

KINETIC MODELING OF THE EXTRACTION PROCESS OF IRON OXIDE OF THE BAUXITE WASTE

Edilson Marques Magalhães, eng.magalhaes@yahoo.com.br

Emanuel Negrão Macêdo, enegrao@ufpa.br

José Antônio da Silva Souza, jss@ufpa.br

João Nazareno Nonato Quaresma, quaresma@ufpa.br

School of Chemical Engineering, Universidade Federal do Pará, UFPA
Campus do Guamá, Rua Augusto Corrêa, 01, 66075-110, Belém, PA, Brazil

Abstract. *The production of alumina from bauxite using the Bayer process generates the residue known by red mud. This material can be used as a source for concentration and recovery of valuable metals such as titanium. The greatest difficulty of concentrating titanium compounds is the large amount of iron oxide present in red mud > 30% by weight. This work is divided into two stages: the first covers the development of a mathematical model that represents the kinetic modeling of extraction of iron oxide present in red mud. The second focuses on the use of the model with experimental data from the extraction of iron oxide red mud in order to obtain the essential parameters that will enable a greater understanding of the process of extraction of iron oxide, such as, the activation energy, rate constant of reaction and controlling stage the extraction process.*

Keywords: *Red Mud, Bayer Process, Leaching*

1. INTRODUCTION

One theory for the uncatalyzed reactions of particles surrounded by a fluid which react with may be treated considering two ideal models simple: progressive conversion model and model without reaction in the core (Balarini, 2009). For the progressive conversion model assumes that reactant fluid enters and reacts in the particle at all times, most likely with different velocities and in different places. Thus, the solid reactant is converted continuously and progressively within the particle. In the model without reaction in the core is assumed that the reaction occurs primarily on the outer surface of the particle. The reaction zone then moves toward the center of the solid and may leave material for the behind completely converted and inert solid (ash), so that at any instant, there is a core of unreacted material which decreases in size during the reaction. However, the outline of this unreacted core does not always have a definite form but, nevertheless, there is evidence that, in most cases, the model without reaction in the core is closer of real particles than progressive conversion model. (Levenspiel, 1999).

In this context, based on the unreacted core model, was performed a kinetic study of reaction solid-liquid (leaching) between the red mud and sulfuric acid solutions in order to extract iron, titanium concentration aiming in the red mud, and to a greater understanding of how to process the extraction of iron oxide, was carried out mathematical modeling of the extraction process, in order of obtain a model which would fit the experimental data, and capable of allowing the obtention of kinetic parameters such as: activation energy, rate constant for the reaction, well how the controller stage of the extraction process.

2. MODELING THE PROCESS OF EXTRACTION OF IRON OXIDE

According to the unreacted core model the stages main of a process of extracting metals from a mineral matrix can be described as follows: Stage 1- Diffusion of the reactant fluid A through the layer surrounding the particle to the surface of the solid. Stage 2 - penetration and diffusion of A through the ash layer to the surface of the unreacted core. Stage 3 - Reaction of the fluid A with the solid in the reaction surface. Stage 4 – Diffusion of the fluid B product through the ashes back to the outer surface of the solid. Stage 5 – Diffusion of B through of the layer of fluid back for into the solution. Figure 1 shows such five stages in more details.

2.1 Main Assumptions of the mathematical model

- 1 - The mathematical modeling is performed considering that the red mud particles are all spherical;
- 2 - considering the leaching process as a reaction system solid-fluid, the mathematical model is developed based on the unreacted core model, then the mathematical modeling is performed using the following stages: Flow of reactant A in the liquid film; Flow of the reactant A in the region $r_c < r < R$; Reaction of the reagent A on the surface of r_c , where r_c is the radius of the core of the unreacted particle and R is the radius of the particle;
- 3 - It is considered that only the iron oxide is being extracted from red mud;
- 4 - The variables main affecting the extraction process are temperature and concentration of sulfuric acid;
- 5 - The extraction process is governed by the third stage, ie, the reaction of the fluid A (H_2SO_4) with red mud particles in the reaction surface.

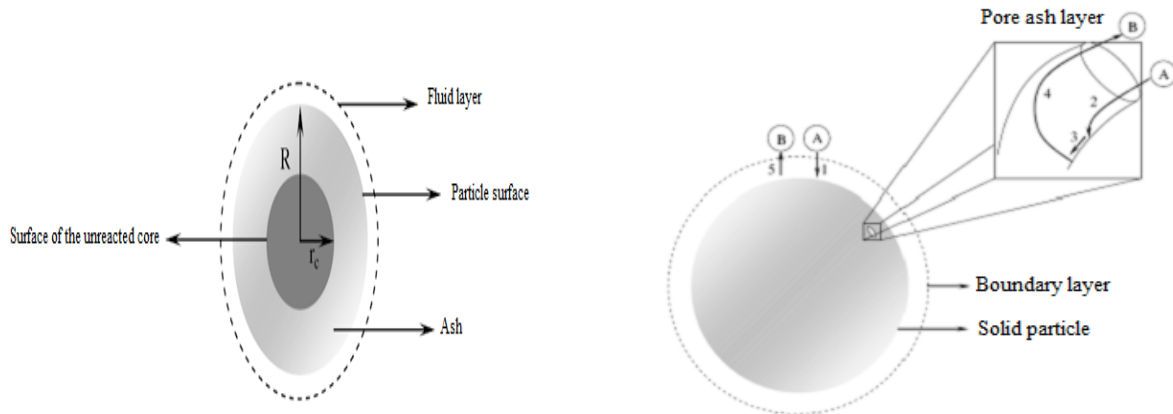


Figure 1. Leaching of a fragment of a mineral matrix. Source: Balarini (2009).

2.2- Development of the mathematical model

2.2.1- Flow reagent A (H_2SO_4) at the liquid film (stage 1)

The flow of reagent A in the liquid film may be given under the definition of a mass transfer coefficient (similar to Newton's law of cooling). For the case in question the mass flow of A to the surface is given by:

$$N_{A_{\infty-P}} = K_m (C_{A_{\infty}} - C_{A_S}) \quad (1)$$

where, K_m is the coefficient of mass transfer in the liquid film, $C_{A_{\infty}}$ is the concentration of A away from of the liquid film and C_{A_S} is the concentration of A on the particle surface. For the case in question, i.e., particles red mud were all considered with spherical shape, and as the flow is variable for the spherical geometries, we will opt to work, for all cases, in terms of rate, thus, Eq. (1), becomes:

$$q_{A_{\infty-P}} = a_p \times N_{A_{\infty-P}} = 4\pi R^2 K_m (C_{A_{\infty}} - C_{A_S}) \quad (2)$$

where a_p is the area of a red mud particle.

2.2.2- Flow reagent A (H_2SO_4) on the region $r_c < r < R$ (stage 2)

The rate on the region $r_c < r < R$ can be obtained according to the Fick's law of diffusion:

$$q_{A_r} = \frac{4\pi D_{ef}}{\left(\frac{1}{r_c} - \frac{1}{R}\right)} \times (C_{A_S} - C_{A_c}) \quad (3)$$

2.2.3 - Reaction of the reagent A (H_2SO_4) on the surface r_c

The reactions which occur on the surface r_c are the reaction between iron (Fe_2O_3) and sulfuric acid solution, well as, may happen the acid reaction with titanium (TiO_2). The total rate of consumption of the reagent A at the surface r_c can be written as follows:

$$q_{A_{r_c}} = SR_{AT}'' = 4\pi r_c^2 \times (K_1 + K_2) \times C_{A_{rp}} \quad (4)$$

where, K_1 and K_2 are the kinetic constants and $C_{A_{rp}} = C_{A_c}$; C_{A_c} is the concentration of A of the unreacted core.

Making an analogy electrical with mass transfer process with chemical reaction (processes in series), we can find the total rate of consumption of A, Eq. (5), as a function of all the mass transport resistance (Flow reagent A in liquid film, Flow reagent A in the region $r_c < r < R$ (2 stage) and Reaction of the reagent A in the surface of the r_c).

$$q_A = \frac{4\pi r_c^2 C_{A\infty}}{\circ_T} \quad (5)$$

where, we have, $\circ_T = \left\{ \frac{r_c^2}{R^2 K_m} + \frac{r_c (R - r_c)}{R Def} + \frac{1}{(K_1 + K_2)} \right\}$; $q_A = \left(\frac{-dn_A}{dt} \right)$ (5.a)

2.2.4 - Consumption of B on the surface r_c

The mathematical models are usually given in terms of extraction of the metals of interest (conversion), in this case the reaction rate for the component B is represented by Eq. (6):

$$\frac{dX_B}{dt} = \frac{3bC_{A\infty}}{\rho_B R \circ_T} \times (1 - X_B)^{2/3} \quad (6)$$

Taking into account the assumptions 3, 4 and 5 of Section 2.1, Eq. (6) takes the following form:

$$\frac{dX_B}{dt} = \frac{3bC_{A\infty} K_1}{\rho_B R} \times (1 - X_B)^{2/3} \times (1 - \alpha_0 X_B) \quad (7.a)$$

It can be seen in Eq. (7.a), that the integral in X_B is a function of α_0 and X_B , then there will be a function of α_0 and X_B . Separating variables and integrates the result, we have the following solution:

$$\Delta F(t) = \mathcal{E}_1 \times t; \quad \Delta F(t) = F(X_B(t)) - F(X_B(0)); \quad \mathcal{E}_1 = 3bC_{A\infty} K_1 / \rho_B R \quad (7.b)$$

where:

$$F(X_B(t)) = D \left\{ 2\sqrt{3} \times \text{Arc tan}(1 - E \times X) - 21 \ln \left[(-1 \times \alpha)^{1/3} X^{1/3} + \alpha^{1/3} \right] + 1 \ln \left[(-1 \times \alpha)^{2/3} X^{2/3} - (-1 \times \alpha \alpha_c)^{1/3} \times X^{1/3} + \alpha_c^{2/3} \right] \right\} \quad (7.c)$$

$$D = \frac{(-1)^{2/3}}{2\alpha^{1/3} \times \alpha_c^{2/3}}; \quad E = \frac{2\sqrt{3}(-1)^{1/3}}{(\alpha_c / \alpha)^{1/3}}; \quad \alpha_c = \alpha_0 - 1; \quad X = 1 - X_B$$

3. RESULTS AND DISCUSSION

3.1. Effect of the temperature and concentration in the reaction constant K_1 (LV-900)

Since the solution for the model given by Eqs. (7.b) and (7.c) was obtained, an algorithm was developed at programming language FORTRAN 90/95 where experimental data of $X_B(t)$ were used to calculate $\Delta F(t)$ as function of time. This procedure was performed by reading the experimental data which were interpolated using the subroutine DCSINT from the IMSL Library and then introduced in Eqs. (7.c) and (7.b), respectively, for each moment (estimate of $\Delta F(t)$). Then, was made linear fit of $\Delta F(t)$ xt to find the value of \mathcal{E}_1 , consequently, K_1 for each leaching temperature.

In Table (1) can be observed values of the reaction constant K_1 for the red mud calcined at 900°C (LV-900). From this table, it can be observed (for both acid concentrations studied) that the reaction constant increases with temperature, as expected.

Table 1. Behavior of K_1 with the leaching temperature (LV-900).

T (°C)	T (K)	1/T (K ⁻¹)	Chemical Reaction			
			K (20%) (s ⁻¹)	ln K (20%)	K (30%) (s ⁻¹)	ln K (30%)
60	333	0.00300	1.50597E-10	-22.616529	2.11319E-10	-22.277654
80	353	0.00283	5.57029E-10	-21.308404	6.25325E-10	-21.192707
90	363	0.00275	1.05016E-09	-20.674320	8.45905E-10	-20.890614

The behavior of the reaction constant K_1 with acid concentration can be analyzed as follows:

- i) For $T = 60\text{ }^\circ\text{C}$, K_1 decreases with concentration;
- ii) For $T = 80\text{ }^\circ\text{C}$, K_1 decreases with concentration;
- iii) For $T = 90\text{ }^\circ\text{C}$, K_1 decreases with concentration.

In this case the red mud calcined at 900°C , the sodium participated of the reactions of calcination and formed a glassy phase. Thus, it is suggested that the mechanism of reaction suffers interference of the following factors that reduce the rate of reaction with increasing concentrations of acid, such factors are: a) the common ion effect, and b) the ionic dissociation of sulfuric acid which is reduced drastically with increasing concentration, (Vogel, 1989).

3.2. Kinetic parameters of the Arrhenius equation (LV-900)

In order to fit the data of Table (1) to the Arrhenius kinetic model, in order to estimate the frequency factor K_0 and activation energy E_a , it was plotted the natural logarithm of $K_1 \times 1/T$ (Fig. (2)). Thus, K_0 and E_a can be obtained by the linear and angular coefficients, respectively. In Table (2) can be observed values of the kinetic parameters of the Arrhenius equation. The activation energy values show that the leaching kinetics is controlled by chemical reaction. This assertion is based on studies that showing that for leaching experiments, the activation energies with values greater than 40 kJ/mol , the controlling step of the kinetics reaction is the chemical reaction.

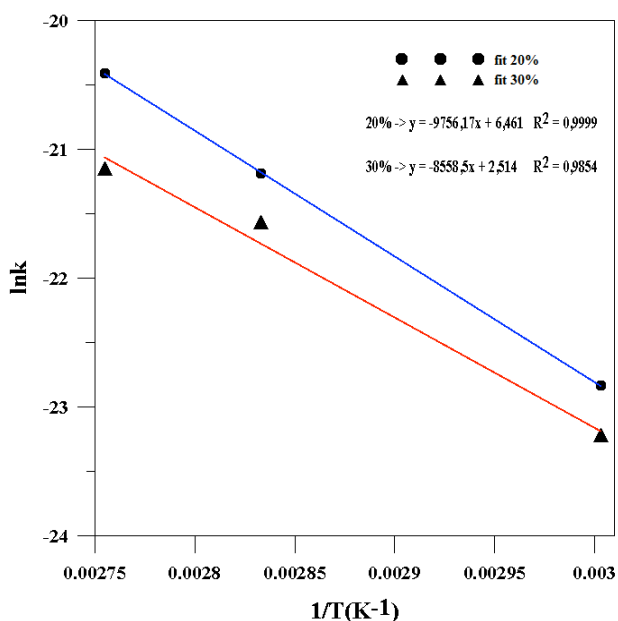


Figure 2. Parameters of the Arrhenius equation (LV-900).

Table 2. Kinetics parameters of the Arrhenius equation (LV-900).

Arrhenius Parameters	Chemical Reaction	
	20%	30%
K_0 (1/s)	6.46	2.51
E_a (KJ/mol)	81.11279738	71.155369

3.3. Effect of the temperature and concentration in the reaction constant K_2 (LV-STT)

In Table (3) can be observed values of the reaction constant K_2 for the red mud without heat treatment (LV-STT). From this table, once again, it can be observed (for both acid concentrations studied) that the reaction constant increases with temperature, as expected.

Table 3. Behavior of K_2 with the leaching temperature (LV-STT).

T (°C)	T (K)	1/T (K ⁻¹)	Chemical Reaction			
			K (20%) (s ⁻¹)	ln K (20%)	K (30%) (s ⁻¹)	ln K (30%)
60	333	0.00300	1.50597E-10	-22.616529	2.11319E-10	-22.277654
80	353	0.00283	5.57029E-10	-21.308404	6.25325E-10	-21.192707
90	363	0.00275	1.05016E-09	-20.674320	8.45905E-10	-20.890614

The behavior of the reaction constant K_2 with acid concentration can be analyzed as follows:

- iv) For T = 60 °C, K_2 increases with concentration;
- v) For T = 80 °C, K_2 increases with concentration;
- vi) For T = 90 °C, K_2 decreases with concentration.

In cases (iv) and (v) which do not follow common sense (which would decrease K_2 with the concentration) suggests that part of the sulfuric acid initially (preferably) was consumed to neutralize the sodium hydroxide present in the red mud.

In the case (vi) where the temperature and concentration are elevated (T = 90 °C and CH₂SO₄ = 30%) (Vogel, 1989) suggests that the mechanism of reaction is influenced by other factors, such as: a) the effect common ion retards the reaction as a whole, since the amount of sulfate is high and therefore the reverse reaction becomes significant, and b) the ionic dissociation of the sulfuric acid which is reduced drastically with increasing concentration and temperature, which contributes to reduce reaction velocity.

3.4. Kinetic parameters of the Arrhenius equation (LV-STT)

The kinetic parameters from the Arrhenius equation for the case LV-STT were obtained analogously for the case LV-900. Thus, K_0 and E_a could be obtained by the linear and angular coefficients of the curves in Fig. 3, respectively. In Table (4) can be observed the values of the kinetic parameters of the Arrhenius equation. Similarly as for the case of LV-900, the activation energy values show that the leaching kinetics is controlled by chemical reaction. The effects observed in Table (4) can be applied for explain the negative value of frequency factor for LV-STT with the acid concentration of 30%.

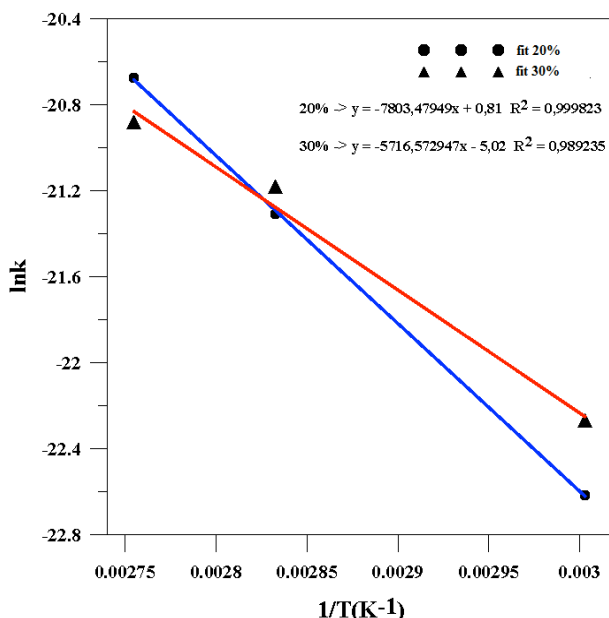


Figure 3. Parameters of the Arrhenius equation (LV-STT).

Table 4. Kinetics parameters of the Arrhenius equation (LV-STT).

Arrhenius Parameters	Chemical Reaction	
	20%	30%
K_0 (1/s)	0.81	-5.08
E_a (KJ/mol)	64.87812848	47.52758748

4. CONCLUSIONS

It was developed a mathematical model based on total resistance to mass transfer in the leaching process. This model has been constructed taking into the consideration of the resistance at the liquid film, the resistance in the region of ash and resistance due to chemical reaction at the surface of the unreacted core.

An analytical solution for the model was obtained considering that the extraction of iron is prevalent in the process and that the reaction rate controls the leaching process. The model was then fitted to the experimental data to determine the kinetic constants and the parameters of the Arrhenius law for each concentration studied.

For the case of LV-STT at $T = 60$ and 80 °C, it was observed that K_2 increases with concentration, this behavior suggests that part of sulfuric acid was consumed preferentially to neutralize the sodium hydroxide present in the red mud. In the case of LV-STT at $T = 90$ °C, one was observed that K_2 decreased with concentration, suggesting that the reaction mechanism interference suffered the common ion effect and ionic dissociation of sulfuric acid. For the case of red mud calcined at 900 °C, the sodium was consumed, and thus, it is suggested that the reaction mechanism only suffer interference of the common ion effect and ionic dissociation of sulfuric acid.

5. REFERENCES

- Balarini, J.C., 2009. "Estudo Cinético do Ustulado de Zinco da Votorantim Metais: Mecanismo não Catalítico Associado à Caracterização e à Determinação de Tempos de Residência", D.Sc. Thesis, School of Engineering, Minas Gerais, MG, Brazil.
- Bayrak, B., 2005. Investigation of Dissolution Kinetics natural magnesite in gluconic acid solutions. Chemical Engineering Journal, Vol 117, (2006), 109-115.
- Levenspiel, O., 2000. Engenharia das Reações Químicas. Edgar Blucher, São Paulo.
- Vogel, A. I., 1989. Textbook of Quantitative Chemical Analysis, Fifth Edition, 1989.

6. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.