MODELS OF ALUMINA DISSOLUTION IN CRYOLITE

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ABSTRACT

Two models for the dissolution of alumina powder in cryolite were formulated and compared with experimental results obtained using modified fast linear sweep voltammetry. The first model, where the rate of dissolution is assumed to be controlled by the rate of chemical reaction at the alumina surface, gave a reasonable fit with the experimental data. The second model, where it is assumed that the rate of dissolution of alumina is mass transport controlled, also gave a reasonable fit with the experimental data. Comparisons of the models with experimental data suggest that the alumina, when added to the electrolyte, forms agglomerates. Heat transfer was shown not to be the dominant rate controlling process in the stirred electrolyte system studied.

1. INTRODUCTION

In the Hall-Heroult process for producing aluminium, refined alumina is added to an electrolyte of molten cryolite (Na$_3$AlF$_6$). The alumina dissolves in the cryolite and is then electrolysed using carbon electrodes to produce aluminium and carbon dioxide. An important consideration in achieving maximum efficiency in production of aluminium is in the rapid dissolution of the alumina in the cryolite bath. Rapid dissolution is necessary to prevent "sludging", the formation of undissolved alumina which settles below the molten aluminium at the bottom of the cell. This sludge is undesirable since in addition to this alumina not being available for electrolysis it causes erosion of the cathode and an increase in cell resistance.

The NaF - AlF$_3$ solvent is a mixture of hexa- and tetrafluoroaluminate anions and the dissolution of alumina in cryolite may be written (1):

$$\text{Al}_2\text{O}_3 + 3\text{AlF}_6^{3-} \rightarrow 3\text{AlOF}_x^{(1-x)^-} + (6 - 3x)\text{F}^-$$
The composition of the bath used in the alumina dissolution tests had a cryolite ratio (moles NaF/moles AlF₃) of 2.4 with 5 wt% CaF. For this composition the predominant oxyanion species formed in solution from the dissolution of alumina would be AlOF₂⁻ and AlOF₃²⁻. These species are the oxygen carrying components of the bath which are reduced at the anode.

In order to better understand the process of alumina dissolution, two simple models for the dissolution of dispersed alumina in a molten cryolite electrolyte have been developed. The first model is one where the rate of reaction depends only on the surface area of the alumina. The dissolving alumina is regarded as shrinking smooth spheres. In this model the rate of dissolution is therefore controlled by the rate of chemical reaction. In the second model it is assumed that the rate of dissolution of alumina is mass transport controlled, so that the concentration of alumina in the electrolyte is important. With the second model the rate depends on the diffusion rate of alumina across a boundary layer at the surface of the alumina.

The predicted shape of the dissolution curves is then compared with the experimental data. This comparison is possible because of the developments in the technique of in situ measurement of alumina dissolution in molten cryolite using a modified form of fast linear sweep voltammetry (2,3,4).

2. EXPERIMENTAL DETERMINATION OF DISSOLUTION RATES

Alumina was added to a stirred electrolyte of cryolite and the dissolution measured with a modified form of linear sweep voltammetry. The equipment setup and the method of dissolution rate measurement have been described elsewhere (3).

Commercial grade alumina was used. This alumina was sieved and the size fraction 63-90μm was used for this work. This alumina had an alpha alumina content of 15% and a surface area, as measured by the BET method of gas adsorption, of 66 m²/g. This area includes the internal surface area which is a result of the very porous nature of the alumina.

A set of three dissolution curves obtained from the commercial alumina were used in this modelling work. The amount of alumina used and the electrolyte alumina concentrations are listed in Table I. The curves obtained are illustrated in Figure 1. These curves are typical of a large number of similar dissolution experiments performed as part of a wider experimental programme.
Table I Initial Mass, Initial Surface Area and Initial Electrolyte Alumina Concentrations for Alumina Dissolutions.

| Dissolution Curve | Alumina Added | Initial Alumina Concentration | Surface Area* |
|-------------------|---------------|-------------------------------|---------------|
|                   | M₀ (g/kg)     | Cᵢ/ρₑ (g/kg)                 | A₀ (m²)       |
| 1                 | 10            | 7.5                           | 0.39          |
| 2                 | 10            | 17.5                          | 0.39          |
| 3                 | 18            | 27.5                          | 0.71          |

* based on smooth sphere model

3. HEAT TRANSFER CONTROL

Heat transfer has been postulated as an important process for limiting the dissolution rate of alumina (5,6,7). Where this is proposed it has generally been assumed that large agglomerates of alumina form, with a frozen shell of electrolyte around the agglomerate.

The time taken to heat 10 g of alumina, with an effective geometric surface area of 0.39 m² (Table I), from 20°C to 975°C, the liquidus temperature of the electrolyte, can be calculated from Equation [1]:

\[ t = \frac{2 C_p M}{W h_b A} \]  

where:
- \( t \) is the time to heat the alumina
- \( C_p \) is the molar heat capacity of alumina (79 J K⁻¹ mol⁻¹)
- \( M \) is the mass of alumina (10 g)
- \( W \) is the molecular weight of alumina (102 g mol⁻¹)
- \( A \) is the effective surface area of the alumina (0.39 m²)
- \( h_b \) is the heat transfer coefficient between the electrolyte and the alumina

Heat transfer coefficients have been reported (5,6,7) in the range 400 - 1200 J s⁻¹ m⁻² K⁻¹. Using these heat transfer coefficients in Equation [1] results the alumina remaining out of contact with the molten electrolyte, due to the existance of a frozen shell, for less than 0.1 seconds. This is negligible when compared with the total
dissolution time and can be ignored.

When large agglomerates of alumina form, as is generally assumed in systems studied previously (5,6,7), the heat transfer becomes much more important because the surface area of the alumina exposed to the electrolyte is much reduced. Also, the cooling of the surrounding electrolyte would result in freezing around the agglomerate. If this were the case, one would expect to observe an initiation time between the addition of alumina and commencement of dissolution, due to the need to remelt the frozen electrolyte. This was not observed in these experiments thus supporting the supposition that some, if not all, of the alumina particles are well dispersed in the electrolyte by the action of the stirrer.

4. FIRST MODEL - CHEMICAL CONTROL

4.1 Derivation of equations

The first model which we propose and wish to test states that the rate of dissolution of well stirred dispersed alumina in an electrolyte of molten cryolite is proportional to its surface area. The rate is not mass transport controlled, but rather, depends on the rate of the surface reaction involving the breaking of strong Al-O bonds by complexing with AlF$_{6}^{-}$. The model assumes that the mass transport is fast relative to the surface chemical reaction.

\[ R = kA \]  

where:
- \( R \) is the rate of dissolution, units g s$^{-1}$
- \( k \) is the rate constant, units g s$^{-1}$ m$^{-2}$
- \( A \) is the surface area of the alumina, units m$^{2}$

We may suppose that the particles of alumina which are added to the cryolite electrolyte are monodisperse smooth spheres each with an initial radius \( r_{0} \). In making this assumption we are supposing that although the alumina is very porous, as shown by the high BET surface area, the electrolyte does not penetrate these pores or if it does then there is no exchange of electrolyte from these pores to the bulk electrolyte. The initial surface area of the total alumina added is then:

\[ A_{0} = \frac{3M_{0}}{r_{0} \rho} \]
where: $A_0$ is the initial surface area of the total amount of alumina added 
$M_0$ is the initial mass of alumina added 
$\rho$ is the particle density

It is readily shown that the surface area of the alumina will decrease as the mass of the undissolved alumina decreases by the relationship:

$$A = A_0 \left( \frac{M}{M_0} \right)^{2/3} \quad [4]$$

where: $A$ is the surface area of all the spheres at time $t$ 
$M$ is the mass of alumina remaining undissolved at time $t$

The mass of alumina remaining undissolved can be related to the concentration of alumina in the electrolyte by the relationship:

$$M = M_0 - (C - C_i) V \quad [5]$$

where: $C_i$ is the initial alumina concentration (g/L) in the cryolite electrolyte 
$C$ is the alumina concentration at time $t$ 
$V$ is the volume of the electrolyte

In order to simplify the equations we will call $C' = C - C_i$, where $C_i$ is the initial alumina concentration, prior to each alumina addition. We therefore obtain an expression for the rate of dissolution of alumina, using the shrinking sphere model:

$$R = \frac{dC}{dt} V = k A_0 \left( 1 - \frac{V}{M_0 C'} \right)^{2/3} \quad [6]$$

By rearranging the equation and integrating with respect to concentration and time, then obtaining the integration constant when $t=0$ and $C'=0$ we get the following expression:

$$t = \frac{3M_0}{A_0 k} \left[ \left( \frac{V}{M_0 C'} - 1 \right)^{1/3} + 1 \right] \quad [7]$$
This can be rearranged to give the concentration of alumina, \( C' \):

\[
C' = \frac{M_0}{V} \left[ 1 + \frac{A_0 k}{3M_0} t - 1 \right]^3
\]

[8]

4.2 Comparison with experimental

Using the shrinking sphere model (Equation 8) a set of calculated experimental curves are plotted in Figure 2, along with the experimental data for comparison. The density of crystalline alumina is 4.0 g/cm\(^3\), however, the density of the individual alumina particles is approximately 2 g/cm\(^3\) due to the high void space within each particle. Based on the estimated median particle diameter of 76.5 \(\mu\)m, and a density of 2 g/cm\(^3\) the surface areas for the alumina additions were calculated as listed in Table I. The rate equation is fitted to the experimental data by a nonlinear regression procedure using a Marquardt-Levenberg algorithm, to obtain a value of the rate constant, \( k \). The values of \( k \) which were found to be the best fit are listed in Table II.

The simple first dissolution model proposed above, where the rate is proportional to the surface area of the alumina supposing the alumina to be smooth spheres gives a reasonable fit to the experimental behaviour. The shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. This could be due to the alumina particles not being completely monodisperse, with some particles breaking up and others forming agglomerates.

Table 2. Rate Constants Obtained for the First Model

| Alumina Addition | Rate Constant \( k \) (g s\(^{-1}\) m\(^{-2}\)) |
|------------------|------------------|
| 1                | 0.22             |
| 2                | 0.19             |
| 3                | 0.11             |
5. SECOND MODEL - MASS TRANSPORT CONTROL

5.1 Derivation of equations

The first rate equation (Equation 2) can be modified by taking into account the diffusion of dissolved alumina away from the surface of the alumina into the bulk of the electrolyte. The driving force for this diffusion is the difference in concentration of dissolved alumina between that at the surface of the alumina ($C_{\text{sat}}$) and that of the bulk of the electrolyte ($C$). It is assumed that diffusion is one dimensional through a constant thickness boundary layer, $\delta$, where $\delta$ is invariant with respect to particle size.

The rate equation may then be written:

$$R = \frac{dC}{dt} V = k_2 A (C_{\text{sat}} - C)$$  \[9\]

Substituting the expression for area as a function of concentration, (4) and (5), the rate equation becomes:

$$\frac{dC}{dt} V = k_2 A_0 \left(1 - \frac{V}{M_0} C'\right)^{2/3} (C'_{\text{sat}} - C')$$  \[10\]

where: $C'$ is the concentration of alumina minus the initial concentration
$C'_{\text{sat}}$ is the saturation alumina concentration for the particular electrolyte composition used minus the initial concentration

This can then be integrated, using algebraic substitution, and the integration constant found for $C' = 0$ when $t = 0$ to yield the expression:

$$t = \frac{2V}{k_2 A_0 a^2 b^2} \left[ \frac{1}{2} \ln \frac{(a+u)^2}{a^2 - au + u^2} + \sqrt{3} \tan^{-1} \frac{2u-a}{a\sqrt{3}} - \frac{1}{2} \ln \frac{(a+b)^2}{a^2 - ab + b^2} - \sqrt{3} \tan^{-1} \frac{2b-1}{a\sqrt{3}} \right]$$  \[11\]
where:

\[ u = \left( C' - \frac{M_0}{V} \right)^{1/3} \]

\[ a = \left( \frac{M_0}{V} - C'_{\text{sat}} \right)^{1/3} \]

\[ b = \left( -\frac{M_0}{V} \right)^{1/3} \]

5.2 Comparison with experimental

The saturation concentration of alumina in the electrolyte used is 164.6 g/L (8). The initial alumina concentration in the electrolyte was 15.8 g/L Al₂O₃ so that the \( C'_{\text{sat}} \) for the first second and third dissolution curves will be 150.9, 129.8 and 108.7 g/L respectively. When these values are used and Equation [11] is plotted for each of the three dissolution runs then the curves shown in Figure 3 are obtained. The rate constants obtained from computer best fits of the calculated curves with the experimental curves are listed in Table III. The rate constants obtained are similar, as should be expected, at the three different initial alumina concentrations.

5.3 Particle interaction

It has been observed (2,4), from dissolution studies of powder alumina added to a stirred electrolyte of cryolite, that the degree of dispersion of alumina in the electrolyte has a large effect on the dissolution rate of the alumina. This dispersion is controlled by the stirring of the electrolyte, by a stirrer in the laboratory cell and in a commercial cell by electromagnetic forces and gas induced stirring. The second model proposed, assumes that the alumina particles are well dispersed so that the diffusion of dissolved alumina away from each alumina particle is not affected by neighbouring particles. This will clearly not be the case for a real system. Where complete dispersion is not obtained there will be some overlap in the boundary layers of adjacent alumina particles, as represented...
Table 3. Best Fit Rate Constants Obtained for the Second Model Using the Actual Values of $C'_{\text{sat}}$ and an Adjusted Value of $C'_{\text{sat}}$ of 80 g L$^{-1}$.

| Dissolution Run | Actual $C'_{\text{sat}}$ | Adjusted $C'_{\text{sat}}$ | $k_2$ (m s$^{-1}$) | $k_2$ (m s$^{-1}$) |
|----------------|-------------------------|---------------------------|-------------------|-------------------|
|                | $C'_{\text{sat}}$ (g L$^{-1}$) | $C'_{\text{sat}}$ (g L$^{-1}$) |                  |                   |
| 1              | 151                      | 80                        | $1.4 \times 10^{-7}$ | $2.9 \times 10^{-7}$ |
| 2              | 130                      | 80                        | $1.5 \times 10^{-7}$ | $2.5 \times 10^{-7}$ |
| 3              | 109                      | 80                        | $1.1 \times 10^{-7}$ | $1.6 \times 10^{-7}$ |

in Figure 4.

We can test this hypothesis by using a smaller concentration gradient in Equation [11]. This can be done simply by using a smaller value for $C'_{\text{sat}}$, which is equivalent to saying that the effective bulk alumina concentration experienced by each particle is greater. When a lower $C'_{\text{sat}}$ is used, as illustrated in Figure 5, a better fit of the model to the experimental data is obtained. These plots are obtained with $C'_{\text{sat}} = 80$ g/L Al$_2$O$_3$.

A better fit still can be obtained using $C'_{\text{sat}} = 40$ g/L Al$_2$O$_3$, as illustrated in Figure 6.

5.4 Estimation of boundary layer thickness from rate constants and diffusion coefficient.

The rate constant, $R$, for the second model is related to the diffusion coefficient, $D$, and the boundary layer thickness, $\delta$, by the relationship:

$$k_2 = \frac{D}{\delta}$$  [12]

The diffusion coefficient for alumina under the conditions employed here is approximately $1 \times 10^{-9}$ m$^2$ s$^{-1}$ (9). Therefore a rate constant of $1.4 \times 10^{-7}$ m s$^{-1}$ gives a calculated boundary layer thickness of $7 \times 10^{-3}$ m. Typically, in a well stirred system, boundary layers are about $10^4$ m. This suggests that the value of $k_2$ obtained with this model is too small or that the surface area calculated is too large. If there was some clumping of the particles taking place then the surface area exposed to the electrolyte would decrease and the rate constant would be smaller. For example a surface area of 0.01 m$^2$ would give a calculated boundary layer thickness of $1.8 \times 10^{-4}$ m. The initiation
time for dissolution due to heat transfer would in this case be of the order of 1 - 4 seconds, which is still negligible. Some small degree of clumping of alumina is therefore suggested by the comparison of this model with the experimental data. As with the first model, the shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. This could be due to the alumina particles not being completely monodisperse, with some particles breaking up and others forming agglomerates.

6. CONCLUSIONS

Two models for the dissolution of alumina powder in cryolite were formulated and compared with experimental results obtained using modified fast linear sweep voltammetry. The first model, where the rate of dissolution is assumed to be controlled by the rate of chemical reaction at the alumina surface, and is therefore proportional to the surface area assuming smooth spheres, gave a reasonable fit with the experimental data. The shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. This could be due to the alumina particles not being completely monodisperse, with some particles breaking up and others forming agglomerates.

The second model, where it is assumed that the rate of dissolution of alumina is mass transport controlled, also gave a reasonable fit with the experimental data. The shape of the experimental curve differs from the predicted curve in that the reaction proceeds more rapidly initially. The fit was improved if it is assumed that dispersion is not complete so that there some overlap between the boundary layers of adjacent alumina particles. The fit could also be improved if it is assumed that the alumina particles are not completely monodisperse, with some particles breaking up and others forming agglomerates. This is supported by a calculation of the thickness of the boundary layer from the rate constants obtained from the second model, and the diffusion coefficients, which suggest that the alumina is clumping to some extent resulting in a reduced surface area.

Heat transfer was shown not to be the dominant rate controlling process in the stirred electrolyte system studied.

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Figure 1. Experimental Dissolution Curves. 600 g Electrolyte (Cryolite with Ratio of NaF/AlF$_3$ = 1.50, 5% CaF$_2$) in 100 cm Diameter Carbon Crucible with Stirrer at 200 rpm, 8°C Superheat (Above Liquidus). Curve 1 and 2 for 1 Mass% Alumina Additions, Curve 3 for 1.8 Mass% Alumina Added. Alumina Added Through a Dropper with a Cone Shaped Spreader, Addition Time Approximately 2 Seconds.

Figure 2. Experimental Curves with Best Fit Curves Obtained Using Equation [7] for the First Model.
Figure 3. Experimental Curves with Best Fit Curves Obtained Using Equation [11] for the Second Model.

Figure 4. Representation of the Overlap of the Boundary Layers of Two Alumina Particles Resulting in an Effectively Lower $C'_{sat}$. 
Figure 5. Experimental Curves with Best Fit Curves Obtained Using Equation [11] for the Second Model with $C'_{\text{sat}} = 80 \text{ g/L Al}_2\text{O}_3$.

Figure 6. Experimental Curves with Best Fit Curves Obtained Using Equation [11] for the Second Model with $C'_{\text{sat}} = 40 \text{ g/L Al}_2\text{O}_3$. 

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