

## A kinetic study of pyrite in the lime roasting of a vertical cyclone

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(Received October 27, 1997)

### 수직 싸이클론의 $\text{Ca}(\text{OH})_2$ 배소에서 $\text{FeS}_2$ 의 열적반응에 관한 연구

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(1997년 10월 27일 접수)

**Abstract** This research has been studied in terms of investigating the reaction behavior of pyrite with a cyclone reactor. The Mathematical model has developed pyrite oxidation and lime sulfation in this reactor. The model assumes a chemical control shrinking core behavior for the pyrite and a fluid film control shrinking core behavior for the lime. The model was solved and characterized numerically. Experiments have been performed to study the influence of reaction parameters such as reactor temperatures, pyrite particle sizes, air flow rates, feeding rates, and mixing ratio of pyrite and lime. The oxidation and sulfation products were characterized chemically and physically.

**요 약** 본 연구는 싸이클론 반응로에서  $\text{FeS}_2$ 의 반응 특성에 관한 조사를 연구하였다. 수학적인 모형으로 이 반응로에서  $\text{FeS}_2$ 의 oxidation과 sulfation 등을 전개하였다. 모형은  $\text{FeS}_2$ 에서 chemical control shrinking core로서 그리고  $\text{Ca}(\text{OH})_2$ 에서 fluid film control shrinking core로서 가정하였으며 수식으로 발전시켰다. 본 실험은 이 반응 파라미터들의 영향에 연구로서 진행하였으며 즉 반응로의 온도변화,  $\text{FeS}_2$ 의 입자크기, 공기 주입비율, 시료 주입비율, 그리고  $\text{FeS}_2$ 와  $\text{Ca}(\text{OH})_2$  비율 등이다. Oxidation과 Sulfation에 의한 반응물들은 화학적 및 물리적으로 특성을 기술하였다.

### 1. Introduction

Refractory precious metal ores occurs in association with pyrite or arsenopyrite. The difficulty in treating these types of ores is not only the lack of complete liberation but also the presence of soluble sulfur, arsenic, and antimony which go into solution, absorb onto the surfaces of free gold particles during their decomposition, thus retarding gold dissolution [1, 2, 3].

Lime roasting of refractory gold ores may be a viable method for treating flotation concentrates of these ores in an economic and environmentally safe manner if the arsenic and sulfur can be retained in the roaster calcines as calcium sulfates or sulfites and calcium arsenates or arsenites [4, 5, 6, 7, 8]. Roasting should be performed under conditions which do not cause fusion and sintering of particles.

The roasting of refractory gold ores is carried out at moderate temperatures (500~700°C) in order to create porosity [9, 10, 11]. If the roasting temperature is too low, then incomplete oxidation results. If the roasting temperature is too high, then sintering occurs and tend to block the gold from subsequent lixiviation with the cyanide solutions. The sulfur dioxide given off from roasting must be either recovered as acid or treated by lime adsorption and scrubbing.

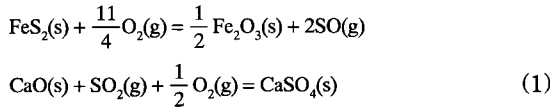
This research presents the initial part of cyclone roasting to evaluate lime roasting of pyrite and to develop a mathematical model and a laboratory reactor to investigate the continuous behavior of the lime roasting of these minerals.

### 2. Mathematical model

The present model describes the oxidation of pyrite particles in a flow reactor in the presence of  $\text{Ca}(\text{OH})_2$ . A system of nonlinear partial differential equation are obtained. These equations are transformed into dimensionless form by introducing characteristic dimensionless groups.

In order to study the kinetics of gas-solid reactions in a moving gas stream, the following assumptions are made in the formulation of the model; (a). There is no temperature gradient within the particle. (b). The particles are spherical and uniform sized. (c). The reactions are first order and are shrinking core in behavior. (d). There is a steady state.

A general equation for pyrite oxidation in the presence of lime may be written as follows;



### 2.1. Pyrite oxidation

When the chemical reaction is rate controlling, the reaction front position in a pyrite particle can be found as;

$$\frac{d}{dt} \left( \frac{4}{3} \pi r_1^3 \rho_p \right) = -4\pi r_1^2 n_{s_1} \text{KC}_{\text{O}_2} \quad (2)$$

This equation will be simplifying as follows;

$$\frac{d\gamma_1}{dt} = \frac{n_{s_1} \text{KC}_{\text{O}_2}}{\rho_{\text{FeS}_2}} \quad (3)$$

The initial condition is given by  $\gamma_1(t=0) = \gamma_0$ . If the concentration of oxygen is constant, the equation can be integrated directly to obtain at constant temperature.

$$1 - \frac{\gamma_1}{\gamma_0} = \frac{n_{s_1} \text{KC}_{\text{O}_2} t}{\rho_{\text{FeS}_2} \gamma_0} \quad (4)$$

The extent of the reaction is defined as;

$$E_1 = 1 - \left( \frac{\gamma_1}{\gamma_0} \right)^3 \quad (5)$$

Assuming an average gas velocity ( $V$ ), then the particle's residence time in the reactor is given by

$$t = \frac{Z}{V} \quad (6)$$

By substituting for  $t$  and  $\gamma_1/\gamma_0$ , we obtain;

$$1 - (1 - E_1)^{\frac{1}{3}} = \frac{n_{s_1} \text{KC}_{\text{O}_2} L}{\rho_{\text{FeS}_2} \gamma_0 V} Z^* \quad (7)$$

$Z^*$  and  $\lambda_1^0$  are given by

$$Z^* = \frac{Z}{L} \quad \lambda_1^0 = \frac{n_{s_1} \text{KC}_{\text{O}_2} L}{\rho_{\text{FeS}_2} \gamma_0 V} \quad (8)$$

$Z^*$  is the dimensionless axial position.

$$1 - (1 - E_1)^{\frac{1}{3}} = \lambda_1^0 Z^* \quad (9)$$

$\beta_1 = \frac{\gamma_1}{\gamma_0}$  is the dimensionless reaction interface position within the pyrite particle. With the initial condition, it is given by  $\beta_1(Z^*=0) = 1$  When temperature and composition changes are taken into account, the following equation is obtained.

$$\frac{d\beta_1}{dZ^*} = -\lambda_1 \frac{X_{\text{O}_2}}{\theta_g^2} e^{-\eta \left( \frac{1}{\theta_p} - 1 \right)} \quad (10)$$

$\lambda_1$  is given by  $\lambda_1 = \frac{n_{s_1} K_D C_T L}{\rho_p \gamma_0 V_O}$ .  $C_T$  is given by  $C_T = \frac{P}{RT_O}$

and  $r_1$  is given by  $\gamma_1 = \frac{E_{A1}}{RT_0}$ .

### 2.2. Lime reaction

The lime sulfation reaction is assumed to be controlled by fluid film mass transfer of the sulfur dioxide. The behavior of the particle can then be described by

$$\frac{d}{dt} \left( \frac{4}{3} \pi R_1^3 \rho_L \right) = -n_{s_2} 4\pi R_0^2 K_D C_{\text{SO}_2} \quad (11)$$

The above equation will be simplifying as follows;

$$\frac{dR_1}{dt} = - \left( \frac{n_{s_2} K_D C_{\text{SO}_2}}{\rho_L} \right) \left( \frac{R_0}{R_1} \right)^2 \quad (12)$$

The initial condition is given by  $R_1(t=0) = R_0$ . If the concentration of sulfur dioxide is constant, this equation can be integrated to obtain at constant temperature.

$$1 - \left( \frac{R_1}{R_0} \right)^3 = \frac{3n_{s_2} K_D C_{\text{SO}_2} t}{\rho_L R_0} \quad (13)$$

$\lambda_2^0$  are given by

$$\lambda_2^0 = \frac{3n_{s_2} K_D C_{\text{SO}_2} L}{\rho_L R_0 V} \quad \beta_2 = \frac{R_1}{R_0} \quad (14)$$

Transforming into dimensionless form is given by

$$E_2 = \lambda_2^0 Z^* \quad (15)$$

With the initial condition, it is given by  $\beta_2(Z^* = 0) = 1$ . When temperature and composition changes are taken into account, the following equation is obtained:

$$\frac{d\beta_2}{dZ^*} = -\lambda_2 \frac{X_{SO_2}}{3\beta_2^2} \frac{\theta_L^3}{\theta_g^2} \quad \lambda_2 = \frac{3n_{S_2} K_D^0 C_T L}{\rho_L R_0 V_0} \quad (16)$$

### 2.3. Oxygen balance

The oxygen rate balance in the system is given by

$$\begin{aligned} \frac{d(QC_{O_2})}{dZ} &= \frac{d}{dZ} \left( \frac{11}{4} \frac{m_{FeS_2}}{M_{FeS_2}} \frac{\gamma_1^3}{\gamma_0^3} \right) \\ &+ \frac{d}{dZ} \left( \frac{1}{2} \frac{m_{CaO}}{M_{CaO}} \frac{R_1^3}{R_0^3} \right) \end{aligned} \quad (17)$$

Using the following equations, they are:

$$V \frac{\partial}{\partial Z} \left( \frac{\gamma_1}{\gamma_0} \right)^3 = - \left( \frac{3N_{S_1} K C_{O_2}}{\rho_{FeS_2}} \right) \left( \frac{\gamma_1^2}{\gamma_0^3} \right) \quad (18)$$

$$V \frac{\partial}{\partial Z} \left( \frac{R_1}{R_0} \right)^3 = - \left( \frac{3N_{S_2} K_D C_{SO_2}}{\rho_{CaO} R_0} \right) \quad (19)$$

The oxygen balance in the system may be transformed into dimensionless form using the following dimensionless parameters.  $\lambda_3 = \frac{m_{FeS_2}}{M_{FeS_2} C_T Q_0}$  is the ratio of the molar flow rate of pyrite to the molar flow rate gas.  $\lambda_4 = \frac{m_{CaO}}{M_{CaO} C_T Q_0}$  is the ratio of the molar flow rate of lime to the molar flow rate of gas.  $X_{O_2} = \frac{C_{O_2}}{C_T}$  is the dimensionless concentration of oxygen in air.  $X_{SO_2} = \frac{C_{SO_2}}{C_T}$  is the dimensionless concentration of sulfur dioxide in air.

$X_{O_2} + X_{SO_2} + X_{N_2} = 1$  is the mole fraction balance in the system. In dimensionless form, the oxygen balance becomes;

$$\begin{aligned} \frac{dX_{O_2}}{dZ^*} &= -\frac{33}{4} \lambda_1 \lambda_3 \beta_1^2 \frac{X_{O_2}}{\theta_g^2} e^{-\eta_2(\frac{1}{\theta_p} - 1)} \\ &- \frac{\lambda_2 \lambda_4 X_{SO_2} \theta_L^3}{2\theta_g^2} \end{aligned} \quad (20)$$

With the initial condition, they are:

$$X_{O_2}(Z^* = 0) = X_{O_2}^0; \quad X_{SO_2}(Z^* = 0) = 0 \quad (21)$$

### 2.4. Sulfur dioxide balance

The sulfur dioxide balance in the system is:

$$\begin{aligned} \frac{d(QC_{SO_2})}{dZ} &= \frac{d}{dZ} \left( 2 \frac{m_{FeS_2}}{M_{FeS_2}} \frac{\gamma_1^3}{\gamma_0^3} \right) \\ &+ \frac{d}{dZ} \left( \frac{m_{CaO}}{M_{CaO}} \frac{R_1^3}{R_0^3} \right) \end{aligned} \quad (22)$$

Using the previous dimensionless groups, the equation becomes;

$$\begin{aligned} \frac{dX_{SO_2}}{dZ^*} &= 3 \lambda_1 \lambda_3 \beta_1^2 \frac{X_{O_2}}{\theta_g^2} e^{-\eta_1(\frac{1}{\theta_p} - 1)} \\ &- \frac{\lambda_2 \lambda_4 X_{SO_2} \theta_L^3}{\theta_g^2} \end{aligned} \quad (23)$$

Figure 1 shows the effect of  $\lambda_1$  on the extent of reaction for pyrite along the dimensionless axial position. As  $\lambda_1$  increases, the extent of pyrite oxidation increases as expected.

The effect of  $\lambda_2$  on the extent of lime sulfation is presented in Fig. 2 as a function of the dimensionless axial position. As the value of  $\lambda_2$  increases, the conversion of lime increases as expected with large average resistance time required for complete

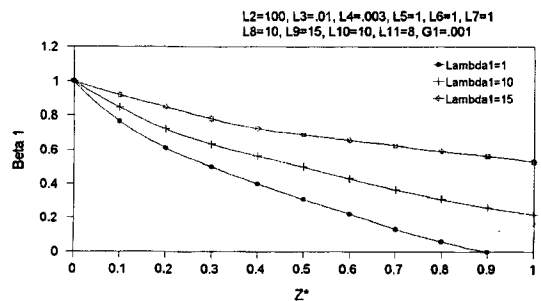


Fig. 1. Effect of Lambda 1 on pyrite oxidation.

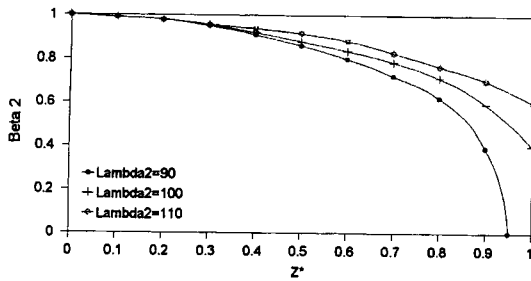


Fig. 2. Effect of Lambda 2 on lime sulfation.

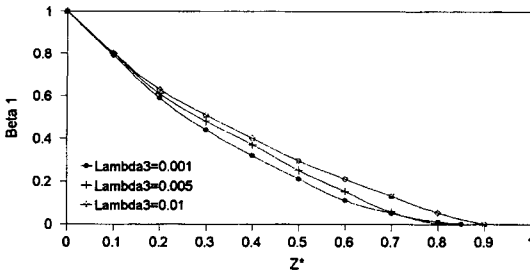


Fig. 3. Effect of Lambda 3 on pyrite oxidation.

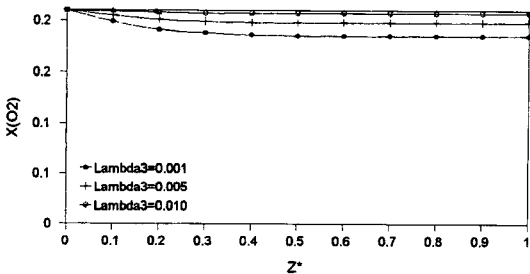


Fig. 4. Effect of Lambda 3 on oxygen concentration.

reaction.

The effect of  $\lambda_3$  on pyrite oxidation and the oxygen concentration is shown in Figs. 3 and 4 as function of the dimensionless axial position. When  $\lambda_3$  becomes small, the oxygen concentration does not change very much within the reactor. There is, however, a large drop in oxygen concentration with

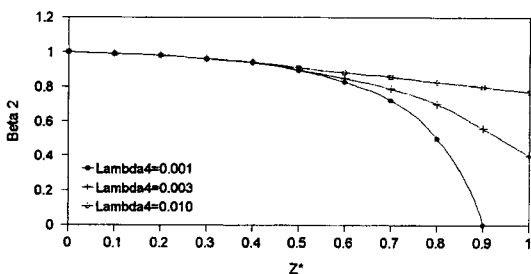


Fig. 5. Effect of Lambda 4 on lime sulfation.

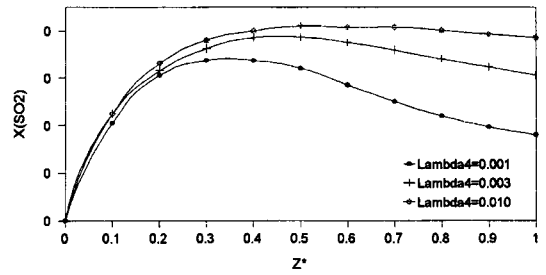


Fig. 6. Effect of Lambda 4 on sulfur dioxide concentration.

an increase in  $\lambda_3$ . This plot shows that the molar flow rate of pyrite should be less than about 0.001 of the molar flow rate of oxygen in order to maintain a constant driving force for oxidation.

Figures 5 and 6 show the lime sulfation and concentration of sulfur dioxide versus axial position for several values of  $\lambda_4$ . At higher value of  $\lambda_4$ , the concentration of sulfur dioxide tends to increase rapidly from the axial position of 0 to 0.1, then it decreases. When  $\lambda_4$  becomes small, the concentration of sulfur dioxide tends to reach a steady value at the discharge of the reactor.

### 3. Experimental procedures

The cyclone roasting oxidation experiments were conducted stainless steel which was 2.5" ID and 33" long. The stainless reactor was encased in silica brick containing a heating coil. There are three thermocouples in the system. All temperatures in the system are continuously recorded by a data acquisition system. The collecting chamber is water-cooled through cooling lines and all water flow rates are controlled by a manometer. A gas analysis system is connected to the end of the reactor using by pass system. Informations of the experimental

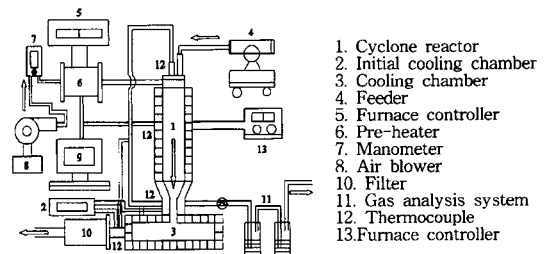


Fig. 7. Schematic of the experimental reactor.

system are collected by a data acquisition system. The cyclone roasting experimental system is shown in Fig. 7.

The pyrite samples were obtained from world national science establishment Inc. The pyrite was crushed to -8--60 meshes. The sample contained 52.69 % sulfur, giving a calculated pyrite content of 98.58 %. A magnet was used to remove pyrotites with the magnetic fraction. The lime and sample were mixed in a ceramic blender and then placed in preheated furnaces for four hours at 50°C prior to feeding into the reactor.

**4. Experimental results and analysis**

*4.1. Effect of changing reactor temperatures on pyrite roasting*

The purpose of these experiments was to find the effect of temperature on the extent oxidation and sulfation. Standard conditions were; air flow rate (7.167 SCFM), sample particle size (-100+200 mesh), and weight ratio of pyrite to lime (1:1.34). The average resistance time of the gas phase was not constant but varied with the reactor temperatures.

Figure 8 shows the best results were obtained at 700°C. The highest temperature would probably result in a sintered calcine and poor gold recoveries. As there are two competing reaction, pyrite oxidation and lime sulfation are the relative kinetics in this result. The rate of lime sulfation must be faster than the oxidation reaction.

*4.2. Effect of particle sizes on pyrite roasting with lime*

The experiments were performed using various

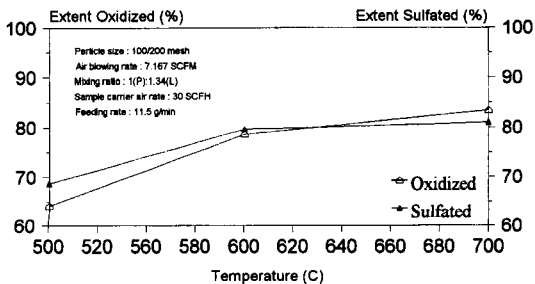


Fig. 8. Effect of temperatures on oxidation and sulfation.

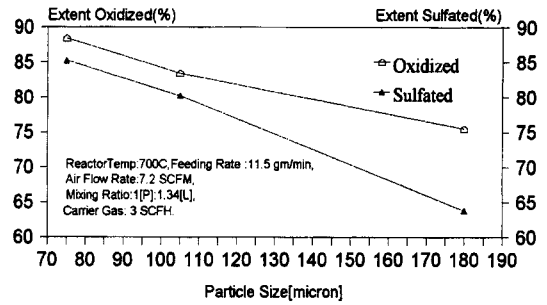


Fig. 9. Effect of pyrite particle sizes on oxidation and sulfation.

pyrite particle sizes (-200 mesh, 100/200 mesh, and 60/100 mesh). The extent of oxidation and sulfation for various pyrite particles sizes are shown in Fig. 9. In creasing the pyrite particle size decreased the sulfur retention because of the slower rate of oxidation and sulfation under this condition.

*4.3. Effect of feed rate on pyrite roasting with lime*

These experiments was performed by fixing all other conditions except the solid feed rates within the rage 6~20 g/min in Fig. 10.

The 20 g/min feeding rate decrease sulfation and oxidation because the oxygen driving force is diminished when solid feed rates exceed 11.6 g/min.

*4.4. Effect of air flow rate and mixing ratio*

The flow rate was varied (4, 5, 7.167SCFM) and other conditions were kept constant. These results show that higher flow rates decreased the percentages of oxidation and sulfation because of the exothermic nature of both the sulfation and oxidation reaction. The sulfur retention increases with the amount of lime added because the retention is proportional to the stoichiometry.

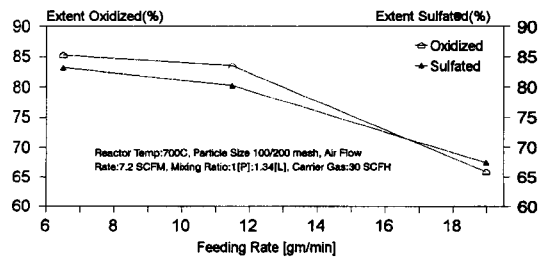


Fig. 10. Effect of sample feed rates on oxidation and sulfation.

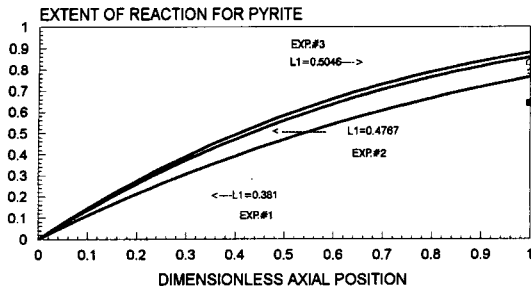


Fig. 11. Predicted vs experimental results for pyrite.

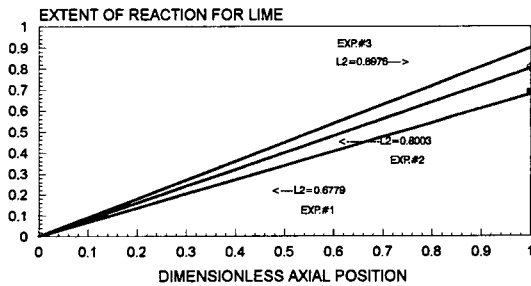


Fig. 12. Predicted vs experimental results for lime.

## 5. Discussion and conclusions

The mathematical model was developed for the oxidation of pyrite and sulfation of lime with air flow. The extent of pyrite oxidation and lime sulfation are related to the values  $\lambda_1$  (0.381, 0.4767, 0.5046) and  $\lambda_2$  (0.6779, 0.8003, 0.8976) in Figs. 11 and 12. The results are single data points because only discharge was sampled and analyzed. On the basis of the experimental and theoretical results, the major conclusions is following;

1) The extent of oxidation and sulfation of pyrite with lime increases with lime increasing reactor temperatures within the range study.

2) The extent of oxidation and sulfation increases with decreasing air flow rates over the range studied.

3) The extent of oxidation and sulfation decreases with increased solid feed rates between 12~20 g/min.

4) The extent of oxidation and sulfation increases only slightly with in an increasing weight ratio of lime to pyrite beyond 1.5.

5) A fundamental theoretical model was developed to characterize the oxidation and sulfation of a pyrite-lime mixture in a flow reactor.

6) The influence of important parameters on the oxidation and sulfation reactions were evaluated theoretically and experimentally.

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## Notation

- K : the chemical rate constant.  
 $n_{s1}$  : the stoichiometric coefficient.  
 $r_1$  : the reaction interface position.  
 $Z$  : the axial position in the reactor.  
 $\lambda_1^0$  : the ratio of the average residence time within the reactor to time for complete reaction of pyrite particle.  
 $V_0$  : the initial gas velocity.  
 $K_0$  : the reaction rate constant at the initial temperature.  
 $n_{s2}$  : is a stoichiometric coefficient.

$\lambda_2^0$  : the ratio of the average residence time in the reactor to the time for complete reaction of the lime particle.

$\beta_2$  : the dimensionless position within the lime par-

ticle.

Q : volumetric gas flow rate [ $\text{cm}^3/\text{sec}$ ].

m : the mass feed rate of pyrite and lime [ $\text{g}/\text{mole}$ ].