

# Kinetics of Recovery of Alumina from Aluminium Casting Waste through Fusion with Sodium Hydroxide

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**Abstract** Aluminium dross containing 72% Al<sub>2</sub>O<sub>3</sub> and 14.0% SiO<sub>2</sub> was fused with NaOH for a period of up to 60 minutes in the temperature range of 500 – 750°C in a stainless steel crucible. The fused mass was dissolved in water. Amount of alumina in the solution was determined by EDTA compleximetric (masking and demasking) chemical method. The optimum condition for alumina extraction was determined as NaOH to aluminium dross weight ratio = 3.5, temperature = 750°C and time 60 minutes. Avrami-Erofeev equation  $[-\ln(1-\alpha) = (k_3t)^m]$ ,  $m = 3/2$  seemed to be most appropriate one to fit the kinetic data of fusion of aluminium dross with NaOH. The activation energy was found to be 6.452kJ/mol.

**Keywords:** alumina recovery, aluminum foundry waste, sodium hydroxide, fusion, reaction mechanism, kinetics, activation energy

## 1. Introduction

Dross is generated during melting of aluminium. Typically 15-25 kg of dross is produced per metric ton of molten aluminium [1]. The main constituent of dross is aluminium, which varies from 8-80% depending upon grades. Apart from aluminium metal, dross may also contain other chemical compounds e.g. MgF<sub>2</sub>, SiO<sub>2</sub> and MgO etc [2]. A number of investigations have been carried out to extract alumina from different types of secondary sources such as micas, anorthite, spent catalysts [3,4], clays and kaolins [5,6], fly ash [7] etc. Attempts have been made to extract alumina from the secondary sources by adopting either pyro- or hydrometallurgical methods [8,9]. All these secondary sources have the potentials to be the industrial raw material as they are rich in alumina content.

Amer carried out the dissolution of waste dross in sulphuric acid in order to produce highly pure aluminum sulfate [10]. However, the process has found little practical application because of the environmental hazard due to the highly corrosive nature of the concentrated acid and alkali involved. Miskufova et al studied the leachability of aluminium from aluminium dross fines in alkaline solution at atmospheric condition [11]. He found a maximum extraction of about 42 % of total Aluminium content by leaching of dross fines in 10 % NaOH solution.

Beaulieu et al developed a process for preparing aluminium chloride by (i) leaching aluminium dross residues with HCl, (ii) hydrochlorinating the liquid to form a precipitate comprising aluminium chloride and (iii) converting aluminium chloride into alumina [12].

Lucheve et al [13] described a process - similar to Bayer's process - for recovery of Al(OH)<sub>3</sub> from black aluminium dross. They leached dross in 10% NaOH solution at ambient temperature for 2 hours and precipitated Al(OH)<sub>3</sub> by bubbling CO<sub>2</sub> through the leach liquor. Park et al also noted that alkaline leaching of aluminium dross followed by precipitation of aluminium hydroxide Al(OH)<sub>3</sub> is a potential method for the recovery of alumina from dross [14]. This method of fine aluminium dross processing is economically and environmentally convenient. However, dross is a very heterogeneous material and applicability and efficiency of proposed method for individual dross samples should be experimentally investigated

In this study, aluminium dross was fused with caustic soda so that sodium aluminate can be formed. This sodium aluminate is useful for the determination of alumina in dross and also for the recovery of alumina. Maximum formation of sodium aluminate is facilitated by a high temperature of fusion.

## 2. Experimental

### 2.1. Material Composition

The compositional analysis of the aluminium dross was done by the x-ray fluorescence analysis and the x-ray diffraction analysis was performed to find out the phases present in it. The result of the analysis is shown in the table below:

**Table 1. Compositional analysis of the dross**

Oxide	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O
Wt%	72	14	2.5	2	1.7

## 2.2. Phase Identification

Figure 1 shows an X-rays diffraction pattern of the fine aluminum dross samples. Almost all of the peaks are

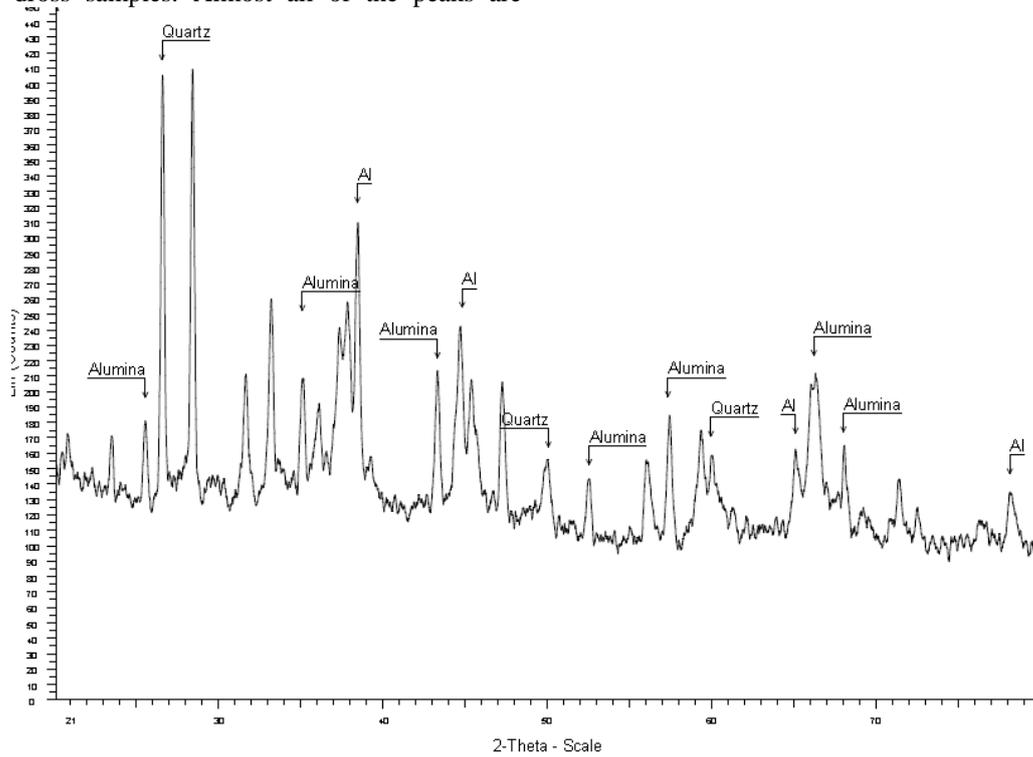


Figure 1.XRD pattern of aluminium dross

Table 2. Phases present in the sample

Name of the phase	Chemical Formula	Other Name
Aluminum	Al	
Aluminum Oxide	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Corundum
Silicon Oxide	SiO <sub>2</sub>	Quartz

## 2.3. Fusion Procedure

Dross of different weight was mixed with a specified amount of sodium hydroxide (NaOH). The mixture was put in a stainless steel crucible, covered with a cap and placed in a muffle furnace. The fused sample was cooled to room temperature and dissolved in distilled water. The solution was filtered and the amount of alumina in the solution was determined by EDTA compleximetric (masking and demasking) chemical method. The effects of NaOH to aluminium dross ratio in the range 2.0-4.0, temperature in the range 500 – 750°C and time of fusion of up to 60 minutes on the extent of alumina recovery were studied. The activation energy of fusion was determined and a kinetic model was fitted for the fusion process.

## 3. Results and Discussion

### 3.1. Compositional Analysis

From Table 1 it can be seen that the alumina constitutes the major portion of the sample and silica is the second major constituent.

### 3.2. Phase Analysis

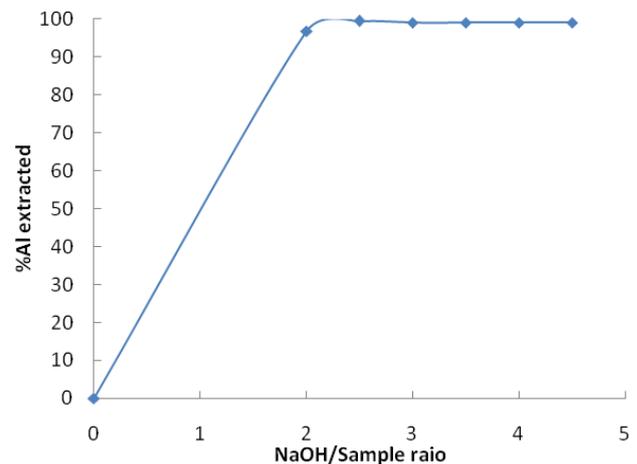
identified. Some very small peaks could not be identified. All phases are mentioned in the Table 2.

Most of the major peaks in the x-ray diffraction pattern correspond to alumina and silica. This is in good agreement with the results of compositional analysis.

## 3.3. Optimisation of Fusion Parameters

### 3.3.1. Optimization of NaOH to Aluminium Dross Ratio

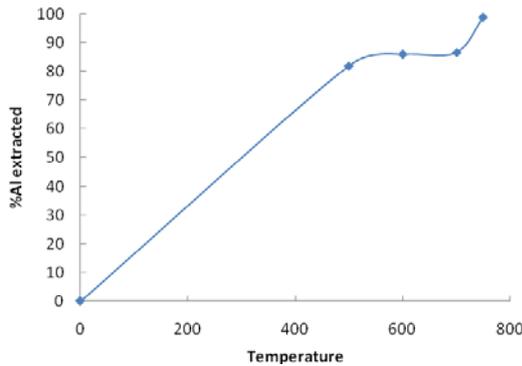
Effect of sodium hydroxide (NaOH) to aluminium dross ratio (weight basis) in the range 2.0-4.0 was studied. The extraction of alumina was found to increase with an increase in concentration of sodium hydroxide in the fusion mixture up to a sodium hydroxide to dross ratio of 3.5 (Figure 2). This ratio sodium hydroxide to dross was taken to be the optimum and was kept constant in the subsequent experiments.



**Figure 2.** Effects of NaOH/Aluminium dross ratios on the extraction of alumina (fusion time: 60 min, Temperature: 750°C)

**3.3.2. Optimization of Temperature**

Figure 3 shows the extent of extraction increased with an increase in reaction temperature up to 750°C.

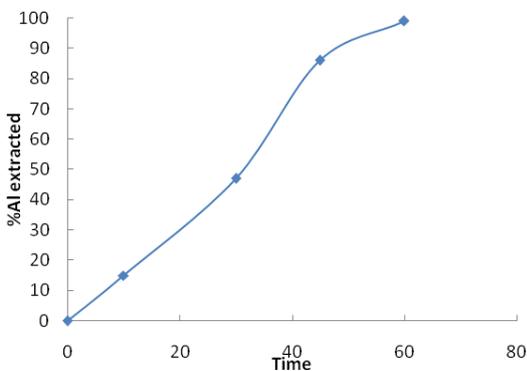


**Figure 3.** Effects of temperature on the extraction of alumina (fusion time: 60 min, NaOH/Dross: 3.5)

These experiments were conducted at a constant NaOH to dross weight ratio of 3.5 and for a time period of 1h. It can be said that the dross and sodium hydroxide mixture fused at 750°C showing the maximum yield.

**3.3.3. Optimization of Time**

To optimize the time of fusion NaOH-dross mixture was fused for different periods of time by using the optimized parameters of fusion (temperature= 750°C, NaOH/dross ratio = 3.5). It was found that maximum yield was obtained after 60 minutes (Figure 4).



**Figure 4.** Effects of time on the extraction of alumina (NaOH/dross ratio: 3.5, Temperature: 750°C)

**3.4. Identification of Reaction Model**

In systems involving solid reactants, the chemical reaction takes place at the interface of the reactants to produce a final compound [14]. Diffusion must then occur through the product for the reaction to continue and the chemical reaction will proceed at the interface of one or both of the reactants. The mechanisms of these steps depend upon the experimental conditions and upon the characteristics of the solid reactants; therefore, the overall rate of the process may be controlled by chemical kinetics or transport processes.

The following Kinetic Models are usually considered for the study of such reactions [14]

1. Ginstling and Brounshtein:  $1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = k_1t$

2. Jander equation :  $[1 - (1-\alpha)^{1/3}]^2 = k_2t$

3. Avrami-Erofeev equation:  $-\ln(1-\alpha) = (k_3t)^m$

where,

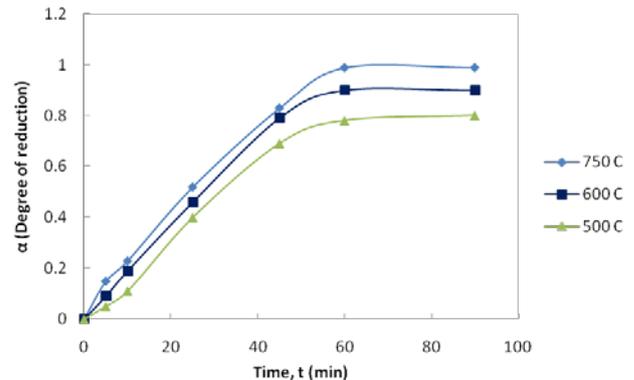
$\alpha$ = fraction of reacted particles

t = time for fraction of reacted particles

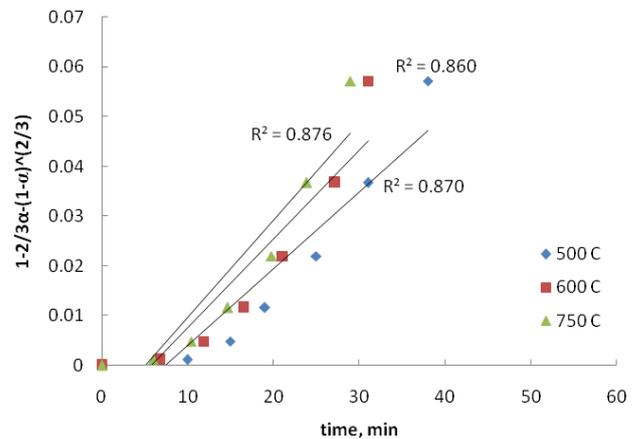
$k_i$  = specific rate constant

m= parameter which depends on geometry

From Figure 5 time required for different fractions of reacted particle of alumina were calculated at 500°C, 600°C and 750°C and then plotted according to equation (1) to equation (3) in Figure 6 to Figure 9. Correlation of coefficient values of the plotted lines are also shown in these figures. It can be seen that the correlation is not high enough for all temperatures and also the lines do not pass through the zero point. Figure 6 suggests that the dissolution of alumina in dross is not follow the Ginstling and Brounshtein equation. Figure 7 suggests that the dissolution does not follow the Jander mechanism. So none of these two mechanisms are suitable for explaining the kinetics of the fusion procedure.



**Figure 5.**  $\alpha$ -t plots at different temperatures



**Figure 6.** Kinetic plots for Ginstling and Brounshtein  $(1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = k_1t)$  model equations. Ginstling and Brounshtein

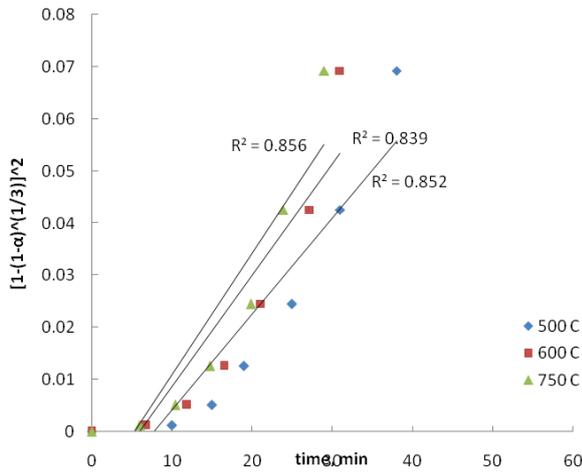


Figure 7. Kinetic plots for Jander equation  $[1-(1-\alpha)^{1/3}]^2=k_3t$  model equations

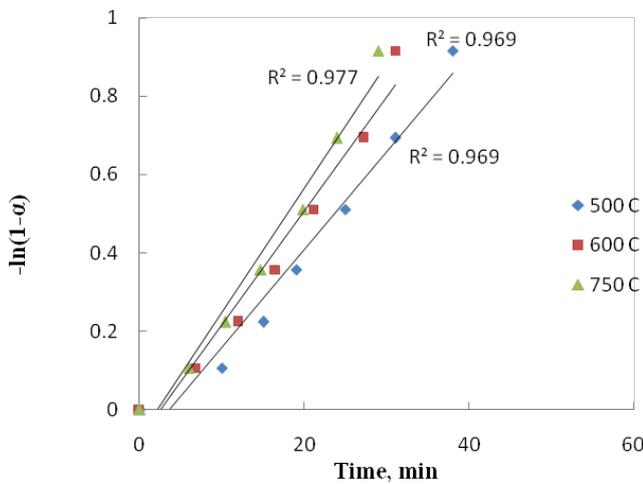


Figure 8. Kinetic plots for Avrami-Erofeev equation  $-\ln(1-\alpha) = (k_3t)^m$  model equations for  $m=1$

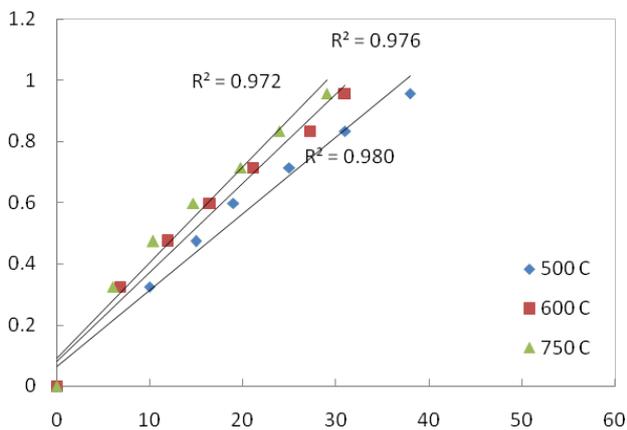


Figure 9. Kinetic plots for Avrami-Erofeev equation  $-\ln(1-\alpha) = (k_3t)^m$  model equations for  $m=2$

In order to investigate if the mechanism represented by Avrami-Erofeev equation i.e.  $-\ln(1-\alpha) = (k_3t)^m$  is the mechanism, the left hand side of Equation (3) for  $m=1, 2$  and  $3$  were plotted against time for different temperatures (Figure 8, Figure 9 & Figure 10). Among all these plots Figure 10 yielded a very high correlation at all temperatures under investigation. Moreover, the plotted lines passed through the zero point.

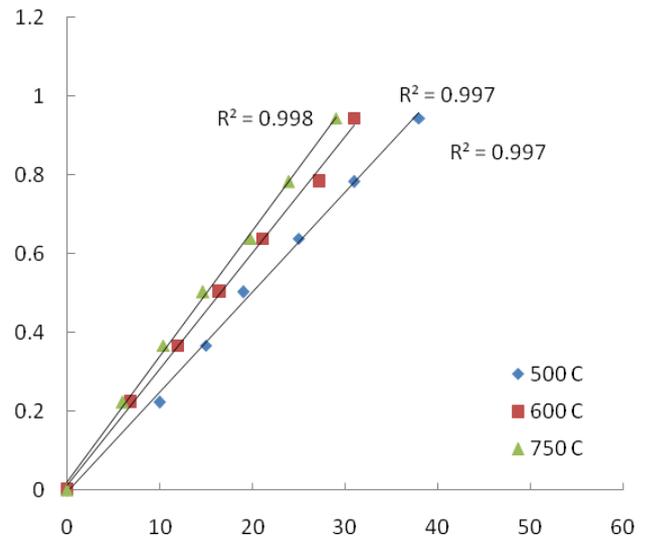


Figure 10. Kinetic plots for Avrami-Erofeev equation  $-\ln(1-\alpha) = (k_3t)^m$  model equations for  $m=3/2$ .

### 3.6. Evaluation of Activation Energy

Both the conventional integral approach and differential approach were used to evaluate the activation energy of the fusion process.

In the integral approach the relationship between the rate constant  $k$  and temperature is given by the Arrhenius equation

$$k = A \exp(-E / RT)$$

where  $A$  is the frequency factor and  $E$  is the apparent activation energy. Apparent activation energy determined from the Arrhenius type plots (Figure 11), where  $-\ln k$  Versus  $1/T$  is plotted for  $F_1$  model. Slope of the plot gave  $E/R$  and activation energy found to be 6.452kJ/mol.

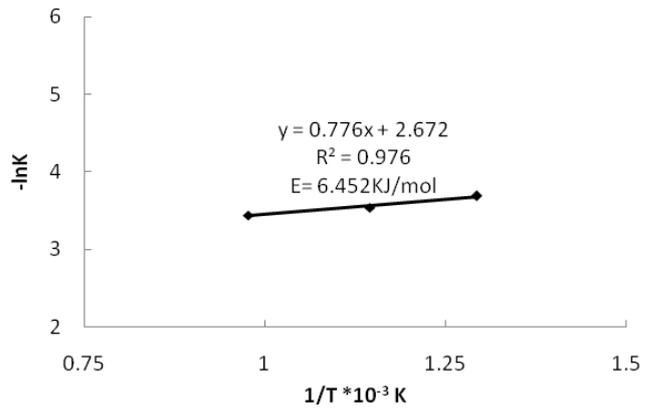
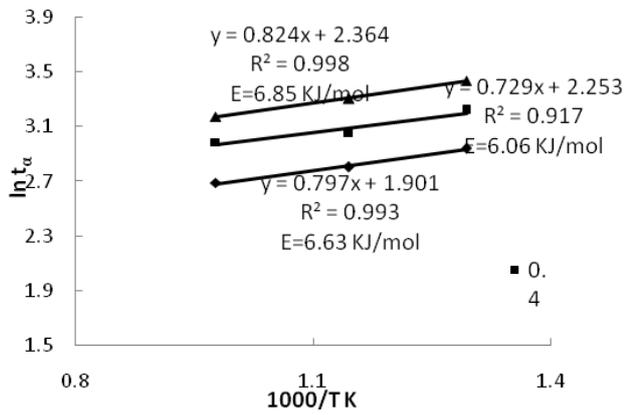


Figure 11. Arrhenius type plots of Figure 10

In the differential approach activation energy was determined in three different extraction levels ( $\alpha$ ) i.e.  $\alpha = 0.3, 0.4$  and  $0.5$  of alumina by differential approach. Time of attaining different extraction level at different temperatures are cross plotted in Figure 12. From these figures we get values of activation energy for  $\alpha = 0.3, 0.4$  and  $0.5$  were 6.63, 6.06 and 6.85kJ/mol respectively.



**Figure 12.** Plots of  $\ln(t_0)$  versus  $1/T$  to determine activation energy (differential approach)

## 4. Conclusions

The optimum conditions for the maximum yield of alumina from dross and the kinetics for the extraction reaction were studied in this work. Several parameters i.e. fusion reagent (NaOH) to dross ratio, temperature of fusion and time of fusion were studied in this study. Maximum extraction of alumina was obtained at NaOH to dross ratio of 3.5 and  $750^{\circ}\text{C}$  at 60 minutes. The rate of alumina extraction followed the Avrami-Erofeev equation:  $-\ln(1-\alpha) = (k_3t)^m$  where  $m=3/2$  with apparent activation energy of about 6.452 kJ/mol.

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