Leaching kinetics of gibbsitic bauxite with sodium hydroxide

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Abstract. In this paper the results of a leaching kinetics study of bauxite ore with sodium hydroxide are presented. The effect of ore particle size, sodium hydroxide concentration and reaction temperature on the Al_2O_3 extraction rate was determined. The results obtained showed that 99% of Al_2O_3 was leached out using -200+270 mesh ore particle size at a reaction temperature of 105 °C for 60 min reaction time with 250 g/L NaOH. The solid-to-liquid ratio was maintained constant at 1:20. The results indicated that leaching of bauxite is the rate controlling process. The activation energy was determined to be 46.04 kJ/mole, which was characteristic for a chemically controlled process.

1 Introduction

Bauxite is an aluminum ore which consists mainly of aluminum hydroxide. There are three types of aluminum hydroxide minerals occurring in bauxite. The first mineralogical form is gibbsite, alumina trihydrate [$Al_2O_3{\cdot}3H_2O$] or [$Al(OH)_3$], which is the most common occurring constituent of bauxite. The other two mineralogical forms are boehmite and diaspore, which have the same chemical formula of alumina monohydrate [$Al_2O_3{\cdot}H_2O$] or aluminum oxyhydroxide [AlOOH] [1].

In 1888, Karl Josef Bayer developed and patented a process, which has become the cornerstone of the aluminum production industry worldwide. The Bayer process is used for refining bauxite to smelting grade alumina, the precursor to aluminum. Typically, depending upon the quality of the ore, between 1.9 and 3.6 tonnes of bauxite is required to produce 1 ton of alumina. The Bayer process involves the digestion of crushed bauxite in the concentrated sodium hydroxide (caustic) solution at temperatures up to 270°C. Under these conditions, the majority of the aluminum containing species in the ore are dissolved, leaving an insoluble residue (called red mud) which is removed. Red mud is composed primarily of iron oxides, quartz, sodium aluminosilicates, calcium carbonate/aluminate and titanium dioxide [2, 3, 4]. Sodium aluminate is separated from the red mud using 7-9 settling tanks with counter-current washing with water. Then, the sodium aluminate solution is diluted and seeded to precipitate aluminum hydroxide. The precipitated aluminum trihydroxide (gibbsite, $Al(OH)_3$) is filtered, counter-current washed with water, dried and calcined at 1000 °C, yielding alumina. The extraction chemical equations can be represented as following:

$$Al(OH)_3(s) + NaOH(aq) \rightarrow NaAl(OH)_4(aq) \qquad (1)$$

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$$AlO(OH)(s) + NaOH(aq) + H_2O \rightarrow NaAl(OH)_4(aq). \tag{2}$$

Processing of different kinds of bauxite from India, Jamaica, Brazil, Guinea, Australia and Greece on in the laboratory and plots scales was reported. It was found that, the optimum leaching temperatures were ranged from 95 to 230 °C for digestion times of 25 to 120 min depending on the bauxite type [5]. Moreover, bauxite from the Um Bogma area, southwestern Sinai (Egypt), containing mainly gibbsite and kaolinite, was leached using sodium carbonate and lime water [6]. The obtained Al_2O_3 recovery was 92% at reaction temperature of 90 °C, reaction time 15 min, Na_2CO_3 concentration 200 g/L, solid content of 30% and CaO/SiO_2 stoichiometric mole ratio of 2.

The present investigation deals with the kinetics of Indian bauxite leaching with sodium hydroxide. The process conditions studied include the particle size of bauxite, sodium hydroxide concentration, temperature and time.

2 Experimental

2.1 Materials and apparatus

A bauxite ore from India was used. It contains mainly gibbsite [$Al(OH)_3$] and hematite [Fe_2O_3] as major minerals as well as boehmite [AlOOH], anatase [TiO_2], quartz [SiO_2], kaolinite [$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$], and alumo-geothite [$Fe_2O_3 \cdot Al_2O_3 \cdot H_2O$] as minor minerals. The ore contains 44.6% Al_2O_3, 25.6% Fe_2O_3, 2.2% TiO_2, 1.4% SiO_2, 0.095% Na_2O, 0.073% MgO, 0.032% CaO and 0.024% K_2O [5, 7]. The ore was ground and sieved. Al_2O_3 contents of the different size fractions was found the same (44.7% ± 0.3%). Sodium hydroxide (purity of 97%) from Fischer Scientific was used in this study. The reaction was performed in 2 liter steel beaker placed in thermostatically controlled oil bath (Fig. 1). Reaction mixture was agitated at a rate of 500 rpm.

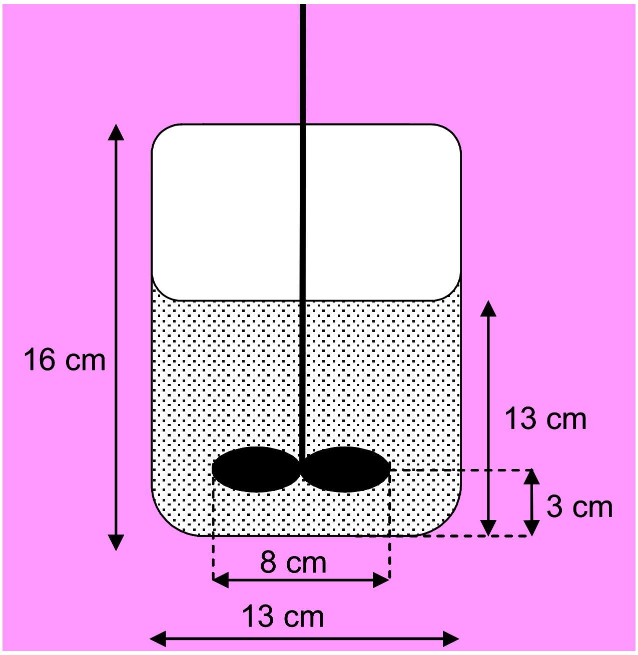

Figure 1. Schematic diagram of reaction vessel.

2.2. Procedure

A sample of 80 g of ground bauxite ore was added to the agitated sodium hydroxide solution (1600 ml) of required concentration at temperature. At selected time intervals, about 2 ml solution of sample was taken using a syringe filter of 1 µm pore size and the solids corresponding to that volume were discarded. Consequently, the solid-to-liquid ratio was maintained constant at 1:20. The cumulative volume removed by sampling was not significantly compared to the original solution (< 2%). Evaporated water was compensated continuously. The samples were chemically analyzed for determination of Al_2O_3 content from which the percentage extraction of Al_2O_3 was calculated.

3 Results and discussion

3.1 Effect of particle size

The effect of particle size on leaching of bauxite was studied using different size fractions (-100+150 mesh, -150+200 mesh and -200+270 mesh). Within the series of tests the initial sodium hydroxide concentration and leaching temperature were kept constant at 200 g/L and 95 °C, respectively. The solid-to-liquid ratio was 1:20. The obtained results (Fig. 2) show that the particle size has a significant effect on dissolution of bauxite and after 30 minutes of leaching. Depending on the ore particle size, an about 43-58% of Al_2O_3 was extracted. In addition, the results show that about 80% of Al_2O_3 present in the fine fraction (-200+270 mesh) of the ore was extracted after 60 min.

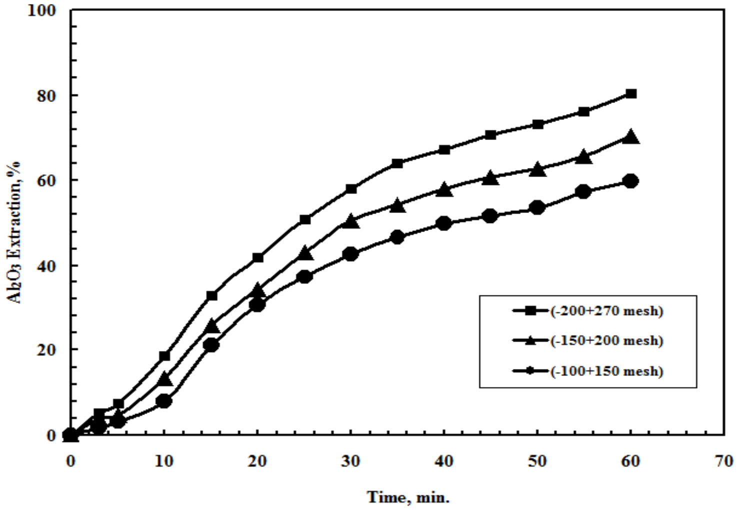

Figure 2. Extraction of Al_2O_3 from different particle sizes of bauxite (at 95 °C, 200 g/L NaOH).

3.2 Effect of sodium hydroxide concentration

A percentage of extracted Al_2O_3 against time is presented in Fig. 3 using fine ore of -200+270 mesh particle size and sodium hydroxide concentration in the range of 150 to 300 g/L at constant temperature of 95 °C. The solid-to-liquid ratio was kept constant at 1:20. It is obvious that the sodium hydroxide concentration also has a pronounced effect on dissolution of Al_2O_3. About 88% of Al_2O_3 present in the fine fraction of the ore was extracted using 250 g/L sodium hydroxide solution after 60 min. The increased sodium hydroxide concentration to 300 g/L had insignificantly increased the Al_2O_3 extraction efficiency.

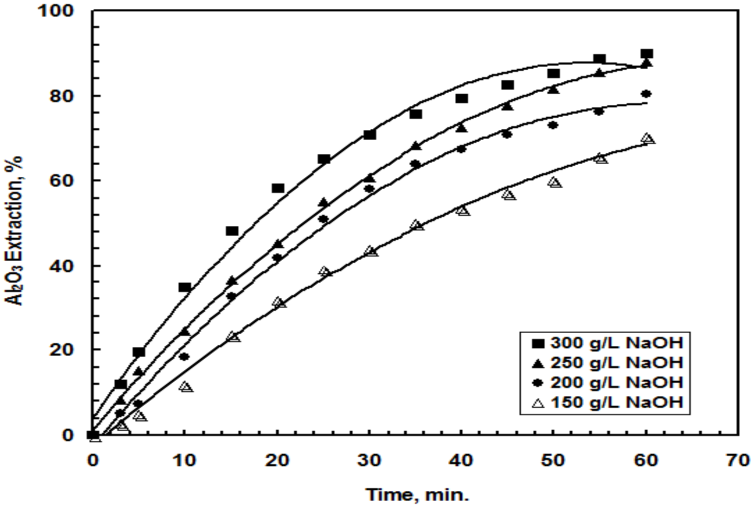

Figure 3. Effect of sodium hydroxide concentrations on extraction of Al_2O_3 (-200+270 mesh particles at 95 °C).

3.3. Effect of reaction temperature

The effect of reaction temperature on extraction of Al_2O_3 at different reaction times is plotted in Fig. 4 using ore of -200+270 mesh particle size and sodium hydroxide concentration of 250 g/L at temperatures in the range of 75 to 105 °C. The solid-to-liquid ratio was kept constant at 1:20. The obtained results show that the studied reaction temperatures had significant effect on dissolution of Al_2O_3. About 99% of Al_2O_3 present in the fine fraction of the ore was extracted after 60 minutes at reaction temperature of 105 °C. At relatively lower temperatures (less than 95 °C), the Al_2O_3 extraction efficiency drastically decreased.

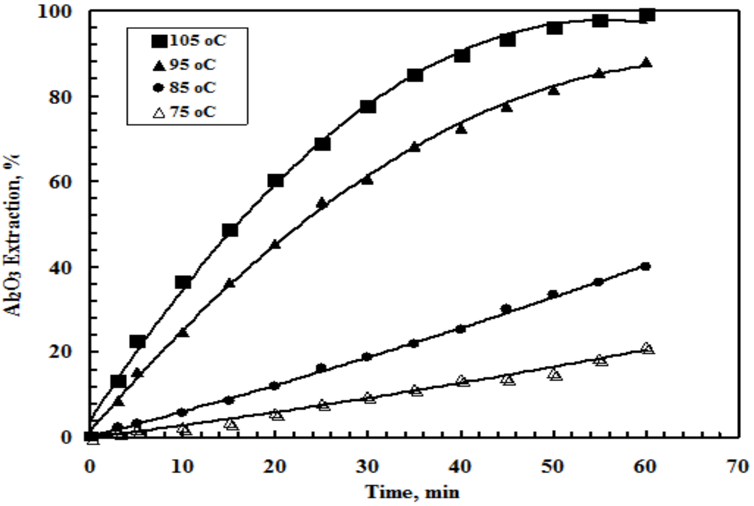

Figure 4. Effect of reaction temperature on extraction of Al_2O_3 (-200+270 mesh particles in 250 g/L NaOH).

3.4 Kinetic aspects

The reaction of bauxite can proceed in a topochemical manner, because the inner core of unreacted particle is decreasing with time. It is clear from Fig. 2 that the rate of reaction decreases with time. This is due to reduction of reactant surface. The rate of reaction is given for models based on control by either chemical reaction at the particle surface, diffusion through the product layer, or combination of both.

The rate control by chemical reaction at the particle surface is [8, 9]:

$$K_c t = 1\text{-}(1\text{-}x)^{1/3} \tag{3}$$

where K_c is the reaction rate constant (min $^{-1}$), t is the time (min), and x is fraction reacted of Al_2O_3 definedas:

$$x = \%\, Al_2O_3\ extraction/100\,. \tag{4}$$

Based on the experimental data presented in Fig. 4, a plot of the right-hand side of Equation (3) versus time is given in Fig. 5. During the whole reaction time, the data in Fig. 5 are linear what indicates that the rate of reaction is controlled by chemical reaction on the surface of bauxite particles. The results are correlated to this model as a straight line and nearly zero point intercept was obtained. In the case of straight lines, the slope equals the rate constant K_c :

$$K_c = MbK_{cc}C/\rho r,\ \mathrm{min}^{-1} \tag{5}$$

where K_{cc} is the chemical rate constant (cm min^{-1}), b is the stoichiometric coefficient (dimensionless), M as molecular weight of the major Al_2O_3 mineral, C concentration of sodium hydroxide (mol/m^3), r radius of unreacted particle (m), ρ as density of bauxite ore (kg/m^3), (pycnometer method = 3660 kg/m^3).

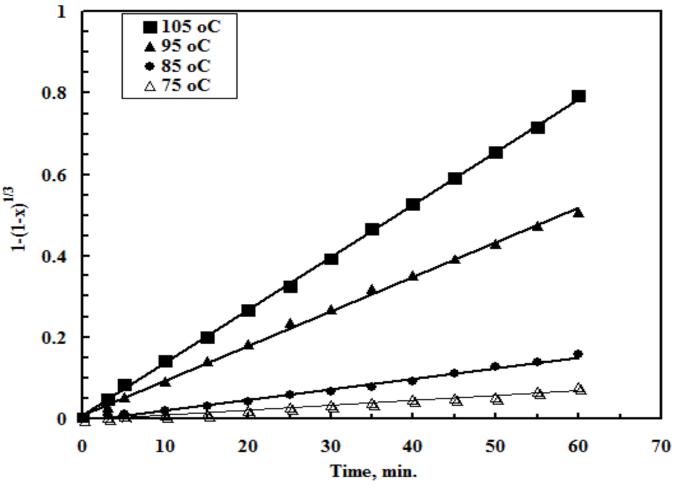

Figure 5. $1\text{-}(1\text{-}x)^{1/3}$ versus time at various reaction temperature (-200+270 mesh particles in 250 g/L NaOH).

When diffusion through the product layer is rate controlling, the kinetics may be correlated graphically using the Valensi equation [8, 9]:

$$K_p t = 1\text{-}\ 2/3x\ \text{-}(1\text{-}x)^{2/3} \tag{6}$$

where K_p = chemical rate constant (cm min^{-1}).

Based on the experimental data in Fig. 4, a plot of the right-hand side of Equation (6) against time is given in Fig. 6. The data cannot be correlated to this model as neither a straight line nor zero point intercept was obtained. In the case of straight lines, the slope is K_p and is equal to:

$$K_p = 2bMDC/\rho r^2 \text{ min}^{-1} \tag{7}$$

where D is the diffusion coefficient of aluminum ions in porous medium (m^2/min).

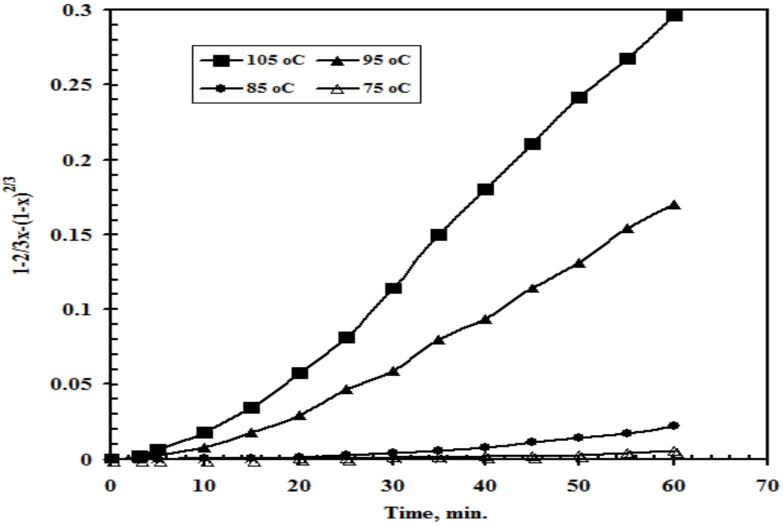

Figure 6. $1\text{-}2/3x\text{-}(1\text{-}x)^{2/3}$ versus time at various reaction temperatures (-200+270 mesh particles in 250 g/L NaOH).

When previous models do not give a straight-line relationship throughout the leaching process, mixed model may be applied. The mixed kinetics equation, in terms of the fraction extracted (x), is [7, 8, 9]:

$$Mbk_{cc}DCt/\rho r^2 = D/r[1\text{-}(1\text{-}x)^{1/3}] + k_{cc}/2[1\text{-}2/3x\text{-}(1\text{-}x)^{2/3}] \tag{8}$$

where $Kr = Mbk_{cc}C/\rho r$

$$Krt = D/r[1\text{-}(1\text{-}x)^{1/3}] + k_{cc}/2[1\text{-}2/3x\text{-}(1\text{-}x)^{2/3}] \tag{9}$$

$$krt = 1\text{-}(1\text{-}x)^{1/3} + B[1\text{-}2/3x\text{-}(1\text{-}x)^{2/3}] \tag{10}$$

where: $B = k_{cc}r/2D$

Two terms on the right side of Eq. (10) represent the chemical and diffusion resistances. To plot Eq. (10), the values of the constant B must be determined, which contains the chemical rate constat k_{cc} and the diffusion coefficient D.

Based on the experimental data from Fig. 4, a plot of the right-hand side of Eq. (10) against time is given in Fig. 7. The data cannot be correlated to this model as neither a straight line nor zero point intercept was obtained.

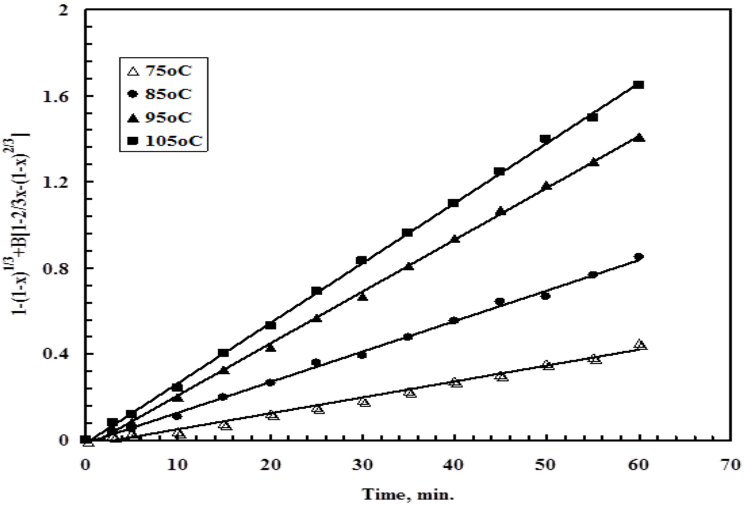

Figure 7. $[1-(1-x)^{1/3}+B[1-2/3x-(1-x)^{2/3}]$ versus time at various reaction temperatures (-200+270 mesh particles in 250 g/L NaOH).

3.5. Calculation of the activation energy

The activation energy of a diffusion controlled process is characterized to be 1 to 3 kcal/mole [8], 2 to 5 kcal/mole [10] or 3 to 6 kcal/mole [11]. In addition, the activation energy for a chemically controlled process is usually greater than 10 kcal/mole [8], or more specifically falls between 10 to 20 kcal/mole [10]. To calculate the activation energy, the values of ln K_c were plotted against $1/T$ (Fig. 8). The activation energy of the overall reaction was calculated to be 11 kcal/mole (45.9 kJ/mole). This value of activation energy confirms that the reaction rate is chemically controlled. This activation energy is in a good agreement with the value of activation energy (48.15 kJ/mole) calculated for oxidative ammonia leaching of sphalerite [12] of chemically rate controlled.

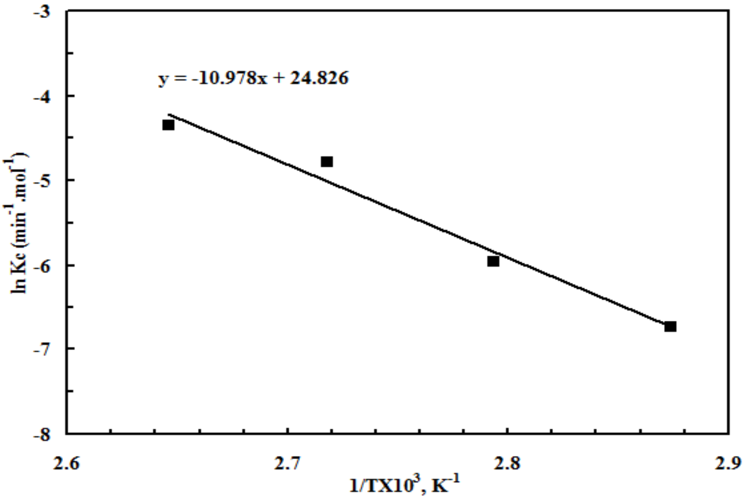

Figure 8. Arrhenius plot for leaching of bauxite ore with sodium hydroxide.

4. Conclusions

The extraction efficiency of about 96% of the Al_2O_3 present in the studied bauxite ore was achieved under the following conditions: particle size -200+270 mesh, temperature 95 °C, reaction time 60 min, sodium hydroxide 250 g/L and solid-to-liquid ratio 1:20. The kinetic study indicated that leaching of Al_2O_3 was the chemically controlled process for all leaching times, and the reaction rate increased with temperature. The activation energy was calculated to be 11 kcal/mole (46.04 kJ/mole), which was consistent with values of activation energies reported for chemically controlled rate.

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