

Solubility of Stibnite Ore in HCl Solutions Saturated With Cl₂ Gas

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In this study, the dissolution of stibnite mineral (Sb₂S₃) in HCl solutions saturated with Cl₂ gas was carried out, taking into consideration the effect of particle diameter, acid concentration and reaction temperature. Using the experimental data, we attempted to establish a kinetic model for the dissolution of the stibnite mineral in HCl solutions saturated with Cl₂ gas. Employing graphical and statistical methods, the following kinetics model, including the effect of the chosen quantities, was established to represent the dissolution process

$$-\ln(1 - X_{\text{Sb}}) = 2.97 \times 10^5 \cdot (d)^{-0.74} \cdot (w)^{1.52} \cdot \exp(-4800/T) \cdot t$$

The activation energy of the dissolution process was found to be 39.87 kJ.mol⁻¹.

Keywords:

Stibnite, hydrochloric acid, dissolution of stibnite, chlorine gas.

Introduction

Antimony and its compounds are mainly obtained from stibnite (Sb₂S₃), which is a sulphuric mineral, and secondly from oxidised minerals, such as cervantite (Sb₂O₃ · Sb₂O₅), valentinite (Sb₂O₃) and kermesite (2Sb₂S₃ · Sb₂O₃)¹⁻³. Stibnite, the most common antimony mineral, is commonly found with quartz in hydrothermal lodes, as replacement particles in limestone, and in hot spring deposits⁴.

Antimony chlorides (SbCl₃ and SbCl₅) are the most consumed antimony compounds and are used in the processes of organic chlorination and polymerization, in electroplating, in the coloration of metals such as iron and zinc^{2,5}. They are produced by reacting stibnite and HCl and/or Cl₂ in solution media, or antimony powder and Cl₂ gas⁵.

Stibnite chlorination has been investigated by various authors. Çopur et al.⁶ proposed a semi-empirical equation for the dissolution (m_s) of stibnite in (v) HCl solutions for low solid-to-liquid quotient (less than 4 : 100 g : mL): $-\ln(1 - X) = 9.79 \times 10^{-10} (d)^{-0.908} (w)^{10.6} (m/V_{\text{HCl}})^{-0.321} e^{-6244/T} \cdot t$ where X is the conversion fraction, d particle (mm), w hydrochloric acid mass fraction (%), m/V_{HCl} solid-to-liquid quotient (g · mL⁻¹), e exponential function coefficient, T reaction temperature K, and t is the time min.

Various kinetics studies on the dissolution of antimony ores in different solutions are present in the literature: In a study carried out by Shestiko et al.⁷, it was found that the leaching kinetics of stibnite in Na₂S was controlled by diffusion through the fluid layer, and the activation energy of the process was calculated as 16.72 kJ · mol⁻¹. In the dissolution process of stibnite in NaOH solutions, Ko et

al.⁸ determined that the dissolution process was controlled by diffusion for the solution of 0.5 mol l⁻¹ NaOH concentration and by chemical reaction for that of 0.05 mol l⁻¹ NaOH. For the dissolution process of stibnite in acidic FeCl₃ solutions, Ko et al.⁹ found that the process was controlled by diffusion of the reactant Fe⁺³ through the sulfur layer for smaller particle diameter than 270 mesh, while for larger particle diameter than 270 mesh, the process was controlled by chemical reaction in the beginning of the dissolution and then by diffusion control as the process progressed. Various authors carried out the reaction of antimony ores with HCl and/or Cl₂ in the solutions to produce pure Sb₂O₃¹⁰⁻¹².

Although there are some investigations on the reactions of stibnite with HCl and/or Cl₂ in the solution, these studies which are patented do not include the process kinetics. In the presented study, the dissolution kinetics of mineral (Sb₂S₃) in stibnite ore was studied in HCl solutions saturated with Cl₂ gas, and the best conditions for the dissolution process were determined for different quantities. It was tried to derive mathematical expression representing the dissolution rate from the experimental results.

Material and methods

The antimony ore used in the experiments was provided from Nidde region in Turkey. After crushing and grinding, the ore was sieved by using ASTM standard sieves and separated into fractions 605, 433, 308, 215 and 152.5 μm. It was determined by X-ray diffractometer that the ore contained mainly Sb₂S₃ and SiO₂. The X-ray diffrac-

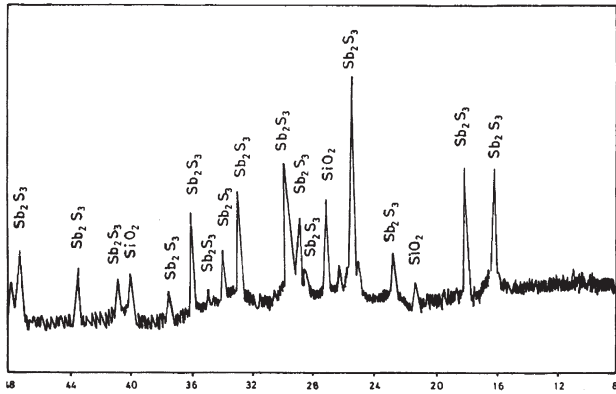


Fig. 1 – X-ray diffractogram of stibnite ore

togram of the stibnite ore is given in Figure 1. The chemical composition of the ore was determined by volumetric and gravimetric methods (Table 1). The dissolution experiments were carried out in a glass reactor of 250 mL volume equipped with a mechanical stirrer having a digital controller unit and a timer. The temperature of the reaction medium could be controlled within ± 1 °C by a temperature regulation system. After adding 100 mL of HCl solution to the reaction vessel and setting the reaction temperature at the desired value, the reactor content was stirred at 500 min^{-1} . The solution was saturated with Cl₂ gas, and 0.5 g solid was then added to the reactor while continuing to stir and add Cl₂ gas. At the end of the reaction period, the contents of the vessel were filtered and the filtered solution was then analysed volumetrically for Sb¹³.

Table 1 – The chemical composition of stibnite ore used in the study

Component	Sb	Ca	Pb	Co	Fe	Mn
%	60.56	2.21	0.029	0.013	0.019	0.008
Component	Ag	Cu	Zn	As	S	SiO ₂
%	0.005	0.014	0.022	0.010	23.118	13.920

The effects of quantities on the dissolution process were investigated using the values given in Table 2 for each quantity. In the experiments, while the effect of one quantity was studied, the values of other quantities shown with asterisk in Table 2 were kept constant.

Results and discussions

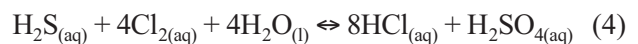
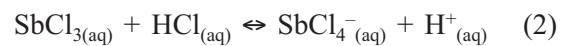
Dissolution reactions

When stibnite ore is added into the hydrochloric acid solution saturated with Cl₂ gas, the reactions taking place in the medium can be written as follows⁶:

Table 2 – Parameters used in this study and their values

Quantities	Values
Reaction temperature, °C	12, 25*, 35, 44
Acid mass fraction, %	23.72, 27.20*, 30.58
Particle diameter, μm	605, 433, 308, 215*, 152.56
Reaction time, min	2.5, 5, 7.5, 10, 15, 20, 30, 40, 45, 50, 60, 70, 75
Stirring speed, min^{-1}	500*
Solid to liquid quotient, $\text{g} \cdot \text{mL}^{-1}$	0.5/100*

*The values kept constant.



Effects of quantities

The data obtained were plotted in the time versus conversion fraction, described as X_{Sb} = the amount of Sb in the solution / the amount of Sb in original stibnite ore.

As seen in Figure 2, the dissolution rate increases, as the particle diameter decreases. This situation can be attributed to the increasing contact surface of the samples as the particle diameter diminishes. Figure 3 shows that increasing reaction temperature has an increasing effect on the dissolution rate, as expected due to the exponential dependence of the rate constant in the Arrhenius equation. The experiments to observe the effect of hydrochloric acid concentration on the dissolution process showed that the dissolution rate increases with increasing acid concentration (Figure 4).

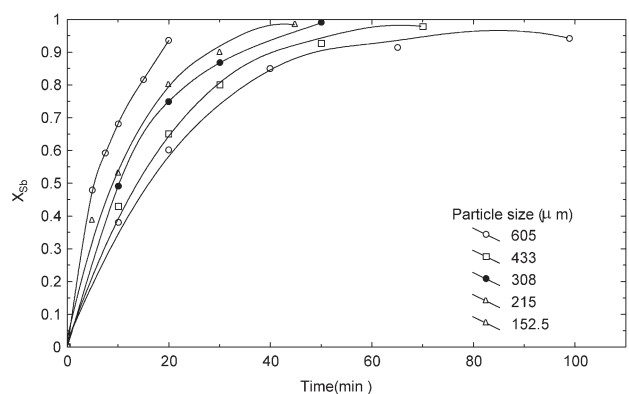


Fig. 2 – Effect of particle size on the dissolution of stibnite ore

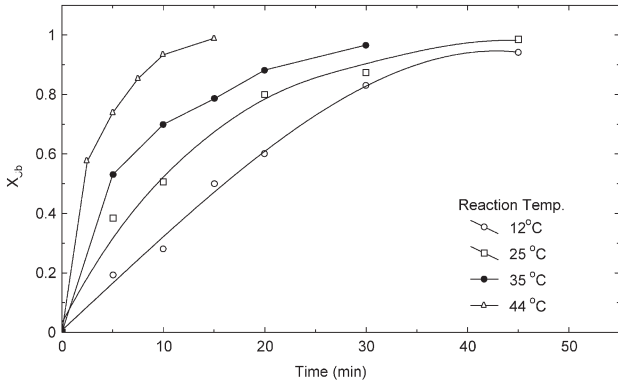


Fig. 3 – Effect of reaction temperature on the dissolution of stibnite ore

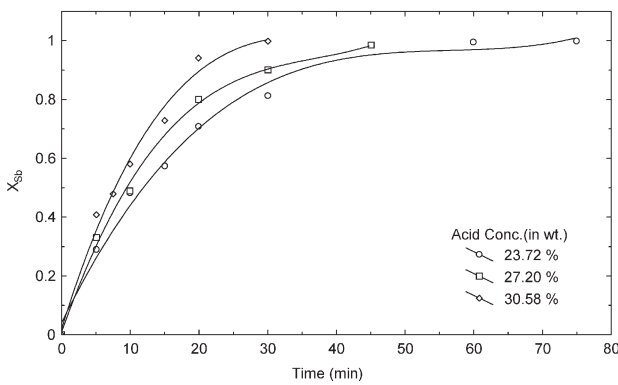


Fig. 4 – Effect of acid concentration on the dissolution of stibnite ore

Kinetics analysis

In a fluid-particle heterogeneous reaction system, the reaction rate can be expressed by one of the following models:

- a) shrinking core model for particle of unchanging size,
- b) shrinking particle model,
- c) pseudo-homogeneous models.

These models can be applicable in both cases of gas-solid reactions and fluid-solid reactions^{14–22}.

In the presented study, the statistical analysis of the experimental data showed that the results fitted to the first order pseudo homogeneous model

$$(dX_{sb} / dt) = k(1 - X_{sb}) \quad (5)$$

When this expression was integrated, the following equations was obtained

$$-\ln(1 - X_{sb}) = k \cdot t \quad (6)$$

As seen in Figure 5, the plots of t versus $-\ln(1 - X_{sb})$ gave straight lines. On the other hand, the quantities such as temperature, particle diameter, HCl concentration, chosen as quantities in the present work, affect reaction kinetics¹⁴. To determine this effect, rate constant, k , in Eq. 6 was expressed in the following form:

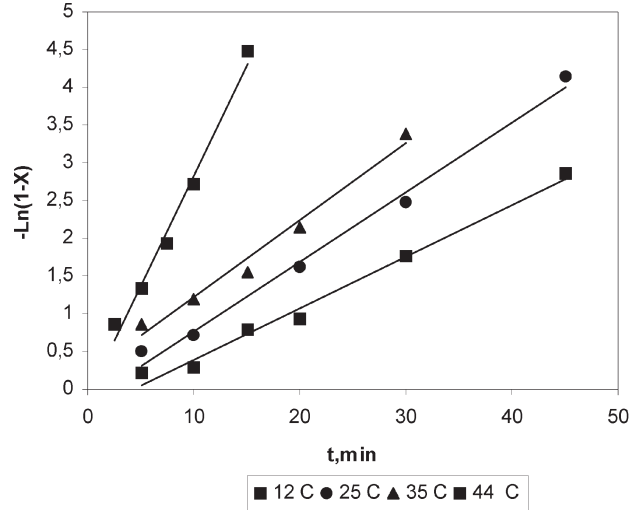


Fig. 5 – Plot of $-\ln(1 - X)$ versus t for different reaction temperature

$$-\ln(1 - X_{sb}) = k_0 \cdot [(d)^a \cdot (w)^b \cdot \exp(-E_A/RT)] \cdot t \quad (7)$$

and, the values of the constants of k_0 , a and b were determined as 2.97×10^5 , -0.74 and 1.52 , respectively, using an statistical program and a PC. Thus Eq. 7 could be written as follows:

$$-\ln(1 - X_{sb}) = 2.97 \times 10^5 \cdot (d)^{-0.74} \cdot (w)^{1.52} \cdot \exp(-4800/T) \cdot t \quad (8)$$

From $E_A/R = 4800$, activation energy (E_A) was calculated as $39.87 \text{ kJ.mol}^{-1}$.

To test the fit between the experimental conversion values and the values calculated from the Eq. 8, the plot of X (experimental) versus X (calculated) was drawn, as seen in Figure 6. The fit between the experimental and calculated values is very good, with a relative mean square errors of 0.1065, calculated by the Eq. 9

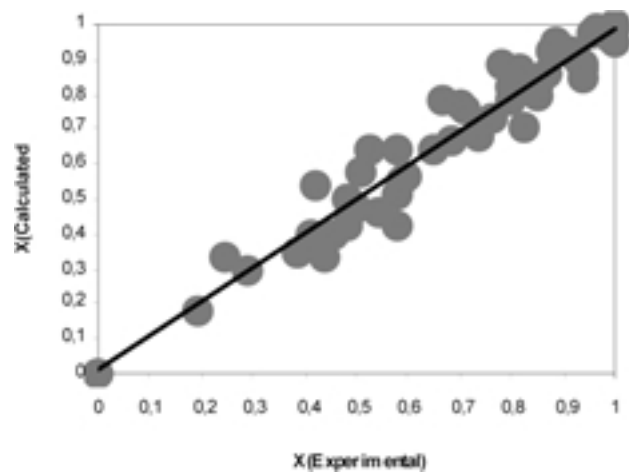


Fig. 6 – The agreement between experimental conversion values and those calculated from the empirical expression Eq. 8

$$ER = \left[\frac{1}{N} \sum_{i=1}^N \frac{(X_{cal} - X_{exp})^2}{(X_{cal})^2} \right]^{\frac{1}{2}} \quad (9)$$

Where X_{cal} is the calculated value, X_{exp} the experimental value, and N the number of experimental data, which is 63 for the present case.

Conclusions

The dissolution of stibnite mineral in hydrochloric acid solutions saturated with Cl₂ gas was investigated in a batch reactor. It was seen that the dissolution process was fitted pseudo-first order homogeneous reaction model and the activation energy of the process was calculated to be 39.87 kJ · mol⁻¹. This semi empirical mathematical model represented the process very well.

Nomenclature

- X_{Sb} – Conversion
 t – Reaction time, min
 a – A constant in Eq. (7)
 b – A constant in Eq. (7)
 k_0 – A constant in Eq. (7)
 d – Particle size, μm
 E_A – Activation energy, kJ · mol⁻¹
 T – Temperature, K
 R – Universal gas constant, J · K⁻¹ · mol⁻¹
 w – Mass fraction, %
 m_s – Mass of stibnite, g
 V_{HCl} – Volume of HCL solution

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