A PRELIMINARY FINITE ELEMENT ELECTROCHEMICAL MODEL FOR MODELLING IONIC SPECIES TRANSPORT IN THE CATHODE BLOCK OF A HALL-HÉROULT CELL

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Abstract

A first 2D transient isothermal model was developed for the modelling of bath penetration in a Hall-Héroult cell cathode block. The model simulates the 'non convective' ionic species transport. The molten cryolite solution system is defined with an ionic model. The migration and diffusion of the ionic species is followed in the cathode block pores and in an overlying bath layer. The evolution of the potential is simultaneously obtained using charge conservation equations. The model includes a linear kinetic model for the electrochemical formation of metallic aluminium. The porous cathode behaviour is modelled using volume averaging based methods. The aluminofluoride ionic equilibrium is implemented by the penalty method and the electroneutrality criterion as a constraint on the FEM weak form. This is the first application of porous electrode theory, adapted for a molten salt, to Hall-Héroult cell cathodes. The results show the early stage evolution of voltage and ion distributions.

Introduction

Presently, the most important research areas in aluminium industry are improvement of energy efficiency and minimisation of waste. An important way to minimize waste is to extend electrolysis cell life. Most cells breakdown due to cathode failure or related problems. Because of the high temperature, electromagnetic environment and highly corrosive properties of the cryolite melt, it is extremely difficult to assess the cathode block state using experimental methods during cell operation. Consequently, it is very difficult to correct operating parameters to avoid too fast degradation of the cathode bloc. Numerical simulation used with more indirect measurements can help to assess cathode block problems. Developing a cathode block model can also help to optimise cells design or materials properties. In this study, a preliminary model is developed for modelling early life of cathode block for start up operations of new cells. The model is a base for developing more complex models for following bath penetration in cathode block and related degradation reactions.

After electric or fuel preheating, the cell start up procedure differs slightly among companies[1]. The bath is poured onto the cathode blocks with the current on. The bath slowly begins to penetrate and after some time, the carbon surface can become sufficiently kinetically activated for metal formation, and eventually the first metal droplets will appear. However, in most practices, some metal is poured to form a stable metal layer before it can form by droplet agglomeration.

This model was not only developed in view of modelling bath penetration but also for assessing some other related physico-chemical process, in particular, modelling phenomena related to aluminium carbides formation, current efficiencies and stability of bath mushy layers. The modelling of aluminium carbide formation could lead to a cathode erosion model. In the case of current efficiency, the need for modelling metal species dissolution could lead to improvement in the cell operating procedure. In the same view: a mushy layer, sludge or muck behaviour model will improve cell operation. All three of these physico-chemical phenomena, in some physico-chemical conditions, are kinetically controlled[1,2,3,4].Consequently, there is a need for a model that could include a kinetic reaction formulation.

Most models [1,5,6] related to bath penetration are not very complex, being steady state, non-ionic and mostly empirical. This kind of model has a very limited range of application and is not useful for detailed studies of bath component behaviour in the cathode block. The main problem of non–ionic, or diffusion based, models is the impossibility of modeling some reactions related to a particular ionic species and thus it is difficult to insert kinetic formulations for chemical or electrochemical reaction. To avoid this limitation, then the model is developed within an ionic frame. In our case, there is also a need to avoid removing one of the species conservation equations by using the electroneutrality criteria or thermodynamic equilibrium equations. The electroneutrality criterion was implanted as a constraint and the ionic equilibrium by the FEM penalty method.

Developing this kind of model is difficult due to the lack of data for the bath properties over CR 3 and the scarcity of studies of carbon/cryolite interfaces under cathodic polarisation[1,2].

Reaction system

The reaction system modeled is $NaF-AlF_3-Al^0$. The model is mainly based on ionic species. The species modeled are Na^+, F^-, AlF_4^-, AlF_6^{-3} and dissolved Al^0. The metallic aluminium behaviour is extremely simplified. In the real system, the metallic sodium is always present as a second product from the following equilibrium:

$$3\,NaF + Al \rightleftharpoons 3\,Na^0 + AlF_3 \qquad (1)$$
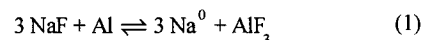
There are disagreements related to the last reaction[2]. It is not clear if metallic sodium comes from a homogenous reaction or from a parallel reaction at the electroactive cathode. Other difficulties are related to the unclear state of the dissolved metallic species (Al^0, Na^0) that make the development of a conductivity model coupled to species conservation equations a very difficult task. Moreover, layers of the bath containing dissolved reduced metals seem to evolve in two zones[7]. Explicitly including metallic sodium is a possible follow up to the model presented in this paper.

Electrochemical reaction

The electrochemical reaction for Al^0 formation is a two steps process[2,8,9]. In this model, for simplification, we only wrote a global interface reaction:

$$AlF_4^- + 3e^- \rightarrow Al^0 + 4F^- \qquad (2)$$
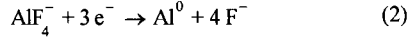
At this step, it was judged too complex to include interface modelling with an extra equation to account for any intermediate species that could be either diffusing outside or adsorbed onto the interface. The dissolution of Al^0 was considered instantaneous and unaffected by its activity as a dissolved species in the bath. Other than the evaluation of density by molar concentration and molar mass, we did not include any effect of Al^0 dissolution in the bath, implying:

a) Transport properties of other species are unaffected
b) The conductivity is not corrected
c) Real molar volume can be different;
d) Effect on electrochemical kinetic parameters is neglected;
e) Modelling of metal nucleation is excluded.

Ionic equilibrium

The ionic equilibrium modeled is the following:

$$AlF_6^{-3} \rightleftharpoons AlF_4^{-1} + 2F^- \qquad (3)$$
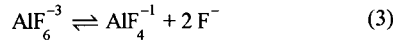
The only cation included in the system is Na^{+1}. The ionic equilibrium in molten salt was defined by using the result from the model of Zhang et al[10]. They used the hypothesis that the activity for $NaAlF_4$ and Na_3AlF_4 are equal to their molar fraction and the following equilibrium were formulated:

$$AlF_3 + NaF \rightleftharpoons NaAlF_4 \qquad (4)$$

$$AlF_3 + 3NaF \rightleftharpoons Na_3AlF_6 \qquad (5)$$
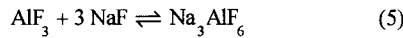
The associated equilibrium constants are then formulated as following:

$$K^{NaAlF_4} = \frac{a_{NaAlF_4}}{a_{NaF}a_{AlF_3}} = \frac{x_{NaAlF_4}}{a_{NaF}a_{AlF_3}} \quad K^{Na_3AlF_6} = \frac{a_{Na_3AlF_6}}{a_{NaF}^3 a_{AlF_3}} = \frac{x_{Na_3AlF_6}}{a_{NaF}^3 a_{AlF_3}} \qquad (6)$$

Using complementary equations and the measured activity for NaF, AlF_3 and other data, Zhang et al.[10] were able to evaluate the equilibrium constants. Using the same hypothesis for the activity of $NaAlF_4$ and Na_3AlF_6 we define the following equilibrium for the ionic equilibrium of interest in our model:

$$Na_3AlF_6 \rightleftharpoons NaAlF_4 + 2NaF \qquad (7)$$
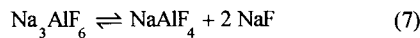
$$K = \frac{a_{NaF}^2 a_{NaAlF_4}}{a_{Na_3AlF_6}} = \frac{K^{NaAlF_4}}{K^{Na_3AlF_6}} = \frac{a_{NaF}^2 x_{NaAlF_4}}{x_{Na_3AlF_6}} \qquad (8)$$

As mentioned earlier, the model has to be defined for ionic species concentration. Then we had to transform the system in molar concentration. The molar fractions were calculated from data on activity and equilibrium constants obtained by Zhang et al.[10] The effect of neutral species (AlF_3, NaF) and of alumina on the equilibrium constant were neglected. The components' molar fractions were calculated from the equilibrium constant and activities. The components were assumed to be completely

ionized as Na^+, F^-, AlF_4^- and AlF_6^{-3}; this allows calculation of ionic molar fractions and subsequently the molar concentration and density[11]. The ionic molar concentration was used to calibrate the ionic species diffusion and mobility coefficients with experimental conductivity data. Following that, the activity data for different CR were defined as a new function of Na^+ concentration. Those functions and equation 8 were used in the penalty formulation of the modeled ionic equilibrium modeled. The system is considered to be isothermal.

Electrochemical reactor

The model is built with a large stagnant zone overlaying the cathode block because it preserves the possibility of modelling an experimental system of metal dissolution and migration. This could subsequently allow comparison of more complex model results with the two-layer dissolved metal zones mentioned earlier[7]. This configuration will also able us to add different effects of turbulent fluid movement.The last point is important because in the industrial conditions, there is a turbulent zone over the cathode block. The cathode below the bath saturation front is not modeled, nor is the advance of this front into the block.

Mathematical models

The model is mainly based on species and charges conservation equations. As mentioned earlier, the domain is split into a fluid only zone and a zone representing the bath saturated porous cathode block. The equations describing the transport in the block are based on a volume averaged model, in which the properties of the carbon and the bath are described in terms of a small number of structure related parameters, such as the porosity, ε, and the intrinsic average species concentrations c_i. The carbon phase is considered non reactive and the porosity independent of time. The general species conservation equations for the species in pore fluid are define by the following equation

$$\varepsilon \frac{\partial c_i}{\partial t} + \nabla \cdot \vec{J}_i - \varepsilon R_i - r_i = 0 \qquad (9)$$

The superficial flux of species $\vec{J}_i$ is referred to the barycentric velocity. The species sources R_i and r_i account respectively for homogenous and heterogeneous reactions. All convective effects are neglected. The flux is averaged on the cross section of the homogenisation volume. The effect of the porous media on transport is modeled with effective transport coefficients. This is discussed later in the transport model section. The species concentration is averaged over the pore fluid and enables us to have continuous species concentration variables between the overlaying fluid domain and the cathode pore fluid.

The electroneutrality constraint is supposed to be valid over the entire domain.

$$\varepsilon \sum_i z_i c_i = 0 \qquad (10)$$

As the electroneutrality criterion is considered valid and we don't take account of convective transport, there is non convective current. The electroneutrality is not implemented in this model in the conventional way by removing one specie's conservation equation; this is discussed more thoroughly in a later section. The charge conservation equations for the porous media are the following:

$$\nabla \cdot \vec{i}_s = r \qquad \nabla \cdot \vec{i}_l = -r \qquad (11)$$

538

The superficial current densities $\vec{i}_s$ and $\vec{i}_l$ are respectively for the graphitised carbon phase and the bath in the pores. As the capacitive effect is neglected, the charge source term r only includes interphase electrochemical reactions. These general equations are the same as the ones generally used in simple porous model[12,13]. The equations for species and charge conservation for the overlaying bath are almost the same as the ones for pore bath. In fact, the sole differences are that we remove the interphase electrochemical reaction source r and instead of using effective diffusion and mobility coefficients in the transport equation, we use standard coefficients.

Transport properties flux model and porosity effect

The species flux in the bath in the cathode pores is driven by migration and diffusion, and is defined by the following equation:

$$\vec{J}_i = -\overline{D}_i \nabla c_i - z_i c_i F \overline{u}_i \nabla \Phi_l \qquad (12)$$

The transport parameters $\overline{D}_i$ and $\overline{u}_i$ are respectively the diffusion coefficient and mobility. The Nersnt-Equation is considered valid [2,7]:

$$\overline{D}_i = RT\overline{u}_i \qquad (13)$$

The species flux for the overlying bath is defined identically, except that transport coefficients are uncorrected for the porous media effect. In the block, a simple porosity effect model is used [12]:

$$\overline{D}_i = D_i \varepsilon^{1.5} \qquad (14)$$

The porosity is defined as constant excepted in a thin layer near the interface between the porous media and free bath. Across this thin layer, the porosity is smoothed to 1 with a polynomial near step function. Normally, for the thin layer, a non zero gradient of porosity should appear in equation 9 but we choose to neglect it for this preliminary model.

Transport coefficient calibration

The ionic species diffusion coefficients for the bath were calibrated from experimental conductivity measurements. The classic ohm law model for ionic solution was used:

$$\sum_i \frac{D_i}{RT} z_i^2 F^2 c_i = \kappa_l \qquad (15)$$

Migration coefficients were obtained using the Nernst-Einstein relation. Bath conductivity κ_l data necessary for the calibration over a wide range of bath molar ratio (CR) without alumina were obtained from an equation calibrated with experimental conductivity measurements collected from literature[14]. The transport properties of dissolved aluminium come from Haarberg et al.[4].

Electrochemical reaction implementation

The interphase carbon/bath surface is considered already kinetically activated for AlF_4^- ion discharge as if it were a carbon surface soaked in bath for some significant time [3] or a molten aluminium surface. For now, this hypothesis is used because almost no kinetic electrochemical studies have been done for the system modeled. Most experimental data are for an aluminium surface. The activation overvoltage η was defined as follows:

$$\eta = \Phi_s - \Phi_l - U \qquad (16)$$

The potential Φ_s and Φ_l are respectively those of the carbon solid phase and liquid bath phase. The open-circuit voltage U is defined as if using a reference electrode of the same kind [12] as our cathode electrode for assessing the voltage. The reference electrode bath for U is CR 1 and saturated with alumina. Using the overvoltage definition, we define the interphase electrochemical reaction charge term with a simple linear form:

$$r = i_0 nA \frac{F}{RT}(\Phi_s - \Phi_l - U) \qquad (17)$$

The parameters i_0, A and n are respectively the exchange current density, specific surface and the number of electrons exchanged in the related electrochemical reaction. The choice of a simple linear model is justified by the fact that the electrochemical reaction is considered to have a small activation overvoltage when occurring on the liquid aluminium surface or on a carbon phase soaked in bath [2,3,8,9]. The electrochemical reaction term for the species conservation equation is defined as follow:

$$r_i = \pm \frac{s_i}{nF} r \qquad (18)$$

The stoichiometric coefficient s_i is for the species "i" in the electrochemical reaction. As discussed earlier, the aluminium dissolves instantaneously and most effects related to metal dissolution are neglected.

Current density

The superficial current density in cathode pore bath is defined from the species flux definition as follow:

$$\vec{i}_l = F \sum_i z_i \vec{J}_i \qquad (19)$$

By substitution of flux definition in the last equation and using equation 11, we obtain the full charge conservation equation for bath in the cathode pores:

$$\nabla \cdot \left(F \sum_i \left[-z_i \overline{D}_i \nabla c_i - z_i^2 c_i F \overline{u}_i \nabla \Phi_l \right] \right) = k^{elc}(\Phi_s - \Phi_l) \qquad (20)$$

The same equation for the bath overlying the cathode is easily obtained by removing interphase electrochemical reaction terms and using standard transport coefficients. The carbon phase is considered to only transport electronic current by ohm's law.

$$\vec{i}_s = -\overline{\kappa}_s \nabla \Phi_s \qquad (21)$$

The full charge conservation equation for the carbon is easily obtained with left equation 11:

$$\nabla \cdot \left(-\overline{\kappa}_s \nabla \Phi_s \right) = -k^{elc} \left(\Phi_s - \Phi_l - U \right) \qquad (22)$$

The parameter $\overline{\kappa}_s$ is the effective conductivity of the carbon phase.

Ionic equilibrium-reaction implantation

The ionic equilibrium is implanted with the FEM penalty method:

$$R_i = \pm S_i k^{ioc} \left[K - \frac{a_{NaF}^2 x_{NaAlF_4}}{x_{Na_2AlF_6}} \right] \qquad (23)$$

The stoichiometric coefficient S_i is for the species "i" in the ionic equilibria. This approach is analogous to a linear reaction-transport model or a kinetic term based on a non-linear

thermodynamic force. As the ionic equilibria is supposed to be fast relative to transport properties and the AlF_4^- ion discharge reaction, the penalty parameter k^{ioc} must be high enough. The activity data for NaF, $NaAlF_4$ and Na_3AlF_6 were redefined as function of Na^+ molar concentration obtained as discussed earlier. Each activity function used was defined as a series of radial functions[15,16] of the following form:

$$a^g(c_{Na^+}) = \sum_{k=1} b_k^g \sqrt{\left(d_k^g - c_{Na^+}\right)^2 + \left(e^g\right)^2} + f^g \quad (24)$$

The radial function parameters(b_k^g, d_k^g, e^g, f^g) for each activity function (a^{NaF}, a^{NaAlF_4}, $a^{Na_3AlF_6}$) were calibrated using Na^+ molar concentration data and a in-house program in Matlab[14]. The three activity functions were calibrated together to minimize the error on the equilibrium constant K. Simultaneous calibration helped to avoid oscillation between calibration data and give a better fit for K.

Electroneutrality constraint

As mentioned earlier, the electroneutrality equation was used to simplify some equations terms, such as the convective current, but not for removing one species conservation equation. The studied system is not very well suited for removing a species because of the many reactions that can be related to those species. Also, the way that ionic equilibrium is dealt with does not really make the species concentration available for such an equation elimination procedure. The electroneutrality criterion is instead applied as a constraint in the FEM formulation. A constraint can be applied to a PDE system solved by FEM using a variational formulation [14]. The applied constraint is the following:

$$\int_V \lambda \left(\sum_i c_i z_i \right) dV = 0 \quad (25)$$

The constraint is inserted in the FEM formulation by the following weak form:

$$\int_V \left(\sum_i c_i z_i \right) \delta\lambda \, dV + \sum_i \int_V \lambda z_i \delta c_i \, dV = 0 \quad (26)$$

However, using this formulation unfortunately introduces a new equation and its associated Lagrangian variable λ that is well defined mathematically but not necessarily on the chemical-physical point of view. We make the hypothesis that the formulation should be good for the averaged concentration inside the cathode pores.

Solving the equations

The system is constituted of the homogenised cathode block and the overlaying bath. The 2D domain for the system is of 0.1 m by a depth of 0.045 m. It is split in two relative to depth to give a cathode block of 0.015 m thick and 0.030 m of overlaying bath. The system is modeled for a temperature of 1300 K. All parameters or data used are for 1300 K excepted for dissolved aluminium transport properties and the exchange current density. The temperature for the dissolved aluminium transport coefficient[4] is 1273 K and for the exchange current density[8,9]

is 1283 K. All other calibrated parameters or literature sources for them can be found in Gagnon [14].

FEM, Initial and Boundary Conditions

The cathode pores are supposed to be completely filled with bath of the same uniform composition of the overlaying bath. The system is initially perfectly electroneutral. The model is started with the bath already in ionic equilibrium and of CR 1.72. The initial bath voltage is of -0.31 V relative to aluminium reference electrode (CR 1 alumina saturated bath). The bath top boundary Dirichlet condition is the initial ions concentration for CR 1.72. and 1 for the Lagrangian variable. The bath top voltage Dirichlet boundary is set to -0.31V. The internal boundary between the cathode block and the overlaying bath is the continuity of all variables except for the graphite current which is isolated. A current of 0.4 A cm^{-2} is put as a bottom boundary condition on the graphite. Any other boundary is the zero flux of Neuman kind. For solving the model by FEM we used COMSOL. A boundary layer mesh is generated near the cathode block and overlaying bath interface. The PDE General Form applications mode was used for the model implementation. The weak form terms related to the electroneutrality constraint were inserted by using the weak form contribution features of COMSOL.

Result and discussion

General result

Figure 1 shows the metal concentration as a function of depth. In a future application, the metal produced inside the pore could be linked to a kinetic relation describing aluminium carbide behaviour. The calculated concentration of aluminium metal is too high. At such a concentration, the nucleation of droplets or formation of aluminum carbide should already be started. The aluminium production reaction would then probably shift onto the metal droplet surface. The real aluminium metal concentration should also be lower because of the formation of metallic sodium as a co-product. The metallic sodium will dissolve and react following other kinetics. For a model more in agreement with reality, metallic sodium modelling will have to be included. Also, the solubility of aluminium metal at high CR is not well known. The study of metallic aluminium in molten cryolite almost always implies side reactions related to metallic sodium. Because of this metallic side reaction, the modelling and the experimental measurements of this kind of system have the same related difficulties.

As observed in figure 2, the CR is rising in the electrochemical reaction zone. The metallic sodium rate or fraction produced will increase in the vicinity of a high CR zone[1,2,6-9]. This fact justifies by itself the necessity to add the metallic sodium modelling for an accurate simulation of aluminium current efficiency. As the CR crosses 3, the bath melting point will rise; this is consistant with a mushy layer formation.

The figure 3 shows that density changes substantially near the interface. The formation of a stagnant bath layer with a higher density could help stabilizing a mushy layer. It is also important to observe that in the real system, the diffusion-migration boundary layer thickness will be smaller because of turbulent mixing by thermal and magnetohydrodynamic forces. It is clear that the model needs to be improved by adding fluid dynamic modelling.

An interesting result will be to assess the mixing inside the porous block by density flow. It is not evident to predict if the density flow will develop or not inside the block and consequently a density layer could be relatively stable inside the cathode bloc. The last remark is true only if the initial bath is of CR lower than 3 because for higher CR, the density begins to lower again. Also, the effect of metal dissolution should be taken in account. The metallic sodium and aluminium dissolution behaviour vary with CR, The behaviour of the cathode and overlaying bath interface zone could also be significantly influenced by thermal Peltier effect.
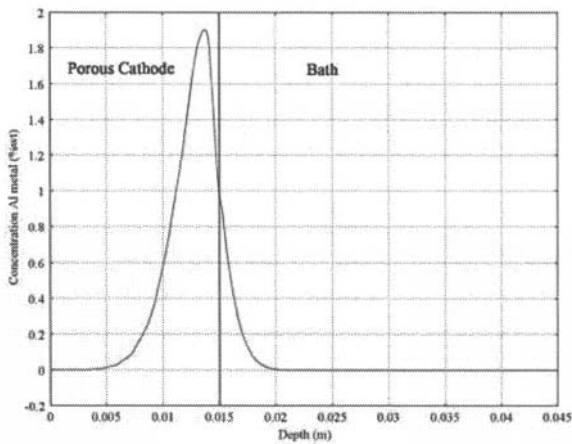
Figure 1. Calculated weight % of Al metal dissolved in the bath at 200 s.
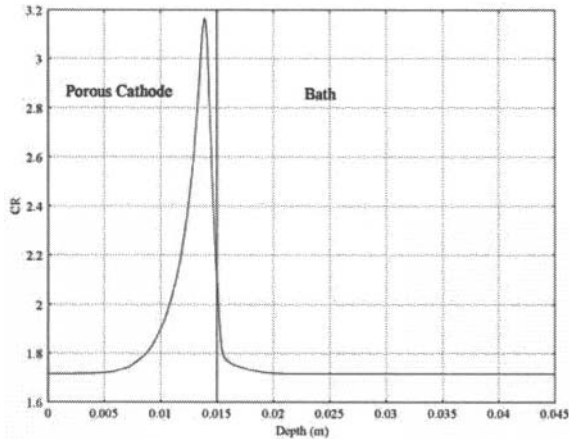
Figure 2. Calculated bath CR at 200 s.

The ion distribution curves shown in figure 4 mostly follow what is predicted by a more simple model [6,9]. Very near the electrochemical reaction zone, the pattern can be explained by the simultaneous effect of the enforced ionic equilibrium, the electrochemical reaction used and ion transport. The table I shows the calculated actvities for two points. Activities are calculated from Na^+ concentration using the three activity functions defined in the form of equation 24. Table I also shows the relative error for the non respect of the equilibrium constant. The free bath is mostly following Ohm's law. The layer where the charge transfer reaction occurs is very thin, about 2 mm. Thus, the height of

cathode block surface defects could be relevant in the reaction distribution and the aluminium carbide related erosion process. The overvoltage and bath voltage are shown in figure 5. The voltage across the bath phase and the overvoltage follows the normal trend that should be observed [1,2,8,9].

Table I. Calculated activities at 200 s for two depths.

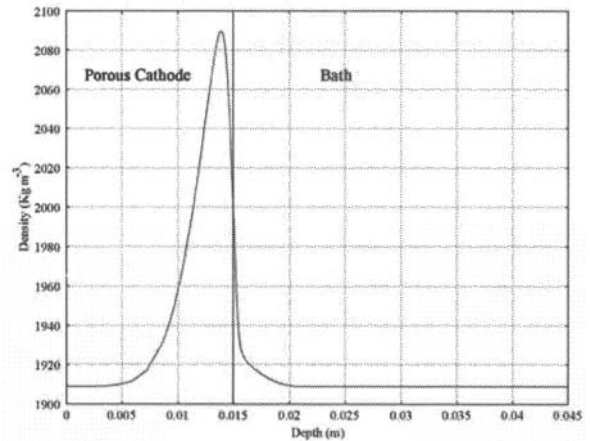| Depth (m)	c_{Na^+} (mmol cm^{-3})	a^{NaF}	a^{NaAlF_4}	$a^{Na_3AlF_6}$	Error (%)
0.035	20.99	0.081	0.61	0.13	0.001
0.016	21.50	0.086	0.59	0.15	0.463

Figure 3. Calculated density of the bath at 200s (includes the supersaturation in metallic Al).
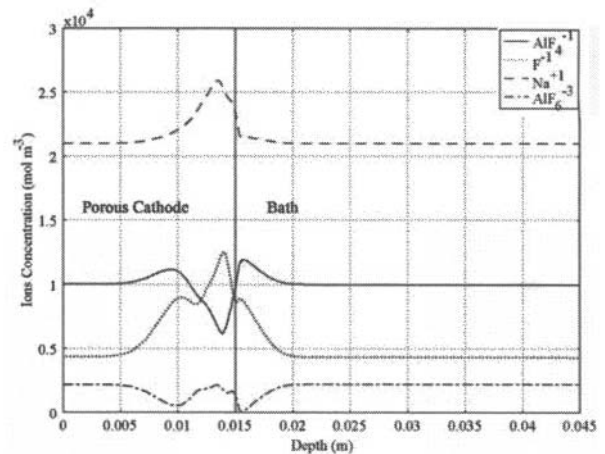

Figure 4. Simulated ion concentrations in the bath at 200s.

Penality method for ionic equilibrium performance

The maximum relative error for not respecting the ionic equilibrium is 0.47%. The largest error is near the strong concentration and voltage gradients but is still within a very good range. The quality of the solution is also function of the size of the penalty constant used in the model. The penalty constant cannot be raised too high because it induces too much numerical instability. In a future model, adding ionic equilibrium related to alumina dissolution should be straight forward but the

optimisation of the penalties constants could be difficult because the ionisation kinetic differences between the different equilibria is not well known.
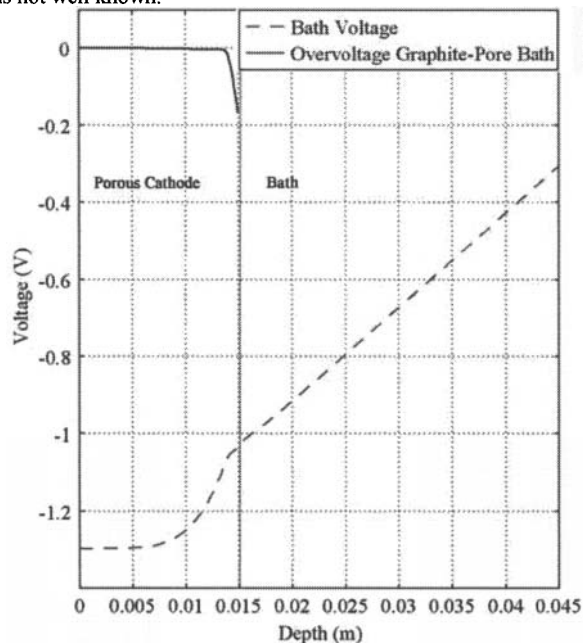

Figure 5. Simulated bath voltage relative to aluminium electrode CR = 1 and charge transfer overvoltage between cathode graphite and pore bath.

Electroneutrality constraint performance

The system remains mainly neutral over the entire domain. It appears that the error follows the element mesh size. This means that we could probably have a smaller charge excess by using smaller element and by the way improving the model solutions. The charge excess seems randomly distributed over the domain. The related residual electric field is calculated with a relative permittivity of 10000 by solving the following equation:

$$\nabla \cdot \left(-e_0 e_r \nabla \Phi\right) = F \sum_i c_i z_i \qquad (27)$$

The maximum voltage error is 0.2 mV. Formally, the relative permittivity of an ionic conductor for non alternative current is almost infinite[17].

Conclusion

The model developed was judged to give good preliminary results relative to the scarce availability of parameters for CR over 3. We were able to observe ionic distributions conforming to what most of the literature predicts from a qualitative point of view. The rising of the CR near the cathode block top was the most interesting result because experimental observations[8,9] suggest indirectly such behaviour. The use of the penalty method for implanting ionic equilibrium was successful. The implantation of electroneutrality as a constraint was also judged numerically efficient for our model. For better modelling of a real system, the model needs to be improved by adding metallic sodium species conservation equation and fluid modelling. The base model developed opens the way for modelling complex phenomena in cathode block pores of a Hall-Héroult cell.

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