Kinetic Modelling of Sphalerite in Sulfuric Acid Solution

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Abstract. The dissolution of sphalerite in aqueous sulfuric acid is studied in the presence of oxygen in an autoclave at 200 C. In the presence of oxygen, and an oxidized hydrogen sulfide there's formation of elemental sulphur and sulfuric acid. The kinetic of the reaction is studied as a function of the mass of zinc sulfide, the concentration of sulfuric acid, the oxygen partial pressure and temperature. A kinetic model taking into account those factors is hence proposed. On the other hand, the role of hydrogen sulfide on the progress of dissolution is highlighted.

Keywords: sphalerite, sulfuric acid, activity coefficients, leaching, kinetic model.

1 Introduction

Zinc is the third largest non-ferrous metal in the world and is conventionally produced from sphalerite. Strict environmental restrictions are imposed on sulfide smelters and the necessity of using complex deposits have stimulated the development of alternative methods in particular hydrometallurgical ones, as to avoid the production of SO2, a pollutant. In the course of this four decades, attention has been granted to the leaching of zinc sulfide ores concentrates with sulfuric acid (Forward and Veltman, 1959; Parker, 1961; Demopoulos and Baldwin, 1999) [1,2, 3], nitric acid (Bjorling, 1954) [4], hydrochloric acid (Mizoguchi and Habashi, 1981; Majima and al. 1981[5,6], and acidified solutions containing ferric ions (Bobeck and Su, 1985; Palencia Perez and Dutrizac, 1991) [7,8].

The hydrometallurgical pretreatment of sulfides can be performed using different methods (Havlik and Kammel, 2000, Havlik and al, 2001a, b) [9, 10, 11].

Weisener and al. (2003, 2004) [12, 13] suggested the rate of dissolution of sphalerite in the acid, the solution being controlled by oxygen diffusion through a porous nS° or polysulfide surface layer. As a result of their batch experiences at pH 2.5 in the presence of O2, Abraitis and al (2004) [14] have found that the main dissolution reaction for sphalerite in these conditions was a none-oxidization. Finally, Malmström

M.Á. Fernández-Izquierdo, M.J. Muñoz-Torres, R. León (Eds.): MS 2013, LNBIP 145, pp. 239–249, 2013.

and Collin (2004) [15] have studied for a long period the dissolution ofsphalerite, using air purged and dissolution experiments by batch at pH values of 1 to 4 and showed that the dissolution rate of sphalerite is dependent on the pH.

(Balaz and Ebert, 1991) [16] Studied the correlation between the changes on the surface and the properties of sphalerite because of the mechanic of activation with a rate of leaching and oxidation of minerals in presence. Hydrogen peroxide was selected as a strong oxidizing leaching model for leaching. This selective leaching agent for copper dissolves all the iron which is often present in the mineral in a large quantity as a precipitate (Anthony and al., 1990) [17] rushes.

This study is about the application of the non-selective leaching agent (H 2 SO 4), which dissolves the zinc and iron from the sphalerite (15.53% Fe), and to evaluate the possible influence of sphalerite; activation by milling on the leaching selectivity defined as Zn / Fe ratio mass.

The Direct leaching of sphalerite concentrate with ferric iron under atmospheric pressure has been described elswhere (Kammel and al. 1987; Crundwell, 1987; Suni and al. 1989; Palencia Perez and Dutrizac, 1991, Cheng and al. 1994; Pedlik and Lochmann, 1995) [18, 19, 20, 21, 22, 23]. As the zinc is leached, the ferric iron is reduced to ferrous iron by the sulfur in the zinc sulfide according to the following overall reaction stoichiometry:

$$Fe2\ (SO4)3(aq) + ZnS(s) \rightarrow 2FeSO4\ (aq) + ZnSO4\ (aq) + S(s)$$

The solid–liquid reaction takes place in acidic environment and elemental sulfur is the solid product formed. In currently applied large-scale zinc dissolution processes, the produced ferrous iron is re-oxidized in order to continue the leaching. However, if the aim is to reduce the ferric iron, the zinc sulfide concentrate can also be used as a reduction agent and is then leached simultaneously.

2 Experimental

Leaching under pressure of sphalerite of Algeria in an aqueous sulfuric acid was studied in an autoclave at temperatures up to 200 ° C with the presence of oxygen. Many parameters were involved in this reaction: influence of time, of the initial mass of zinc sulfide, of the oxygen pressure, of the temperature and of the concentration of sulfuric acid. A kinetic model taking into account these factors is proposed. In the other hand, the role of hydrogen sulfide on the progress of dissolution is highlighted. The sample used as a 98.495 in sphalerite. Analysis by atomic absorption of the sample employees gave the following composition s= 32.15% and Zn = 66,345%.

3 Results and Comments

3.1 Influence of Time

The experiment consists in attacking 5g of concentrate ZnS with 400ml of initial concentration of sphalerite (0.125 M and 0.5 M) at a pressure of 106Pa for 2 to 120 minutes at a temperature ranging from 50 °C to 200 °C.

In the sulfuric acid medium of 0.125M, the concentration of total dissolved zinc is plotted versus time in Figure (1). This graph shows that the part of the curves corresponding to the oxidation reactions is linear between 15 and 120 min and at temperatures at or below 180 ° C.

In case where the temperature is 130°C, and time of less than 15 minutes, the curve represents the dissolution of zinc sulfide with sulfuric acid

$$ZnS + H_2SO_4 \rightleftharpoons ZnSO_4 + H_2S$$ **R-1**

This reaction is too fast, and the measures are not precise as to obtain a significant initial velocity.

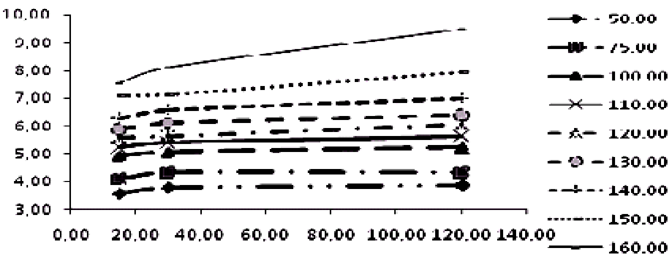

Fig. 1. Dissociation of Sphalerite as function of time between 50 and 160°C

From 15 minutes time, the slope of this line is used to define an average rate of reaction which corresponds to the linear part of the dissolution curves

This equation is of the form [Zn +2] t = Kt + [Zn +2] eq E-1

Thus the reaction is very slow, which correspond to the oxidation of hydrogen sulfide and sulfur.

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S°$$ R2

$$S° + \frac{3}{2}O_2 + H_2O \rightarrow H_2SO_4$$ R3

$$H_2S + H_2SO_4 \rightarrow H_2O + H_2SO_3^- + S°$$ R4

At 190 and 200 ° C, the curves in Figure (2) have a slight concavity turned toward the time axis. The equilibrium corresponding to the first reaction can be considered as reached.

In case of the temperature at 190 ° C, the concentration of the total dissolved zinc is plotted versus the time in Figure (2). This graph shows that the slope of this line is used to define the average rate of reaction.

The relationship [Zn 2 +] t = [Zn 2 +] eq + kt is not well verified because of the strong contribution of the oxidation reactions of hydrogen sulfide and sulfur. The reactions of sulfur oxidation and decomposition of the hydrogen sulfide are added to the oxidation reaction of hydrogen sulfide.

In a sulfuric medium of 0, 5M, the concentration of total dissolved zinc, is plotted versus time in Figure (3).

This graph shows that the curves of the [Zn 2 +] = f (t), corresponding to the oxidation reactions is linear between 15 and 120 min and at temperatures at or below 150°C. In addition, the curves are more concave, but the average rate of reaction will always be taken as

$$\Delta\ [\mathrm{Zn}\ 2\ +] = ([\mathrm{Zn}2\ +]\ 120\mathrm{mn} - [\mathrm{Zn}\ 2\ +]\ \mathrm{eq}). \tag{E2}$$

The curves observed here are in good agreement with the decrease in total moles of gas system over time. After a period (20 minutes) of establishment of equilibrium, there is an almost linear decrease in the number of moles versus time for temperatures below 170-180 ° C.

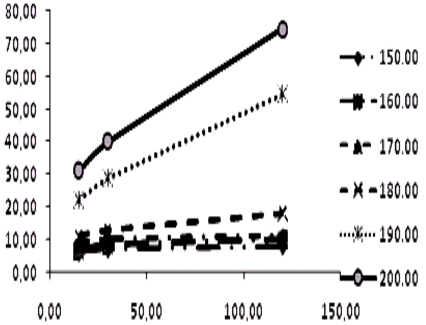

Fig. 2. Dissociation of Sphalerite as function of time between 150 and 200°C

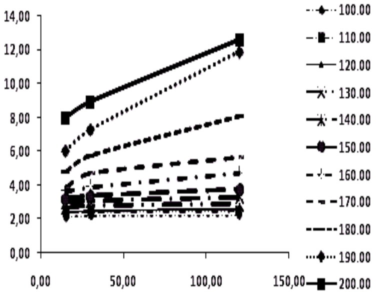

Fig. 3. Dissociation of sphalerite as function of time between 100 and 200°C

3.2 Influence of the Initial Mass in Zinc Sulfide

The experiment consists in attacking 5 to 50g of concentrate ZnS with 400ml of initial concentration of sphalerite (0.125 M) at a pressure of 106Pa for 120 minutes at a temperature ranging from 130 °C to 200 °C.

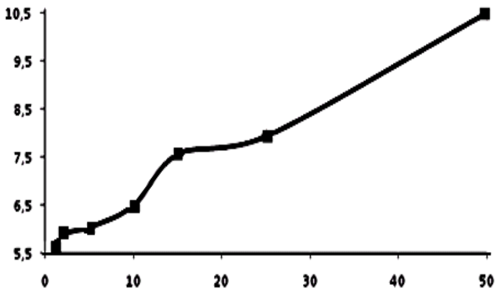

Fig. 4. Dissociation of Sphalerite as function of the initial mass of ZnS at 130°C

The figure (4) shows that the reaction of dissolution of zinc sulfide presents, within the temperature range studied, a single regime as function of the initial mass of solid:

$$[Zn\ 2\ +]\ t = [Zn\ 2\ +]\ eq + kmt \qquad E3$$

[Zn 2 +] eq is independent of the initial mass of zinc sulfide provided that it is sufficient.

After rapid dissolution (time t0), the reaction is strongly inhibited by the presence of hydrogen sulfide and the reaction rate is of order 1 in relation with the initial mass of zinc sulfide.

3.3 Influence of Oxygen Partial Pressure

The experiment consists in attacking 5 g of concentrate ZnS with 400ml of initial concentration of sphalerite (0.125 M et 0.5M) at a pressure of 105Pa to 4 106Pa for 120 minutes at a temperature ranging from 130 °C - 150°C and to 180 °C.

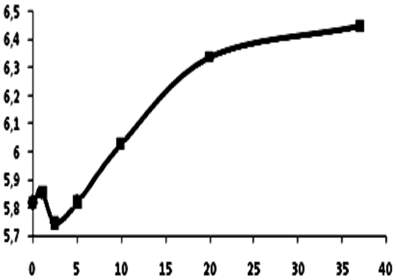

Fig. 5. Dissolution of sphalerite as function of partial pressure of oxygen at 130°c in an aqueous sulfuric medium at 0.125 M

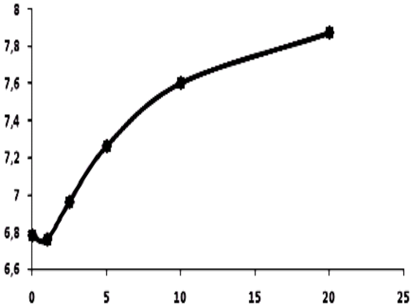

Fig. 6. Dissolution of sphalerite as function of partial pressure of oxygen at 150°c in an aqueous sulfuric medium at 0.125M

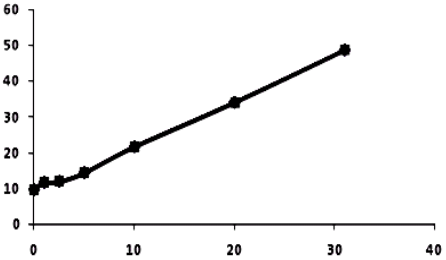

Fig. 7. Dissolution of sphalerite as function of partial pressure of oxygen at 180°c in an aqueous sulfuric medium at 0.125 M

Figures (5), (6) and (7) show that regardless to the temperature, the rate of dissolution of zinc sulfide is directly proportional to the oxygen pressure in the pressure range of (0 to 4.10 6 Pa) and the maximum temperature considered (180°C). At low concentrations and at temperatures below 150-160°C, dissolution increases slightly with oxygen pressure (1.36 10 -6 mol dissolved by additional 10 5 Pa). At 180°C, the oxidation reactions are strongly activated, dissolution increases significantly with the oxygen pressure (1.01 mole dissolved by additional 10 5 Pa).

In all cases: $[Zn^{2+}]_t - [Zn^{2+}]_{eq} = kP_{tO_2}$ E4

Time, temperature, concentration and the initial mass are fixed.

The dissolution rate obtained corresponds to the following reactions:

$$H_2S + 1/2\,O_2 \rightarrow H_2O + S^\circ \qquad R5$$

$$H_2O_2 + O_2 \rightarrow H_2SO_4 \qquad R6$$

$$S^\circ + H_2O + 3/2\,O_2 \rightarrow H_2SO_4 \qquad R7$$

The curves obtained do not pass through the origin.

3.4 Influenced of the Initial Concentration of Sulfuric Acid

The experiment consists in attacking 5g of concentrate ZnS with 400ml of initial concentration of sphalerite (0 M et 1M) at a pressure of 106Pa for 120 minutes at a temperature ranging from 130°C to 180 ° C.

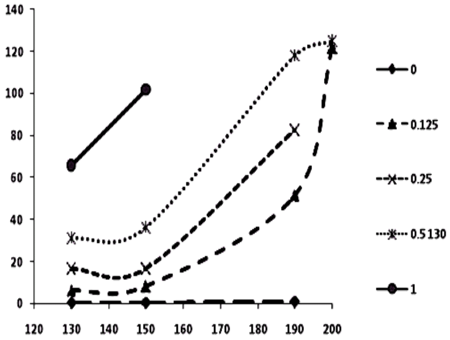

Fig. 8. Dissolution of sphalerite as function of initial concentrations for in sulfuric acid

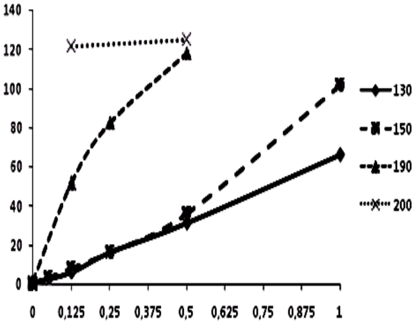

Fig. 9. Dissolution of sphalerite as function of temperature for different initial concentrations in sulfuric acid

The figures (8 and 9) show that for the temperature 130 ° C, the concentration of dissolved zinc is quad when the acidity passes from 0.125 to 0.5 M.

The analyses show that the solutions at 180 ° C are always accompanied by the production of sulfur which increases with acidity. At 130 ° C, the production of hydrogen sulfide increases as a function of acidity. At low temperatures, the dissolution is held following an electrolytic process, the rate of the reaction depends, for low acidities, on the acidity of the solution. The increase of H + ions in the solution helps the dissolution.

At high temperatures (> 160 C), the overall reaction is strongly activated; hydrogen sulphide is almost completely oxidized as sulphur for sulfuric acid concentrations above 0.5 M.

The rate of reaction, whatever the temperature below 200°C, and taking into account the dissolution without oxygen, can be written

$$[Zn^{2+}] = [Zn^{2+}]_{eq} + k\,[H_2SO_4]\,t \qquad \text{E5}$$

$[Zn^{2+}]_{eq}$ is proportional to the initial concentration of sulfuric acid.

3.5 Influence of Hydrogen Sulfide in the Solution

The test is to attack an amount of ZnS (5g) by a sulfuric acid solution (0.125 M) at temperatures between 130,150 and 180 ° C in an autoclave at a partial pressure of oxygen of 106 Pa for a time 120 min.

Figures (10 and 11) show that whatever is the temperature, the dissolution of zinc sulfide increase greatly.

Activated carbon acts as an adsorbent for hydrogen sulfide and allows a significant dissolution, even at relatively low temperatures (90-130°C), shifting the equilibrium reaction in the direction of dissolution. On contrary, the presence of hydrogen sulfide at high pressure delays considerably the dissolution and almost stops it when the pressure is of 10 6 Pa. At 180°C, hydrogen sulfide reacts with sulfuric acid to give mainly sulfur. Sulfur, which coats the grains of sulfur, creates an additional resistance to diffusion which delays the dissolution.

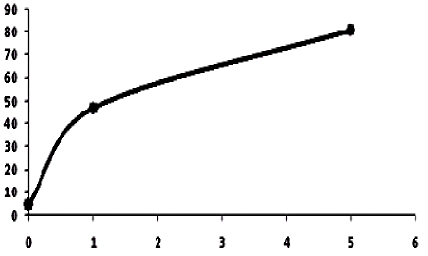

Fig. 10. Dissolution of sphalerite as function of mass activated carbon

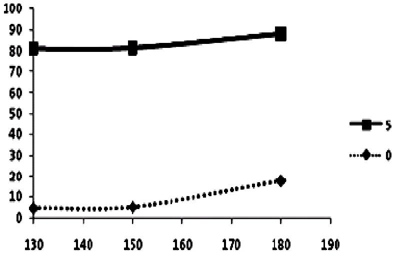

Fig. 11. Dissolution of only sphalerite in presence of activated carbon as function of temperature

Figures (12 and 13) show that whatever is the temperature, the reaction of dissolution is strongly delayed when the partial pressure of hydrogen sulphide increases. A pressure of 106 Pa of hydrogen sulphide completely stops completely the reaction for the considered temperatures.

For a temperature equal to 130°C, the final concentration of acid is considerably more important than the initial concentration.

For a temperature equal to 180°C, the final concentration of acid is also greater than the initial concentration excepted for the partial pressures of 106 Pa of hydrogen sulfide.

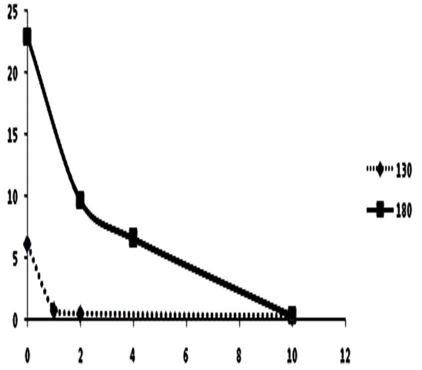

Fig. 12. Dissolution of sphalerite as function of partial pressure of hydrogen sulfide at 130°C and 180°C

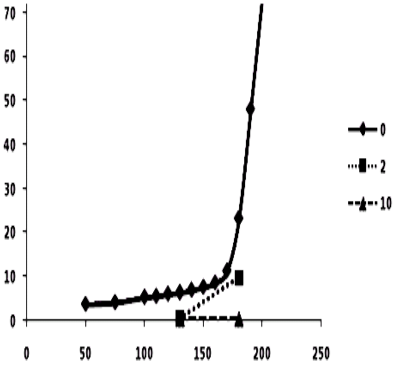

Fig. 13. Dissolution of sphalerite as function of temperature for different partial pressures of hydrogen sulfide

3.6 Effect of Temperature

The test is to attack an amount of ZnS (5g) by a 400ml sulfuric acid solution (0.125 M and 0.5 M) at temperatures of 50 to 180 ° C in an autoclave at a partial pressure of oxygen of 106 Pa for a time of 120 min.

The resulting graph (Figure14) is divided into two areas as for the previous concentrations of sulfuric acid.

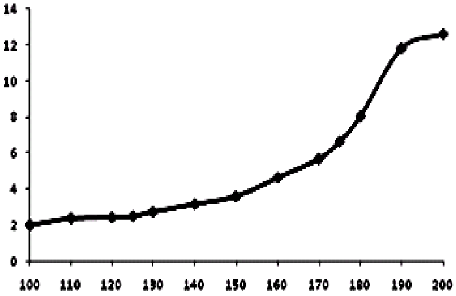

Fig. 14. Dissolution of sphalerite as function of temperature for different partial pressures of hydrogen sulfide

3.6.1 In the Area 120-170 ° C

The concentration of dissolved zinc by the reaction of dissolved oxygen under pressure can be expressed as a function of concentration [Zn 2 +] eq corresponding to the balanced relationship in the absence of oxygen:

$$[Zn^{+2}] = [Zn^{+2}]_{eq+}3.5.m.t.P_{O_2}[H_2SO_4].e^{\frac{-11.21}{T}} \qquad \text{E6}$$

With P O2 (Pa), m (g) t (min) [H 2 SO 4] mole of sulfuric acid per liter;

The concentration [Zn2+] eq can be calculated from the relation giving the equilibrium constant of the reaction without oxygen. This concentration depends only on the temperature and the initial concentration of sulfuric acid.

This model corresponds to the slow reaction of oxidation of hydrogen sulfide. The dissolution rate is of order 1 with regard to the oxygen pressure in the initial mass of zinc sulfide and sulfuric acid concentration. The reaction takes place according to an electrochemical oxidation of hydrogen sulfide, but it is also limited by diffusion through a layer of liquid sulfur on the surface of the grains.

3.6.2 Above 160 ° C to 200 ° C

The kinetic model corresponding to the second step is of the same form as before:

$$[Zn^{+2}] = [Zn^{+2}]_{eq+}m.t.P_{O_2}[H_2SO_4].e^{\frac{-20.58}{T}+22.765} \qquad \text{E7}$$

With P O2 (Pa), m (g) t (min) [H 2 SO 4] mole of sulfuric acid per liter;

The reaction is faster than temperatures at 160 ° C. Hydrogen sulfide and elemental sulfur are rapidly oxidized as sulfuric acid. The oxidation of hydrogen sulfide and the complex reactions of hydrogen sulfide in sulfuric acid constitute the limiting steps of the dissolution reaction.

4 Conclusion

This present study is related to a dissolution process of sphalerite in aqueous solution of sulfuric acid. Leaching experiments of this study are covering the temperature range of 25 ° C to 200 ° C,

In the presence of oxygen, two areas above 120 ° C can be distinguished.

Between 120 and 160 ° C the reaction takes place according to an electrochemical process. It is divided into two stages. The first corresponds to the dissolution of zinc sulfide which quickly reaches its equilibrium. And hydrogen sulfide is oxidized very slowly. The kinetic model thus proposed in this second step is

$$[Zn^{+2}] = [Zn^{+2}]_{eq+}3.5.m.t.P_{O_2}[H_2SO_4].e^{\frac{-11.21}{T}}$$

[Zn 2+] eq is the concentration of dissolved zinc in equilibrium, corresponding to the equilibrium reaction without oxygen. This concentration depends only on the initial concentration of sulfuric acid and temperature. The overall reaction is limited mainly by the reaction of oxidation of hydrogen sulfide and diffusion through a layer of liquid sulfur on the surface of the grains.

Between 160 and 200 ° C the reactions of oxidation are faster, and the kinetic model is

$$[Zn^{+2}] = [Zn^{+2}]_{eq+} m.t.P_{O_2}[H_2SO_4].e^{\frac{-20.58}{T}+22.765}$$

The overall reaction is limited by parallel chemical reactions oxidation of hydrogen sulfide, the reaction of hydrogen sulfide with sulfuric acid superimposed on the direct oxidation reactions. Elemental sulfur resulting from these reactions is itself oxidized as sulfuric acid.

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