# Investigation of Alkaline Leaching Parameters on Stibnite Concentrate



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#### Abstract

According to critical statistical studies, antimony is one of the rarest elements in the world, and global resources could be exhausted by 2050. In light of these observations, its extraction will be costly due to poor-quality ore, deep mining, remote locations, and high energy consumption. In the present study, an alkaline leaching process was carried out on stibnite concentrate to evaluate the effect of reaction parameters on the percentage of antimony extraction. The leaching efficiencies of different sulfur and hydroxide sources were studied and compared to one another to create a better understanding of the reaction process. Kinetic models were investigated to identify the reaction pathway and calculate the activation energy. The activation energy of the stibnite dissolution was assessed as 19.13 kJ/mol using a two-dimensional diffusion-reaction model. The value of activation energy indicates the quantity of energy necessary for a reaction to proceed. As expected, potassium hydroxide leaching was significantly more successful than was sodium hydroxide; however, in terms of economics, the use of sodium hydroxide was found to be more cost-efficient. Interestingly, this finding indicated that caustic leaching is still the most effective method for stibnite extraction.

Keywords Stibnite · Antimony · Alkaline · Leaching · Extraction

# 1 Introduction

Antimony is a brilliant white metalloid with a bluish tinge and has a rhombohedral crystalline structure. The melting point and boiling point of antimony are 630 °C and 1635 °C, respectively. It starts to become appreciably volatilized at about 1500 °C. Air has no effect on antimony at ordinary temperatures, but when antimony is heated to redness in air, volatile antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) is formed [1]. Antimony trioxide is toxic even at a low concentration, and some of its salts may be carcinogenic upon long-term exposure. Antimony has been employed extensively both in industry and in daily life since the nineteenth century; however, antimony sulfides have been known since around 4000 BC. Its most significant application is as a flame retardant in the manufacture of electronics and

Serdar Aktaş serdaraktash@yahoo.com textiles, as a catalyst for plastic fabrication, and as paint pigment and fining agent in glassware, opacifier in ceramics and an alloying element in ammunition and battery manufacturing plants. It is also utilized in vehicle brakes and tires. Brake pads contain stibnite, the sulfide compound of antimony. In particular, stibnite is used in automobiles as a lubricant, vibration reducer, and friction stability improver. Anthropogenic activities are the primary source of antimony in the atmosphere [2, 3]. As a result, global consumption of antimony has increased to over  $1.4 \times 10^5$  t each year, with China being the most significant producer [3].

Antimony mining activities produce residues that frequently contain high levels of antimony in the form of sulfides, such as Sb<sub>2</sub>S<sub>3</sub>. These residues, oxidized when exposed to air or humidity in the air, are one of the major sources of the antimony present in the environment and of antimony contamination and pollution near smelter areas, which also require vast amounts of energy consumption (>3.6 GJ t<sup>-1</sup>) [4, 5]. In addition, pyrometallurgical processes require higher-quality and higher-grade antimony containing minerals or concentrates. However, according to a report from Henckens et al. [3], antimony is one of the rarest elements in the world, and global

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resources could be exhausted by 2050; therefore, its extraction costs will increase due to poor-quality ore, deep mining, remote locations and high energy costs [3]. In order to provide alternatives to address many of these problems, several hydrometallurgical processes have been developed, and various leaching methods have been proposed in both acidic and alkaline media due to the amphoteric character of antimony and its compounds, such as hydrochloric acid [6], HCl with tartaric acid [7], ferric chloride [8, 9], ozone [10], both ozone and HCl [5], H<sub>2</sub>SO<sub>4</sub> and NaCl [11], H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, tartaric acid, HCl with ferric ions, KOH and hydroquinone [12], NaOH [13], and a mixture of NaOH and Na<sub>2</sub>S [9, 12–14].

Apart from these, stibnite has a detrimental influence on gold leaching even at low concentrations. Hence, cyanidation is an effective method for extracting several elements in goldbearing ores, including Au, Cu and Sb [15]. In a recent study, cyanidation experiments carried out on a Barika multielement-bearing ore sample containing antimony of 619.7 g/ t and many other elements including Ag, Au and Cu led to an increase in antimony extraction to 43.10% from 23.73% without roasting [16]. In another cyanidation study, the concentration of Sb in the solution was reduced by around 33.33% with the addition of lead. Also, an increase in gold grain passivation was found to be related to the precipitation of antimony. Therefore, better control of cyanide might prevent the precipitation of Sb as well as Fe and Cu [17]. As cyanidation has hazardous effects on the environment, other leaching and extraction methods have been applied. For example, instead, thiourea leaching was used to leach an antimony-rich concentrate in New South Wales, Australia [18].

Worldwide, an alkali sulfide system has been used industrially for ten decades [19–24]. Metallic antimony with a purity of over 99.5% can be obtained from this basic system using electrolysis [20-26].

Hydrometallurgical methods for extracting antimony by acidic systems are less common than alkaline systems. However, many studies have been done in this area [27–30]. The concentrations of Cl<sup>-</sup> and OH<sup>-</sup> determine the stability of the SbCl<sub>3</sub> system. When this equilibrium changes, the antimony ion may form a precipitate, or the precipitate may redissolve. Depending on the pH of the solution and the chloride concentrations, oxychloride compounds such as Sb<sub>4</sub>O<sub>5</sub>Cl<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, Sb<sub>4</sub>O<sub>3</sub>(OH)<sub>5</sub>Cl and SbOCl may be formed by this hydrolysis process [31, 32]. Studies on the hydrolysis balance of the Sb<sup>3+</sup>-Cl<sup>-</sup>-H<sub>2</sub>O system [33] are limited to theoretical data and have not yet been confirmed by experimental studies. Due to deficiencies in different complexometric calculations of antimony in these theoretical analyses, the control mechanisms of this system are not fully understood [31].

In previous studies, it was claimed that alkaline  $Na_2S$  solutions were universal leaching agents for antimony-bearing compounds, while the solubility of other minor or trace elements such as As, Hg or Sn was very low, which ensures selective leaching. The possible reactions were given as follows:

$$Sb_2S_3 + 3Na_2S = 2Na_3SbS_3 \tag{1}$$

$$3Na_2S + 6H_2O = 3H_2S + 6NaOH$$
 (2)

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

$$Sb_2S_3 + 2NaOH = NaSbOS + NaSbS_2 + H_2O$$
 (4)

As mentioned in Raschman and Sminčáková [14], the dissolution-reactions of stibnite were summarized using these equations. It was assumed that leaching of antimony proceeds as per Eq. 3. Another article supported these reaction equations. Sb extraction was attributed to both Eqs. (1) and (3), with Eq. (1) being the more effective. Excess NaOH and Na<sub>2</sub>S were used, and the minimum molar ratio of Na<sub>2</sub>S:Sb<sub>2</sub>S<sub>3</sub> was 18:6. The rate-controlling step was identified as the leaching reaction at the stibnite particle surface. In all experiments, a surplus of leaching solution consisting of higher molar ratios of caustic to antimony was added. The residual sodiumcontaining products are water-soluble. It was found that at pH < 13.6, complex trivalent anion  $SbS_3^{3-}$  was present in the solution, and there were mainly two different mechanisms-chemical reactions and external mass transfer—controlling the initial stage of the process. However, in the above-mentioned study [14], the grade of the sample was lower, and there were impurities such as Si, Fe and Zn. Also, only Na<sub>2</sub>S as the sulfur source and NaOH as the alkaline media were investigated. It was reported that the reaction rate between stibnite and sodium sulfide was higher than that between stibnite and sodium hydroxide.

In the present paper, the purpose of this research was to investigate the effect of hydroxide type and molarity on the extraction of Sb from the stibnite concentrate. Additionally, the effect of the sulfide/sulfur-based components including Na<sub>2</sub>S, thioacetamide (C<sub>2</sub>H<sub>5</sub>NS), thiourea (CH<sub>4</sub>N<sub>2</sub>S), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), ammonium sulfide (NH<sub>4</sub>)<sub>2</sub>S and elemental sulfur (S°), as well as their molarity, was investigated. Parameters including stibnite quantity, time, temperature, stirring rate, the kinetics of these systems, and the synergistic action of the different hydroxide and sulfur sources on the leaching behavior of the stibnite concentrate were also studied.

## 2 Materials and Methods

The stibnite concentrate was obtained from a mineral processing plant in Ödemiş–Halıköy (Turkey). The chemical composition of the stibnite concentrate was confirmed using a flame atomic absorption spectrometer (AAS, Shimadzu AA-7000, Japan). The AAS was operated in standard background (i.e., D<sub>2</sub> lamp) mode, which is the approved method for antimony and arsenic analysis. The sulfur content of the concentrate was analyzed using a carbon/sulfur analyzer (Eltra, CS-800). Xray diffraction (XRD) analysis of the stibnite concentrate was carried out in the 2(theta) range of  $5-105^{\circ}$  using a Rigaku vertical diffractometer with Cu-K $\alpha$  radiation at a step size of  $0.02^{\circ}(2\theta)$  in 2-s intervals under conditions of 40 mA and 40 kV. The mineral phases that generated the diffraction pattern were identified by the PANalytical X'Pert HighScore Plus analysis program (Philips). Before starting the XRD analysis of the concentrate, the concentrates were ground to a fine powder, dried at 105 °C to remove moisture, and cooled in a desiccator. The fine powder was then placed in the holder of the instrument. A Malvern Mastersizer 3000 (USA) was used to determine the particle size of the stibnite concentrate using distilled water as the dispersant.

This experimental procedure is thus intended to shed light on the kinetics of these systems. The experimental conditions are summarized in Table 1. The studied reaction parameters are summarized in the following sections.

The effects of alkaline lixiviant concentration, stirring speed, solid/liquid ratio, reaction temperature and reaction time, as well as the effect of a catalyst on leaching antimony, were investigated using a 0.50-L Teflon beaker as a reactor. The beaker was immersed in a water bath at a constant temperature condition. The reaction temperature was adjusted using a digitally controlled hot plate. All chemicals were of analytical grade unless otherwise stated. During the experimental procedure, the reactor was covered with a Teflon lid that was inert to strong acid/base/alkali media to prevent the evaporation of the leaching solution. A half-milliliter of the solution was sampled at different time intervals to measure the concentration of antimony present in the solution. Afterward,

Table 1 Leach test conditions

Parameters	Reagent	Concentration
Hydroxide type	NaOH	0.25–4.00 M
	KOH	0.25–4.00 M
	NH <sub>4</sub> OH	0.25–1.25 M
	Ba(OH) <sub>2</sub>	0.25–1.50 M
Sulfur-based reagent type	Na <sub>2</sub> S	0–1.00 M
	S°	0.250 M
	$(NH_4)_2S$	0.250 M
	$CH_4N_2S$	0.250 M
	C <sub>2</sub> H <sub>5</sub> NS	0.250 M
	$Na_2S_2O_3$	0.125 M
Stirring rate		0-1000 rpm
Liquid/solid ratio (L.kg <sup>-1</sup> )		40-100
Temperature (°C)		25–55
Time (min)		15-720
Particle size (D <sub>90</sub> )		350 µm

the extraction percentage was calculated using Eq. 5.

Extraction of Sb (%) = 
$$[C_t/(C_o)] \times 100$$
 (5)

where  $C_o$  is the concentration of antimony in the stibnite concentrate and  $C_t$  is the antimony concentration in the solution at time *t* (min).

## **3 Results and Discussion**

The elemental assay of the stibnite concentrate is shown in Table 2. The possible trace elements are not given, since they did not follow in the experimental studies.

The stibnite concentrate was characterized by XRD before commencing the leaching experiments. The XRD patterns are shown in Fig. 1. As can be seen, the stibnite was detected as the major phases, and no minor phase was found.

A plot of the particle size distribution is given in Fig. 2, which shows that the average particle size of the powder  $(D_{90})$  was 350  $\mu$ m.

#### 3.1 NaOH Concentration

In this experimental series, the effect of NaOH concentration on the extraction of antimony was investigated. The results are shown in Fig. 3. The experiments were carried out using 5 g stibnite concentrate in 250 mL of NaOH solution of at 100 rpm stirring speed for 1 h at 25 °C.

As shown in Fig. 3, the extraction percentage increased almost linearly to 59% in 1 h at 25 °C, along with an increase in the NaOH concentration up to 1 M. After that point, the dissolution rate nearly leveled off. In a similar study focused on the leaching kinetics of natural stibnite from mines in Slovakia [34], the performance of alkaline lixiviant solutions comprising 1, 2, 4 wt.% (0.025, 0.05, 0.1 M) NaOH, and with the addition of stibnite in particle size fractions of 0.18–0.25 mm (180–250  $\mu$ m) and 0.25–0.50 mm (250–500  $\mu$ m) at temperatures between 298 to 348 K, was compared to determine the optimal conditions. The increasing trend in our work was found to be similar to that of Sminčáková et al. [34].

Table 2 Elemental assay   of the stibnite concentrate	Element	Wt.%	
	Sb	69.0	
	As	0.12	
	S	28.6	
	Fe	1.10	
	Al	0.30	
	Si	0.40	
	Others*	0.47	

\*Trace elements





## 3.2 Comparison of NaOH and KOH

In this experimental series, the effect of different hydroxide types on antimony extraction was investigated. The experiments were carried out using 5 g stibnite concentrate in separate 250-mL alkaline solutions of KOH and NaOH at 100 rpm stirring speed for 1 h at 25 °C. The results are given in Fig. 4, which details the comparison of the antimony extraction percentages of NaOH and KOH in the concentration range of 0.25 M to 4.0 M. The efficacy of potassium hydroxide on the antimony extraction percentage was significantly higher than that of sodium hydroxide, as it enhanced the extraction 74.8% to 54.7% in 1 M leaching solution. In both cases, no

significant further benefit resulted from leaching with more concentrated solutions. However, when one considers that NaOH is two-thirds the price of KOH on the international market, the use of NaOH is expected to be more economical.

### 3.3 Hydroxide Type

The experiments were carried out separately using stibnite concentrates of 5 g in 250-mL alkaline solutions of different hydroxide ions for 1 h at 100 rpm and 25 °C. In addition to NaOH and KOH, Ba(OH)<sub>2</sub> and NH<sub>4</sub>OH were evaluated for the effect of hydroxide type on Sb extraction from the stibnite concentrate. It is known that Ba(OH)<sub>2</sub> is a strong base and that



Fig. 3 Effect of NaOH concentration on Sb extraction %



 $(NH_4)OH$  is a good complexing agent. It appeared that, practically, there was no change when  $Ba(OH)_2$  was added to the solution, as the amounts of barium hydroxide added to the solution were superabundant considering its relatively low solubility—3.89 g in 100 mL of water. Also, the involvement of ammonium hydroxide in the system exhibited an increasing trend, though the antimony extraction percentage was extremely limited in terms of a comparison of KOH and NaOH, as presented in Fig. 5.

Furthermore, in stark contrast to the performance of KOH (74.8% Sb extraction) and NaOH (54.7% Sb extraction), Fig. 5 shows that  $Ba(OH)_2$  and  $NH_4OH$  did not even achieve 1%

Sb extraction at 25 °C in 1 h, despite concentrations as high as 1.5 M, making them ineligible for consideration. Thus, NaOH was selected as the alkaline reagent for further experiments carried out in this study.

## 3.4 Sulfur-Based Reagent Type

The experiments were carried out using 5 g stibnite concentrate in 250 mL of 0.25 M NaOH plus 0.250 M sulfurcontaining reagent solution at 100 rpm for 1 h at 25 °C. A highly basic media was created by the sodium hydroxide in the solution; however, the sulfur ions were the driving force



**Fig. 4** Comparison of NaOH and KOH on Sb extraction %

**Fig. 5** Comparison of hydroxide type on Sb extraction %



behind the reaction between stibnite and the alkaline medium, as the rates of reaction between stibnite and sodium sulfide were higher than those of sodium hydroxide and stibnite, as reported in the studies of Sminčáková et al. [35, 36]. According to these findings, the effect of various sulfur sources including sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), thioacetamide (C<sub>2</sub>H<sub>5</sub>NS), ammonium sulfide ((NH<sub>4</sub>)<sub>2</sub>S) and thiourea (CH<sub>4</sub>N<sub>2</sub>S), in addition to the absence of sulfur ions, is given in Fig. 6.

Additionally, in contradistinction to the efficiency of  $Na_2S$  combined with NaOH (about 38% Sb extraction), the

performance of other sulfur-based reagents was inefficient, showing almost the same efficacy—about 10%—with no use of sulfur, or worse—less than 10%—in the case of thiourea and sodium thiosulfate. Figure 6 points out that the achievement obtained using elemental sulfur was almost the same as with no use of sulfur. Only ammonium sulfide surpassed the threshold of 10% extraction efficiency. The main alternative to sodium sulfide was found to be ammonium sulfide, since the latter has a similar molecular formula as the former. However, sodium ions belonging to the metallic group 1A in the periodic table show higher basicity, resulting in higher extraction efficiency.





#### 3.5 Na<sub>2</sub>S Concentration

The experiments were carried out using 5.0 g stibnite concentrate in 250 mL of 0.25 M NaOH solution containing Na<sub>2</sub>S of different molarities at 100 rpm for 1 h at 25 °C. The results of this test series are shown in Fig. 7.

Figure 7 shows that the influence of sodium sulfide was remarkable, and its extraction efficiency of 99.56% was attained at a concentration of 0.75 M. But even the leap in extraction efficiency between the addition of 0.25 M and 0.50 M Na<sub>2</sub>S was significant—from 63.01% to 98.87%—in accordance with the literature survey [16, 35, 36]. To further understand the effect of the experimental parameters on the extraction of Sb, 0.25 M Na<sub>2</sub>S was used for the next experimental series.

#### 3.6 Stirring Rate

After investigating the Na<sub>2</sub>S concentration, a new series of experiments were carried out using 5.0 g stibnite concentrate in 250 mL of 0.25 M NaOH plus 0.25 M Na<sub>2</sub>S solution for 1 h at 25 °C. The effect of the stirring rate is regarded as one of the most critical parameters in leaching studies. In this experimental series, the stirring rate was varied from 0 to 400 rpm while other reaction conditions were kept constant. The recorded recoveries are shown in Fig. 8.

Stirring permits solvent molecules to interact with each other, also with undissolved solute, and helps the transportation of dissolved solute. It is related to the speed of dissolution. In the case of stibnite leaching, even without stirring dissolution, and a transportation mechanism exist, and the antimony extraction rate was about 48% without any stirring.

Furthermore, the extraction percentage increased to 94.38% from 48% when a stirring rate of 200 rpm was employed. However, no further significant increase in Sb extraction occurred with an additional increase in the agitation rate, which may be attributed to vortex formation at increased stirring speed complexing particle interaction as the stirring speed increased from 200 rpm to 400 rpm, with extraction of 94.38% and 95.12%, respectively. A stirring rate of 200 rpm for this system may be adequate and was proposed due to the possible lack of vortex formation and stable conditions. At 200 rpm stirring rate, however, the effect of reaction temperature and time is more difficult to understand. For this reason, a stirring rate of 100 rpm was used for the subsequent experimental studies.

## 3.7 Effect of Reaction Temperature and Time

The experiments were carried out using 5.0 g stibnite concentrate in 250 mL of 0.25 M NaOH plus 0.25 M Na<sub>2</sub>S solution at 100 rpm for 12 h at 25 °C, 35 °C, 45 °C and 55 °C. A series of experiments were carried out to observe the effect of temperature and time.

As seen in Fig. 9, with an increase in temperature from 25 °C to 45 °C, the Sb extraction percentage increased from 62% to 81% during the first hour. After 3 h of extraction, approximately 90% Sb extraction was achieved at 25 °C; 97% Sb extraction was obtained at 45 °C. An increase in temperature thus has a significant effect on the extraction of Sb. After 180 min, the antimony extraction percentage was generally leveled off, but a fluctuation was observed at 25 °C. For instance, approximately 30% of the increase was obtained



**Fig. 7** Effect of Na<sub>2</sub>S concentration on Sb extraction %





when the temperature increased from 25  $^{\circ}$ C to 55  $^{\circ}$ C. Thus, temperature is found to play a vital role in this process.

#### **3.8 Leaching Kinetics**

The kinetic model can be calculated from the reaction order via experimental data using the integrated rate law. In this study, the leaching kinetics of antimony extraction process values were extracted from Fig. 9, and various kinetic models were used to investigate the underlying mechanism. The studied kinetic models and their equations are given in Table 3.

Among all computed kinetic equations, the twodimensional diffusion model was best fitted to the dissolution of stibnite concentrate (i.e., only the best-fitted plot is given in the text).

As shown in Fig. 10, a high correlation coefficient derived by fitting experimental data confirms a good fit for the twodimensional diffusion kinetic model, implying a diffusionand chemical reaction-controlled leaching process.



**Fig. 9** Effect of temperature and time on the Sb extraction %

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Reaction model	Kinetic equation
Two-dimensional diffusion	$(1 - X) \ln(1 - X) + X = kt$
Three-dimensional diffusion	$1 - (2/3)X - (1 - X)^{2/3} = kt$
Jander equation (three-dimensional)	$[1 - (1 - X)^{1/3}]^2 = kt$
First-order kinetics	$-\ln(1-X) = kt$
Two-dimensional phase boundary reaction	$1 - (1 - X)^{1/2} = kt$
Three-dimensional phase boundary reaction	$1 - (1 - X)^{1/3} = kt$
Avrami equation	$[-\ln(1-X)]^{1/2} = kt$
Erofeev equation	$[-\ln(1-X)]^{1/3} = kt$

Here, k is the rate constant, t is the time (min), and X is the fraction of extracted antimony in the stibnite concentrate

Accordingly, an Arrhenius plot was drawn using the twodimensional diffusion-reaction equation, which was extracted from Fig. 10.

Figure 11 was plotted using the Arrhenius equation, which was given in Eq. 6, and the activation energy ( $E_a$ ) was calculated from the plotted figure. As can be seen, when the lnK is plotted versus the inverse of the temperature, the slope is a straight line. The value of the slope is equal to  $-E_a/R$ .

$$\ln k = \ln A^{-} E_{a}/R^{*1}/T \tag{6}$$

Here, k represents the rate constant,  $E_a$  is the activation energy, R is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), and T is the temperature expressed in Kelvin (K). A is known as the frequency factor, having units of (L mol<sup>-1</sup> s<sup>-1</sup>), and takes into account the frequency of reactions and likelihood of correct molecular orientation.

The value of activation energy indicates the quantity of energy necessary for a reaction to proceed. The activation energy using the two-dimensional diffusion-reaction model was calculated to be 19.13 kJ/mol. This result indicates that the leaching of antimony from the stibnite concentrate includes both diffusion- and chemical reaction-controlled processes verified by the study of Raschman et al. [14], where the kinetics of leaching of stibnite by mixed Na<sub>2</sub>S and NaOH solutions was investigated. In that study, the leaching of the natural stibnite ore was found to be a chemical- and diffusioncontrolled process. Furthermore, this finding is consistent with the data shown in Fig. 8, displaying the effect of the stirring rate. The reaction is found to be more dependent on the stirring rate than on temperature.

## **4** Conclusions

In this work, a chemical route for the stibnite concentrate provided by a mineral processing plant in Haliköy, Izmir, was proposed to obtain the highest Sb extraction percentage and to compare the leaching efficiencies of several sources of sulfur-based leaching reagents and hydroxide types. The main goal was to investigate unused leaching reagents and also to identify improved leaching conditions and evaluate the reaction kinetics. The obtained results are summarized as follows:

The highest Sb extraction percentage reached nearly 100% using a lixiviant solution of 0.25 M NaOH + 0.25 M Na<sub>2</sub>S at 100 rpm and 45 °C for 180 min. Interestingly, similar extraction of Sb was recorded using



**Fig. 10** Relationship between [(1 - (X)\*ln(1 - (x) + X)] and time as a function of temperature





a lixiviant solution of 0.25 M NaOH + 0.75 M Na<sub>2</sub>S at 200 rpm and 25 °C for 60 min. Based on these findings, a new understanding of the essence of the Sb extraction process for utilizing stibnite concentrate was put forward in this work.

- The efficacy of KOH, which has higher basicity in terms of the extraction of antimony, was significantly greater than that of sodium hydroxide. However, considering the economic aspect of the process, the use of NaOH is more cost-effective because its international price is less than two-thirds that of KOH. Its consumption and price/performance ratio render sodium hydroxide a more eligible dissolving agent. Unfortunately, other hydroxide types (i.e., Ba(OH)<sub>2</sub> and NH<sub>4</sub>OH) did not represent a high Sb extraction percentage in stibnite concentrate.
- The activation energy of the stibnite dissolution was calculated as 19.13 kJ/mol using a two-dimensional diffusion reaction. This activation energy value is generally in agreement with previously published research articles.

Further studies are recommended to increase the extraction of Sb using a better stirring method, which may remove the sulfur product layer and hence improve the kinetics of leaching. Additionally, antimony precipitation tests should be conducted in further studies for producing special antimony compounds such as  $Sb_2O_3$  (antimony trioxide) and  $Na_2(SbO)_2C_8H_4O_{10}$  (sodium antimony(III) oxide tartrate).

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# **Compliance with Ethical Standards**

**Conflict of Interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

**Symbols**  $C_o$ , Concentration of Sb in stibuite concentrate;  $C_t$ , Concentration of Sb in solution after leaching for time t; T, Leach time (min); k, Rate constant; A, Frequency factor (min<sup>-1</sup>);  $E_a$ , Activation energy of the reaction (kJ mol<sup>-1</sup>); R, Universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>); T, Absolute temperature (K); X, Fraction of leached antimony in the stibuite concentrate

#### References

- Gowland W (1914) The metallurgy of the non-ferrous metals fourth edition. Charles Griffin and Company, Limited, London, pp 438– 456
- AlSioufi L, Sánchez de la Campa AM, Sánchez-Rodas D (2016) Microwave extraction as an alternative to ultrasound probe for antimony speciation in airborne particulate matter. Microchem J 124: 256–260
- Henckens MLCM, Driessen PPJ, Worrell E (2016) How can we adapt to geological scarcity of antimony? Investigation of antimony's substitutability and of other measures to achieve a sustainable use. Resour Conserv Recycl 108:54–62
- Hu X, Guo X, He M, Li S (2016) pH-dependent release characteristics of antimony and arsenic from typical antimony-bearing ores. J Environ Sci 44:171–179
- Tian Q, Wang H, Xin Y, Li D, Guo X (2016) Ozonation leaching of a complex sulfidic antimony ore in hydrochloric acid solution. Hydrometallurgy 159:126–131
- Guo X, Xin Y, Wang H, Tian Q (2017) Leaching kinetics of antimony-bearing complex sulfides ore in hydrochloric acid solution with ozone. Trans Nonferrous Metals Soc China 27:2073– 2081

- Iyer RK, Deshpande SG, Rao GS (1972) Studies on complexes of tartaric acid—I: antimony(III)-tartaric acid system. J Inorg Nucl Chem 34(11):3351–3356
- 8. Ye L, Ouyang Z, Chen Y, Chen Y (2019) Ferric chloride leaching of antimony from stibnite. Hydrometallurgy 186:210–217
- 9. Anderson CG (2012) The metallurgy of antimony. Chem Erde 72(S4):3–8
- Tian Q, Wang H, Xin Y, Yang Y, Li D, Guo X (2016) Effect of selected parameters on stibnite concentrates leaching by ozone. Hydrometallurgy 165:295–299
- Bahamondes OCC (2018) Cinética de Lixiviación de antimonita en medio H<sub>2</sub>SO<sub>4</sub>-NaCl a presión atmosférica, Dissertation. Departamento de Ingenieríai Facultad de Ingeniería, Metalúrgica, Universidad de Concepción
- 12. Gök Ö (2014) Catalytic production of antimonate through alkaline leaching of stibnite concentrate. Hydrometallurgy 149:23–30
- Sminčáková E, Komorová Ľ (2007) Kinetika lúhovania Sb<sub>2</sub>S<sub>3</sub> v roztoku NaOH. Acta Montanistica Slovaca Ročník 12(číslo 4): 328–333
- Raschman P, Sminčáková E (2012) Kinetics of leaching of stibnite by mixed Na<sub>2</sub>S and NaOH solutions. Hydrometallurgy 113-114: 60–66
- Guo H, Deschênes G, Pratt A et al (2005) Leaching kinetics and mechanisms of surface reactions during cyanidation of gold in the presence of pyrite or stibnite. Mining, Metallurgy & Exploration 22:89–95. https://doi.org/10.1007/BF03403120
- Abdollahi H, Karimi P, Amini A et al (2015) Direct cyanidation and roasting combination of a semi-refractory massive sulfide ore. Mining, Metallurgy & Exploration 32:161–169. https://doi.org/10. 1007/BF03402284
- Deschênes G, Xia C, Fulton M et al (2009) Determination of the leaching parameters for a refractory gold ore containing aurostibite and antimony minerals: part II — AD zone. Mining, Metallurgy & Exploration 26:114–120. https://doi.org/10.1007/BF03403428
- Celik H (2004) Extraction of gold and silver from a Turkish gold ore through thiourea leaching. Mining, Metallurgy & Exploration 21:144–148. https://doi.org/10.1007/BF03403316
- Anderson CG, Nordwick SM, Krys LE (1992) In: Reddy RG, Imrie WP, Qeuneau PB (eds) Processing of antimony at the sunshine mine. Residues and effluents—processing and environmental considerations. AIME-TMS, San Diego, pp 349–366
- Anderson CG et al (1994) Antimony separation process. US Patent No. US5290338A, March 1
- Anderson CG, Krys LE, (1993) Leaching of antimony from a refractory precious metals concentrate. Proceedings of the Fourth

International Symposium on Hydrometallurgy, TMS-SME-AIME, Salt Lake City, UT, August 1–5, pp 341–363

- Nordwick SM, Anderson C (1993) Advances in antimony Electrowinning at the sunshine mine. In: Hiskey B, Wadsworth M (eds) Proc. AIME meeting "hydrometallurgy-fundamentals, technology and innovations". Littleton, pp 1107–1128
- 23. Trifonoff A, Gardner D (1914) Method of treating antimony and arsenic ores. US Patent No. US1097897A, May 26
- Annable HWC (1934) Process for separating gold and antimony contained in antimony suphide ores. US Patent No. US1964781A, July 3
- Awe SA, Sandström Å (2013) Electrowinning of antimony from model sulphide alkaline solutions. Hydrometallurgy 137:60–67
- Ackerman JB, Anderson CG, Nordwick SM, Krys LE (1993) Hydrometallurgy at the sunshine mine metallurgical complex. In: Hiskey B, Wadsworth M (eds) Proc. AIME meeting "hydrometallurgy-fundamentals, technology and innovations". Littleton, pp 477–498
- 27. Kim SS (1975) Leaching of antimony with ferric chloride. Taehan Kwangsan Hakoe 12(4):35–39
- Motang T (1981) New techniques for treating the Dachang jamesonite concentrate. J Central South Inst Min Metall 198(4): 18–27
- 29. Li W, Xu B (1984) A trial process for direct hydrometallurgical production of antimony white. Hunana Metallurgy 4:20–23
- Thibault J et al (1998) Process for producing antimony trioxide. International Patent US Patent No. US005783166A, July 21
- Liu L, Hu Z, Cui Y, Li B, Zhou X (2010) A facile route to the fabrication of morphology-controlled Sb<sub>2</sub>O<sub>3</sub> nanostructures. Solid State Sci 12(5):882–886
- 32. Han-ying J (1984) Physical chemistry of hydrometallurgy. Metallurgical Industry Press, Beijing
- Xin-ling D (2012) Research on the hydrolysis equilibrium of antimony trichloride in the Sb<sup>3+</sup>-cl<sup>-</sup>-H<sub>2</sub>O system. China Nonferrous Metallurgy 41(5):75–79
- Sminčáková E (2009) Leaching of natural stibnite using sodium hydroxide solution. JOM 61:32–35
- Sminčáková E, Raschman P (2012) Leaching of stibnite by mixed Na<sub>2</sub>S and NaOH solutions. Acta Technica Corviniensis- Bulletin of Engineering Fascicule 1:35–39
- Sminčáková E, Raschman P (2011) Leaching of natural stibnite using Na<sub>2</sub>S and NaOH solutions. Int J Energy Eng 1(2):85–89

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