

As natural stibnite is always accompanied by minor elements, the objective of this experimental investigation was to study the effect of temperature and leaching time on the behaviour of antimony , iron, copper, nickel and mercury during alkaline leaching in Na_2S+NaOH aqueous solutions having constant concentration.

The effect of ratio of solid to liquid phase (s:l) on the recovery of antimony and mercury was investigated during agitation leaching by changing the weight of solid stibnite sample and the volume of the leaching solution used in experiments.

2. METHODOLOGY

Sample of natural stibnite taken at Pezinok Mine (Slovak Republic) was used for testing. Table 1 summarizes the chemical composition of the sample in weight percents (wt. %). Other elements present in the sample(wt.%) are as follows: 19.15% S, 10.4% Si, 1.81% Ca, 0.65% Al, 0.63% Pb, 0.37% Mg and traces of Ti, Mn, As, Sn, Bi, Ag.

Table 1. Chemical analyses of the initial antimony concentrate

Element	Sb	Zn	Fe	Cu	Hg	Ni
Weight %	49.3	5.43	0.84	0.115	0.015	0.0018

Before leaching, sample was crushed and ground. Ground sample was then screened to obtain the size fraction -0.25 mm. The specific surface area determined by BET method on Geminy 2360 (Micromeritics, USA) testing equipment was 0.4287 $m^2 g^{-1}$. Antimony, zinc, iron, copper and nickel concentrations in the leaching solutions were analyzed by Atomic Absorption Spectrometry (AAS) (VARIAN, model Spectr AA-20 Plus, Australia). The parameters used for analyses are summarized in Table 2.

Table 2. AAS parameters of analysis

Element	Supply current /mA	Wavelength/nm	Gap/nm	Range of calibration/ $\mu g\ cm^{-3}$
Sb	10	217.6	0.2	0.4 – 100
Fe	5	372	0.2	1 – 100
Cu	15	324.6	0.7	0.03 – 10
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: 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.

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 [12]. With the volume of samples used for analyses (200μl) and the minimum 0.2 ng Hg of the range, the mercury determinability was about 1 μg dm^{-3}.

In all experiments that were carried out with the objective to find out the effect of solid and liquid phase on recoveries of antimony and mercury the leaching time was 30 minutes, temperature 297 K and the aqueous leaching solution contained 1wt.% Na_2S+ 1wt.% NaOH.

Leaching experiments were carried out in a 250 cm^3 glass reactor. Leaching solutions were prepared by dissolving pure NaOH and $Na_2S.9H_2O$, p.a. (Lachema, Brno, Czech Republic) in distilled water. The leaching medium was 50 cm^3 aqueous solution containing 1wt.% Na_2S + 1wt.% NaOH. One gram of sample was kept in suspended state in the leaching solution by a glass stirrer that was rotated at the speed 10 s^{-1}. The solid to liquid ratio s:l = 1:50 was maintained constant during all experiments. The leaching tests were carried out at the following temperatures: 294 K, 304 K, 315 K, 323 K and 341 K. The constant temperature was maintained in each experiment by water thermostat. In order to study the effect of temperature on leaching, samples of leaching solution were withdrawn from the reaction vessel after 15 minutes of leaching and then analyzed for Zn, Fe, Cu and Ni. Antimony and mercury were analyzed in the solutions after 5 minutes leaching time.

3. RESULTS AND DISCUSSION

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. The effect of solid to liquid ratio (s:l= g:cm^3) on antimony and mercury recovery is summarized in Table 3.

Table 3. Antimony and mercury recoveries at different solid to liquid ratios (temperature 297 K, 1wt.% Na_2S + 1wt.% NaOH)

Solid to liquid ratio s : l = g:cm^3	1:10	1:25	1:40	1:50	1:100
Sb/%	35.4	62.6	90.1	96.8	96.8
Hg/%	0.68	1.93	2.33	2.53	3.73

From the comparison of the antimony recoveries at the above solid to liquid ratios used in leaching it follows that the maximum, i.e.96,8% antimony recovery was reached at s:l= 1:50. When of this ratio was further decreased there was no additional corresponding improvement in antimony dissolution in the leaching solution. All other experiments were therefore carried out at this optimum solid to liquid ratio. The mercury recoveries listed in Table 3 suggest that increasing solid to liquid ratio has favorable effect on mercury recovery. The maximum recovery (3.73%) was achieved at s:l=1:100.

The favorable effect of temperature on antimony recovery during leaching is shown in Fig.1. When temperature increased by 47 K that is from 294 K to 341 K the antimony recovery after 5 or 15 minutes of leaching increased by approximately 24%. Maximum antimony recoveries of leaching at 341 K were 69.9% and 85.3% after 5 and 15 minutes respectively. Antimony recoveries increased with leaching time at all temperatures. The leaching tests revealed that within the given temperature range copper and nickel remained insoluble, i.e. did not pass into the leaching solution. This has a favorable effect on selectivity of antimony leaching.

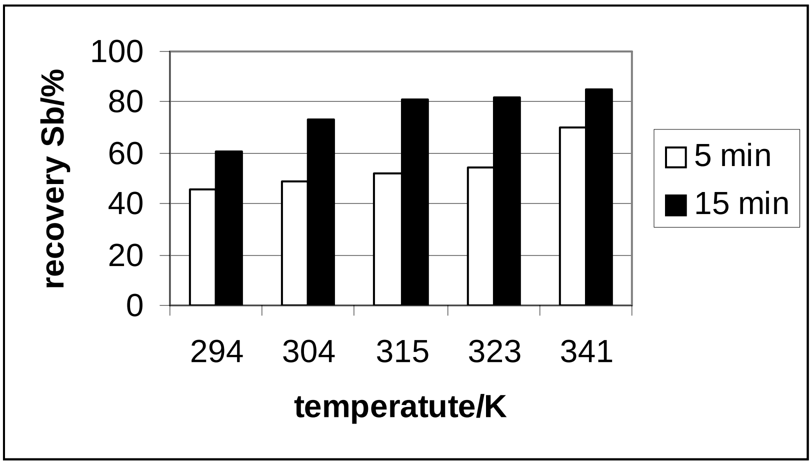

FIGURE1. Antimony recovery versus temperature at two times of leaching (1wt.% Na_2S + 1wt.% NaOH, s:l = 1:50)

Effect of temperature on mercury recovery during leaching is summarized in Fig.2. It is obvious that temperature does not have any favorable effect on mercury recovery as after 15 minutes of leaching at 304 K in solution 1wt.% Na_2S + 1wt.% NaOH its maximum recovery was only 2.98%. This result is in agreement with observations by other researchers [13, 14, and 15] and mercury passes into the solution according to reaction (7).

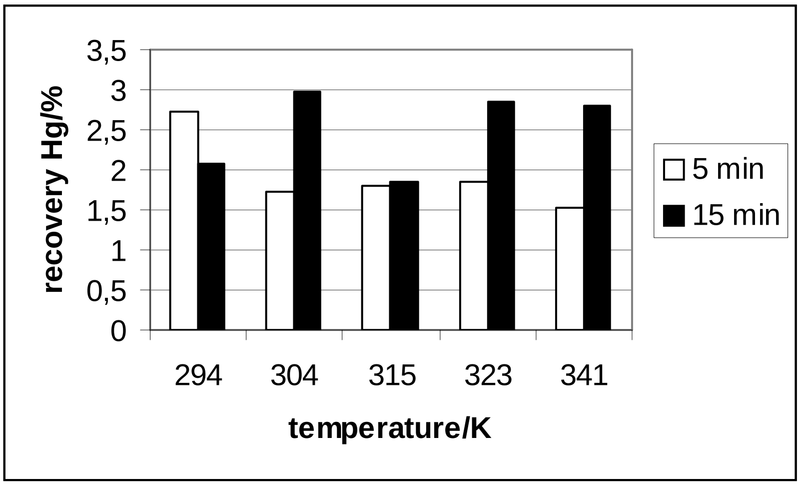

FIGURE 2. Mercury recovery versus temperature at two leaching times (1wt.% Na_2S + 1wt.% NaOH, s: l = 1:50)

Results summarizing the behavior of iron during leaching shown in FIGURE 3 suggest that the recovery after 15 minutes of leaching in solution 1% Na_2S + 1% NaOH is below 0.9%. The maximum iron recovery, 0.83%, was determined at 341K. Low recoveries at all temperatures were identified for zinc as can be seen in Fig.3. Zinc recoveries were in the range 0.04 to 0.06%.

Table 4 is the summary of recoveries of all studied elements after 15 minutes of leaching in 1% Na_2S + 1% NaOH solution at 341 K. Sodium sulphide being generated by reactions (8) and (9) that is one of the components of the leaching solution has a beneficial effect on reaction (1).

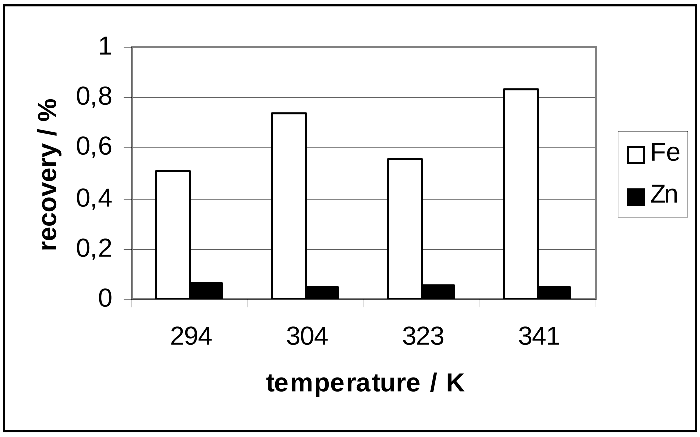

FIGURE 3. Variation of iron and zinc recoveries with temperature
(1wt.% Na_2S + 1wt.% NaOH, s: l = 1:50, 15 min)

Table 4. Recoveries of Sb, Hg, Fe and Zn obtained in leaching tests

Experimental conditions: 1%Na_2S+1%NaOH 341 K, 15 min	Recovery /%			
	Sb	Hg	Fe	Zn
	85.3	2.79	0.83	0.049

4. CONCLUSIONS

Laboratory leaching tests of natural stibnite in mixed leaching solution 1% wt. Na_2S + 1 wt.% NaOH were carried out with the objective do reveal the effect of temperature and leaching time on recoveries of Sb, Hg, Fe, Zn Cu a Ni into solution. The test results can be summarized as follows:

1. The sample used for leaching consisted of stibnite, quartz, pyrite and wurtzite as was determined by X-ray diffraction analysis.
2. The optimum solid to liquid ratio (s:l) for transfer of antimony into aqueous solution is 1:50. The maximum antimony recovery achieved at this condition was 96.8%. Maximum mercury recovery. 3.73%, occurred at s:l = 1:100.
3. Both temperature and leaching time favorably affect the antimony recovery into leaching solution. The maximum antimony recovery was determined as 85% after 15 minutes of leaching at 341 K.
4. The effect of temperature on recoveries of Hg, Fe and Zn was rather negligible. The recoveries of those accompanying metals varied in the following ranges: mercury from 1.85% to 2.98 %, iron from 0.5% to 0.8 % and zinc from 0.04% to 0.06 %.
5. Neither copper nor nickel dissolved in the alkaline solution under experimental conditions used in this investigation.

Leaching of stibnite in alkaline aqueous solution is highly selective for antimony. Antimony recovery increases with time and temperature of leaching. Iron, zinc and to some extent also mercury sulphides are left behind in the solid residue.

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