

Decoding Alumina Dissolution by Navigating the Dynamic Interplay of Bath Composition

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Abstract

Efficient dissolution of alumina is essential to maintain ideal conditions in an aluminium reduction cell. Too little alumina dissolved in the electrolyte provokes the so-called anode effect, while a surplus favours the muck formation under the metal pad. In the two cases, the energetic and environmental performance of the electrolysis cell decreases rapidly, in opposition to the priorities of the aluminium industry.

This work presents an intricate model to reproduce the alumina dissolution process to assess the influence of the chemistry and bath properties on the alumina dissolution kinetics.

Simulation results are compared with the ones obtained from an extensive experimental parametric study to validate the behaviour and understand the kinetics involved. From these results, the limiting factor to the raft dissolution is the internal diffusivity of the dissolved alumina. An increase of the fluoride content, aluminium, and calcium, within the bath increases the diffusivity of the dissolved alumina, thus increasing its dissolution rate. However, this beneficial impact can be counterbalanced by the lower solubility of the alumina in the bath. Accordingly, the relationship between the bath composition and the raft dissolution kinetics is presented at different superheats to understand this delicate equilibrium. Subsequently, the differences in the dissolution conditions between the experimental setup and industrial cells are described. Finally, a pathway to reach an optimal composition for industrial cells is presented.

Keywords: Alumina rafts, Bath composition, Alumina dissolution.

1. Introduction

The production of primary aluminium through the Hall-Héroult process needs a constant input of alumina to sustain the reaction. Therefore, alumina powder is fed every minute or so at three to five points in the electrolysis cell. These injections of typically one kilogram of alumina rapidly aggregate to form solid rafts that are difficult to dissolve and create a significative lag between the injection and the reduction. Moreover, undissolved alumina can migrate in the electrolysis cell creating spatial heterogeneity in the dissolved alumina concentration. The spatial and temporal heterogeneity create instabilities in the electrolysis process, such as anode effect or muck formation, which promotes instability, loss of production, greenhouse gas generation, and degradation of the cell. With such a focus on energy efficiency and environmental emissions reduction, a deep understanding of alumina dissolution is essential to maintain the process in a narrower band of stability. In this way, the work presented here compares experimental results obtained with a gravimetric method to a unidimensional model, previously presented in [1],

relying solely on the bath chemistry and the temperature of the bath and alumina to predict the dissolution behaviour of powdered alumina.

2. Methodology

2.1 Experiments

This study is based on two elements, aiming to compare the results from several laboratory experiments to a one-dimensional alumina dissolution model to assess the latter's accuracy. The gravimetric method was employed to create alumina powder injection samples in cryolite baths of various chemical and thermal conditions. A stainless-steel ring with a diameter of 12 cm was brought down to the bath-air interface level. The ring also had overlapping wires at the interface level. Then a mass of 40 grams of alumina was injected using a funnel to the bath surface and constrained to the ring dimensions. This enabled the alumina to attach to the metal ring and the horizontal pins at its bottom wires. Subsequently, the apparent weight of our samples was monitored as they underwent infiltration, sintering, and dissolution.

In the meantime, a video recording of the sample was made. This was helpful to the understanding of the behaviour observed in the gravimetric curves. However, the top of the furnace needed to be open for visual access during the whole test. This created a large radiative heat loss on the top of the bath and the sample. Therefore, the initial superheat of the cryolitic bath was increased by 5 °C before the injection. In most cases, the heat losses decreased the bath temperature steadily by an amount of about 20°C from the beginning to the end of the test. This value depends on the condition used but was uniformly imposed on the model calculations.

Three injections using primary alumina were done for each of the five test conditions. Since the same electrolytic bath is used, a slight change in the alumina mass fraction of the electrolyte is present between each sample. Worst-case scenario calculations indicate that the augmentation of concentration is lower than 0.3 % between each reported test. However, as the complete dissolution of the samples was only achieved in a few cases, the plausible change in concentration is even lower than 0.3 %.

2.2 Mathematical Modelling

For the scope of this study, a model presented at TMS 2024 was reused [1]. An important hypothesis of this model is that the alumina injection dynamic is so fast that no crust can be created around the heap of powder. The bath solidification is only considered when the particles are at rest. This hypothesis was allowed by the observation of the video recording of the experimental tests. During these tests, the infiltration front of the sample moves almost constantly toward the centre of the raft. This invalidates the hypothesis that a solid crust shell is present around the alumina because that phenomenon would prevent the continuous infiltration of the raft. In the meantime, Figure 1 shows the progression of the infiltration front during the first ten seconds after the injection. It clearly shows a progression of the infiltration by about 20 % of the raft radius in 10 seconds. The infiltration seen in Figure 1 is a combination of radial and vertical infiltration, while some test observations show the predominance of vertical infiltrations. A crust shell frozen around the raft cannot allow this behaviour. Therefore, the model should be initialized without any crust around it.

counterbalanced by the augmentation of the diffusivity. However, be aware that this is only true when the raft has a significant thickness, in which the diffusion is significant. This is an important statement that explains the difference between the results of this work with the results of other works, where the thickness of the raft was usually negligible. If the raft is very thin, the dissolution of the raft is controlled by convective mass transfer, itself driven by the alumina solubility. However, a taller raft will bring more dissolved alumina to the lower face of the raft by the diffusion in its pores.

These results state that the limiting factor for the alumina dissolution is the diffusivity of the dissolved alumina in the cryolite melt. Therefore, increasing the mass fraction of additives in the bath can promote dissolution. Nevertheless, be aware that this conclusion is strongly dependent on the calculation of the alumina diffusivity from the Wilke-Chang equation, as presented in [4].

5. Conclusions

A model for the alumina dissolution using thermal and chemical conditions has been developed in this work. This model simulates the main reactions of the dissolution of an alumina raft:

- Bath infiltration and solidification
- Alumina sintering and dissolution
- Heat transfer and enthalpy changes

This model was compared to five experimental conditions of alumina powder injection. The model can predict the actual weight of the raft created in the conditions near industrial cells. The model was then used to find the main effects of the thermal and chemical conditions on the raft dissolution. This sheds light on the raft dissolution that is limited by its internal diffusion. Therefore, increasing the diffusivity of the dissolved alumina within the raft body will enhance the overall dissolution rate of the raft. An augmentation of the additive content is then favourable to the dissolution of the raft with a significative thickness. In the case of a thin raft, the diffusivity has a lesser impact on the dissolution rate as it is controlled by fluid convection.

The next step to improve the prediction capabilities of the model is to understand the bubble dynamics inside the raft and its influence on the dissolution rate of alumina.

6. References

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