EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling

Mathematical modelling of dissolution of alumina

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1. Introduction

Background

Aluminium plays a big role in many parts of life, even though it is a metal that was discovered only recently (in the early 19th century). Because its production was hard, it was initially viewed as a symbol of wealth, used to create sculptures and cutlery for the rich. In the late 19th century Martin Hall and Paul Héroult independently discovered a scalable industrial process for producing aluminium from alumina (Al_2O_3) which is now known as the Hall-Héroult electrolytic process. This discovery was made possible by two other scientists, Pierre Berthier who discovered Bauxite ore, which is an ore containing high amounts of aluminium in bound form, and Carl Bayer who introduced a process for extracting alumina from bauxite. With these crucial parts in place, there was a scalable way to produce aluminium which involves mining bauxite, using the Bayer process to produce alumina, and using alumina and large amounts of electricity to get high purity aluminium metal. This led to a rapid growth in the production of aluminium, resulting in millions of tons of aluminium produced by the means of these processes today.

Aluminium is a multipurpose metal and, even though large amounts are produced, the process can still be improved

Many different industries rely on the steady supply of aluminium, because of its advantageous properties such as high strength to density ratio and malleability which makes it a popular material in the aerospace and automotive industry. It is also a good conductor of heat and electricity and used to make heat sinks in computers. Besides these more technological uses that aluminium has, it found a way into households where the list of uses is long, for example it is used in cans, aluminium foil, mirrors, cutlery, pots etc. All of this is made possible by the fact that aluminium can be recycled without losing its advantageous properties.

The Hall-Héroult process is based on the process of electrolysis. Alumina particles are added at the top of the process vessel into a bath of hot molten cryolite (the electrolyte). The process uses large amounts of electric current to heat the fluid and drive an electrolytic reaction which converts the alumina to aluminium. In perfect circumstances, the alumina added at the top of the vessel enters the cryolite and dissolves rapidly. However, in some cases it forms rafts that float on top of the fluid slowing down the dissolution, decreasing throughput, and inducing harmful side reactions. The reaction is extremely sensitive to the amount of dissolved alumina in the electrolyte, and there is a very narrow operating window for the process.

Even though there are large amounts of aluminium produced each year using the Hall-Héroult process, due to the harsh physical and chemical conditions required there is still uncertainty about the details of the effects that take place and about how to make the production of aluminium more efficient and environmentally friendly. Norsk Hydro and Teknova are thus interested in models for the Hall-Héroult process and, in particular, how the local composition of the electrolyte affects the dissolution of the alumina process. We restrict our attention to one aspect of the process, the "feeding of alumina". In this part of the process, solid room-temperature alumina dissolves into a bath of cryolite where the electrolysis takes place.

Glossary

- Electrolysis: Separation of complex molecules by the means of conducting electrical current through an ionized fluid called electrolyte.
- Bath: Term used to refer to the hot electrolyte fluid made up of cryolite (among other chemicals), which can dissolve alumina.
- Overheat: Temperature difference between the melting point of the electrolyte and the temperature of the bath. For efficiency, this must be as low as possible.
- Stefan condition: Interface condition describing how the position of a phase-change interface evolves depending on the heat flowing in and out from it.

We focus on the behaviour of a small alumina particle in a hot and chemically aggressive fluid. The interesting part of this problem is that the cryolite is just above its melting point (with about a 5K overheat) and the temperature of the particle is well below this, but at the same time the temperature of the fluid is below the melting point of the particle. An everyday analogue of this problem would be throwing in -200°C piece of sugar into water near 0 degrees, while asking how fast does the sugar dissolve?

Since there are large differences in the temperature between the particle and the surrounding fluid, we expect that the fluid next to the particle will freeze rapidly and then, because of the high temperature, this frozen shell will melt away. While this is happening, the dissolution is inhibited, since no fluid is in contact with the particle, but after the shell melts the dissolution process can initiate and the particle dissolves into the solution. These effects can be seen on Figure 1.

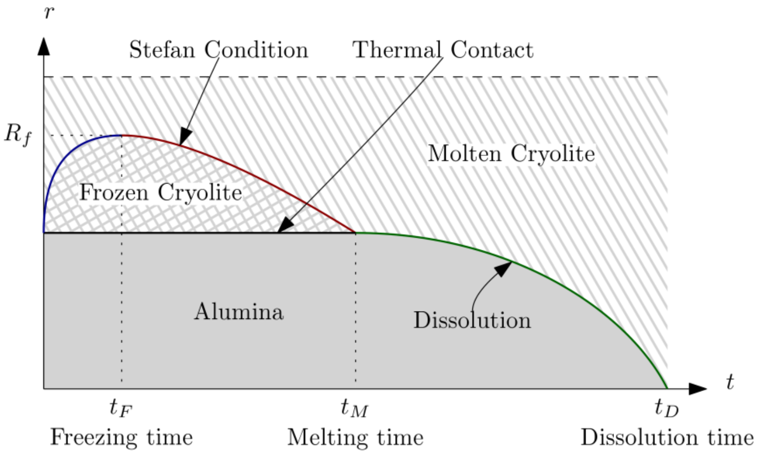

Figure 1: Various effects that happens after placing the particle into the bath. The length of the effects is not drawn to scale.

There are number of questions arising from these observations, such as: what is the maximum size of the frozen shell? When does this maximum occur? When does the frozen shell melt away? When does the particle completely dissolve into the fluid? How do these times depend on the process parameters? In general, all these questions can be answered if we can determine how the effective radius of the particle changes with time. Our aim is to build models for heat and mass transfer in and around a single alumina particle to address some of these questions.

Neglecting flow and spherical symmetry results in a one-dimensional problem which is easier to solve, yet still has valuable insight

2. Model for the formation of frozen cryolite layer

We consider a single particle residing in a semi-infinite bath of cryolite. There is potentially one big complication we have not discussed, namely the flow of the fluid in the bath, which may make the thickness of the frozen shell nonuniform. Luckily, for small particles we can show that this flow effect is negligible, so we do not include it in our model. We assume spherical symmetry, and that the density of the frozen layer and the fluid are the same.

We track the temperature in the particle, the frozen shell, and the surrounding cryolite bath. Our model comprises coupled partial differential equations (known as diffusion equations) with a free boundary at the edge of the frozen region which moves in time. This situation is commonly known as a Stefan problem. We assume that the far-field temperature of the cryolite bath is constant, that the temperature is continuous across the alumina-frozen cryolite and frozen-molten cryolite boundaries, and that the temperature is bounded in the centre of the particle. On the boundary between the alumina particle and the frozen layer the heat flux is continuous. Between the frozen and liquid shell, we assume that the temperature is at the melting point and that the difference between the heat fluxes drives the movement of the boundary.

We scale the model to identify the key parameters which describe the behaviour. We find that there are multiple important parameters: θ_m, which describes how close the melting temperature of the cryolite is to the temperature of the hot bath, and St, the Stefan number, which describes how much heat is necessary to move the boundary by a certain amount, and κ, which is the ratio of the thermal diffusivities of the cryolite and the alumina. Finally, β and υ, are relative conductivities. The parameters are defined by:

$$\theta_m = \frac{T_m - T_A}{T_c - T_A}, \qquad \mathrm{St} = \frac{c_A \rho_A k_f (T_c - T_A)}{L \rho_f k_A}, \qquad \kappa = \frac{k_c \rho_A c_A}{k_A \rho_c c_c}, \qquad \beta = \frac{k_f}{k_A}, \qquad \upsilon = \frac{k_c}{k_A},$$

where ρ is the density, c is the heat capacity and k is the conductivity, L denotes the latent heat of fusion, T_m the melting point of the bath; subscripts A, c and f denote the alumina particle, the cryolite bath and the frozen shell respectively. Here, T_A and T_c are the initial temperatures in the particle and bath, respectively.

3. Solution of the model

We exploit the fact that the Stefan number is small and solve the approximate model to find explicit formulae for the temperature profiles and the effective radius of the particle. In all the figures, blue lines correspond to freezing, red lines to melting, and green lines to the dissolution.

In Figure 2 we show how the radius of the frozen shell varies with time. We see that the freezing occurs very quickly and that the subsequent melting occurs much more slowly. In particular, we find an explicit expression for the time at which the frozen layer has completely melted.

The approximate melting time can be calculated by only dealing with the melting part of the solution

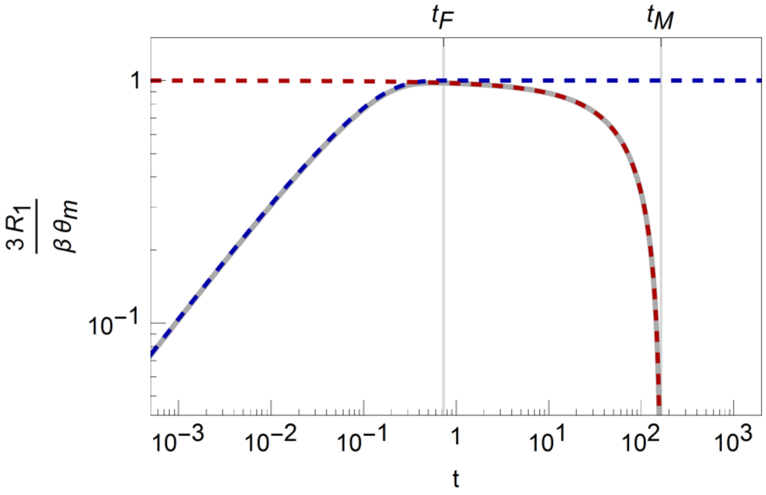

Figure 2: Graph showing how the thickness of the frozen shell, R_1, varies as a function of time (grey line) using logarithmic scales. The fast freezing is shown in blue and the slower melting is shown in red. t_F denotes the time that the frozen layer reaches its maximum radius and t_M denotes the melting time.

In Figure 3 and 4, we plot the temperature as a function of position for various times in the cryolite and the particle, respectively. We see that the particle heats up swiftly and that the particle cools down the surrounding cryolite. We note that, although we show the steady state temperature profile in the cryolite, this would not be achieved in practice because the frozen region completely melts before the steady state is reached.

In Figure 5, we plot the heat fluxes flowing into the phase change boundary. The heat flux due to the particle is shown as a blue curve and the heat flux due to the cryolite is shown as a red curve. We see that the flux due to the particle decreases much faster than the flux due to the cryolite. We calculate the short-time and long-time behaviour of the system and use this to determine formula for the fluxes in these two limits, which are shown as dashed lines in Figure 5. The intersection of the two solid curves represent the time at which the shell transitions from freezing to melting. We obtain an upper bound for t_F by considering the intersection of the long-time behaviour of the heat flux due to the particle and the short-time behaviour of the heat flux due to the cryolite.

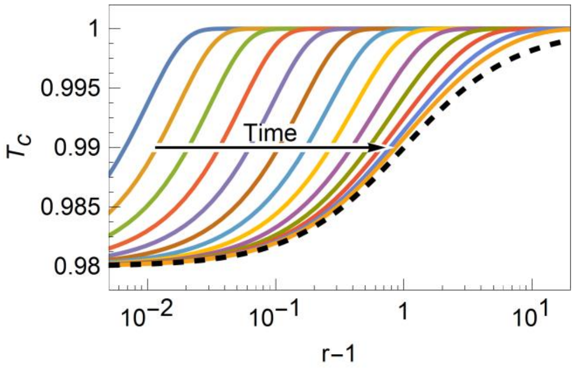

Figure 3: Graph showing how the temperature varies across the cryolite bath at different times (using a log scale). The dashed line shows the steady state profile.

The temperature rapidly increases to the bath temperature; after 5 particle diameters away, the effect is negligible

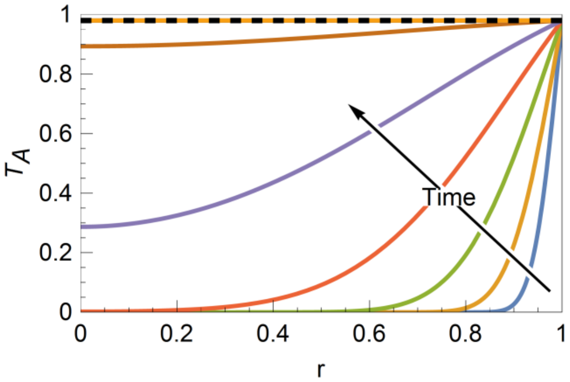

Figure 4: Graph showing how the temperature varies in the particle for different times. The dashed line shows the steady state profile.

An upper bound can be calculated for the freezing time by looking at the long-time behavior of the heat flux from the bath

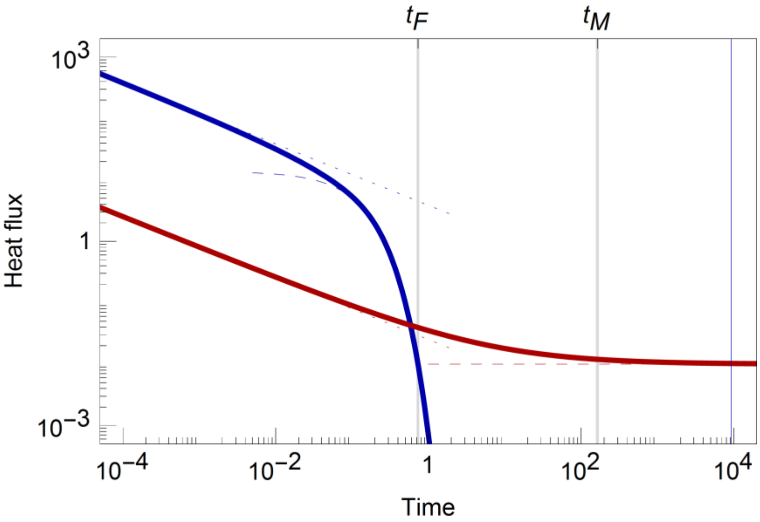

Figure 5: Graph showing how the heat fluxes into the moving boundary vary with time. The heat flux due to the particle is shown in blue and the heat flux due to the cryolite is shown in red. The intersection of these curves gives the freezing time. Long time and short time behaviours are given by dashed and dotted lines, respectively.

4. Modelling of dissolution

After the freezing and melting processes, the cryolite is in contact with the alumina particle which means that there is a surface reaction which dissolves it into the cryolite. We keep track of the concentration of the alumina in the cryolite by using conservation of molecules. To solve the system, we prescribe the far-field concentration, and assume that the concentration is saturated at the interface. As before, the difference in concentration drives the movement of the interface.

By suitably scaling the system, we get one important parameter which play a similar role to the Stefan number and encapsulates how much the interface moves for a given mass flux, namely

$$\sigma = \frac{C_s - C_0}{\rho_A \left(1 - \frac{C_s}{\rho_c}\right)},$$

where C_s is the saturation concentration, C_0 is the far-field concentration. For real material properties, σ is small and the dissolution problem can be solved explicitly. We find that the particle dissolves in finite time, and there is a simple relationship between the square of the radius and time.

In Figure 6, we show how the freezing, melting and dissolution times vary with the initial temperature difference between the particle and the cryolite. Each vertical slice can be interpreted as the solution for the given temperature difference. We see that there is a regime where the temperature difference is too small and freezing does not happen. We also determine expressions for the freezing and melting times in the limit of large initial temperature difference, which we plot as dashed lines in Figure 6. We see that these expressions accurately capture the behaviour. Finally, we conclude that, at the parameter values at which the cell operates, we always expect to have freezing, melting and dissolution, and the large initial temperature difference approximations accurately capture the behaviour.

If we vary the temperatures there are values where the freezing may not even happen

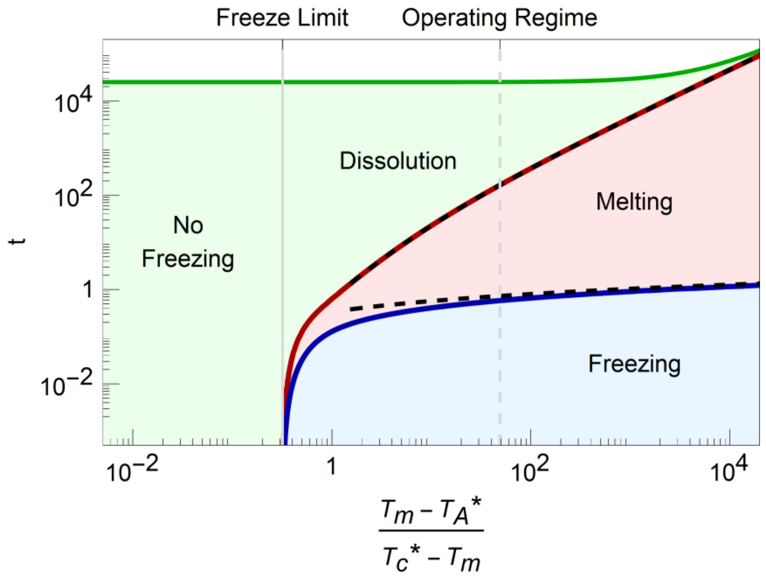

Figure 6: Graph showing how t_F (shown in blue), t_M (shown in red), and the dissolution time vary with the initial temperature difference between the particle and the cryolite changes. All the other parameters kept as constant. The large-temperature-difference behaviours are show as dashed lines. Colours denote the regions where freezing, melting, and dissolution occur.

5. Discussions, Conclusions & Recommendations

We have built mathematical models to describe two key aspects of the "feeding" stage of the Hall-Héroult process, namely the freezing and the subsequent melting of a thin solid cryolite layer around a single particle, and the subsequent dissolution of the particle into the bath. We have analysed these models to find some key results:

- Using real material properties, we find that there is a clear separation of timescales between the thermal processes and dissolution. Freezing occurs over the shortest timescale, followed by melting, then dissolution, and finally fluid flow. We derived simple approximations for these timescales.
- The model yields a maximum particle size which can be verified with back of the envelope energy-based calculations and is in the regime of applicability. Also from the temperature distribution, a distance can be identified where the effect of the particle on the bath is negligible.
- We have found insight into the minimum temperature difference between the particle and the cryolite to have freezing.

Further experiments will be needed to verify the applicability and the accuracy of the models.

Extending the model

The key extensions for future work are to:

- solve the model numerically in the case when the Stefan number is not small;
- consider multiple particles, which may form rafts of clumps, and the effect of the shape of the particles on dissolution;
- include the fact that the particles are porous;
- couple the local model close to the particle with the larger-scale model for the flow in the bath, including chemical reactions.

6. Potential Impact

The work has provided Norsk Hydro with the understanding of the freezing, melting and dissolution time when dropping a small alumina particle into a hot cryolite bath. Norsk Hydro will work on integrating the results into their existing modelling tools and investigate the dissolution of particles in the full reduction cell to get a better understanding of where the dissolution happens. This information will be useful to help achieve better distribution of alumina in the bath by modifying the feeder design and control. This is likely to improve production efficiency and avoid undesirable environmental impact.

Outside of the company, these analyses could result in the reduction in energy consumption and reduction in the emission of harmful PFC gases. This may lead to smaller carbon footprint while producing aluminium.

Eirik Manger, Principle Engineer, said "*I was impressed how much progress one can make by using mathematical methods and scale analysis. I did not realize that the freezing and melting times were so short compared to the dissolution time, which provided me with new information. We are very pleased with the progress and look forward to continue the work in the research project.*"