# CONCENTRATION GRADIENTS OF INDIVIDUAL ANION SPECIES IN THE CATHODE BOUNDARY LAYER OF ALUMINIUM REDUCTION CELLS

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## Abstract

It is well known that the system $NaF$-$AlF_3$, which constitutes the "backbone" of the electrolyte used in primary aluminium manufacture, forms $Na^+$, $F^-$, and a number of fluoro-aluminate anion complexes in the molten state. Since mainly the $Na^+$ ion carries electric current, the aluminium-containing complexes must diffuse towards the cathode, resulting in concentration gradients in the cathode boundary layer. Starting from a structural model for the melt containing five anion species, it was possible to calculate the concentration gradients of the individual ions using the Stefan-Maxwell equation for diffusion in a multi-component system. Generally, $AlF_4^-$ and $Al_2F_7^-$ were transported towards the cathode, while $F^-$ and $AlF_6^{3-}$ moved away from the cathode. For $NaF$/$AlF_3$ molar ratios higher than 2.0, $AlF_5^{2-}$ moved towards the cathode, while it diffused away from the cathode in more acid melts.

## Introduction

Molten salts consist of a mixture of anions and cations. Upon melting, the system $NaF$-$AlF_3$ forms $Na^+$, $F^-$, and a number of fluoro-aluminate anion complexes. The exact nature of the fluoro-aluminate complexes is still a controversial issue, mainly because structural models can only be derived indirectly by a combination of modelling and different kinds of experimental information.

A number of fluoro-aluminate complexes have been suggested, as shown in Table I. The references represent the supposedly first time the species was mentioned in the literature. Besides $Na^+$, which is regarded as being the only cation, the "classic" structure model for the system $NaF$-$AlF_3$ involves only $F^-$ and two complex anions; these are $AlF_6^{3-}$ and $AlF_4^-$. $Al_2F_7^-$ was introduced to explain the existence of melts with $NaF$/$AlF_3$ ratios (r) smaller than one.

It is well known that because the current in the electrolyte is transported mainly by the $Na^+$ ion, the cathode reaction in aluminium cells involves diffusion of aluminium containing ions towards the cathode (surface of the aluminium), while sodium fluoride diffuses away from the cathode. Therefore, the electrolyte at the cathode contains less $AlF_3$ and higher concentrations of $NaF$ than the bulk of the electrolyte. This gives rise to the cathodic concentration overvoltage. The mass transfer conditions also influence the concentrations of dissolved metal at the cathode (sodium, Al-species with reduced valance), and thereby, the current efficiency. At present, it is not clear if the loss in current efficiency should be described as mass transport of dissolved metal, in particular Na [7] or as the result of electronic conductivity following the presence of dissolved Na [8].

Table I. Fluoro-aluminate complexes suggested in the literature.

| Ion | Author(s) | Year | Reference |
|---|---|---|---|
| $AlF_6^{3-}$ | Arndt and Kalass | 1924 | [1] |
| $AlF_4^-$ | Piontelli | 1940 | [2] |
| $AlF_5^{2-}$ | Grjotheim | 1956 | [3] |
| $Al_2F_9^{3-}$ | Brynestad et al. | 1959 | [4] |
| $Al_2F_{10}^{4-}$ | Brynestad et al. | 1959 | [4] |
| $Al_3F_{14}^{5-}$ | Cochrane | 1967 | [5] |
| $Al_2F_7^-$ | Dewing | 1972 | [6] |

It is the present author's opinion that it is probably not possible to fully understand the cathode process without considering the behaviour of the individual species or compounds constituting the electrolyte. The main aim of the present work was, therefore, to apply a structure model in combination with the Stefan-Maxwell equation for diffusion in a multi-component system to reveal the transport and concentration of individual species at the cathode. To the author's knowledge, the only serious attempt to carry out such a calculation was performed by Thonstad and Rolseth, who determined the concentrations of $Na^+$, $F^-$, $AlF_6^{3-}$, and $AlF_4^-$ at the cathode and in the bulk of the electrolyte [9].

## Choice of Structure Model. Activity Models

Six different structure models were discussed by Solheim and Sterten [10]. The models contained either four or five of the following compounds; $NaF$, $Na_3AlF_6$, $Na_2AlF_5$, $Na_4Al_2F_{10}$, $Na_3Al_5F_{14}$, $Na_2Al_2F_9$, $NaAlF_4$, and $NaAl_2F_7$. As explained below, the activities of these compounds were fitted in such a way that the mixture would become as close as possible to an ideal solution, defined by unit sum of activities in the entire composition range.

Solheim and Sterten's work was based on their empirical model concerning the formal activities of $NaF$ and $AlF_3$ in the system $NaF$-$AlF_3$ [11, 12]. These activity data were based on the Gibbs-Duhem equation and fitting of different types of experimental information (mainly heats of mixing, liquidus temperature, and vapour pressure), but no structure model was applied in the derivation.

In the previous work by Solheim and Sterten [10], it was shown that models composed of $NaF$, $Na_3AlF_6$, $NaAlF_4$, and $NaAl_2F_7$ and

one of the compounds $Na_2AlF_5$, $Na_4Al_2F_{10}$, $Na_5Al_3F_{14}$, or $Na_3Al_2F_9$ all formed near ideal solutions. Today, the model containing $Na_2AlF_5$ seems to be the least controversial throughout the aluminium community. Therefore, although this model was not the one that performed "best" or "most ideally" in the previous work, it was chosen as a basis for the present work. A closer description of the model is given in the following.

## Thermodynamic Activities

In deriving thermodynamic activity models, the $NaF-AlF_3$ melt is treated as a mixture of $NaF_{(l)}$ and compounds of the type $Na_aAl_bF_{a+3b}(l)$. The activity (a) of a Na-Al-F complex is related to the formal activities of $NaF(l)$ and $AlF_3(s)$ [10, 11] by

$$a\,NaF(l) + b\,AlF_3(s) = Na_aAl_bF_{(a+3b)}(l);$$
$$a_{Na_aAl_bF_{a+3b}} = C \cdot a_{NaF}^a \cdot a_{AlF_3}^b \qquad (1)$$

where C is the equilibrium constant. The standard state is the liquid compound $Na_aAl_bF_{(a+3b)}$. In the previous work [10], it was used as a criterion that at the melt composition corresponding to the stoichiometry of a compound (e.g., at 25 mol% $AlF_3$ for $Na_3AlF_6$), the sum of the numerical values of all the activities should be unity,

$$\sum_{i=1}^{m} a_i = 1 \qquad (2)$$

The chosen model contains five compounds (including NaF), and it was straightforward to adjust the individual equilibrium constants by numerical iteration so that Eq. (2) was satisfied at the five different compositions. The standard state activities are temperature functions, except for pure molten NaF, where both the activity and the equilibrium constant are unity by definition (see Eq. (1)). By performing the calculation at different temperatures, the equilibrium constants could be described as temperature functions. Provided that the criterion in Eq. (2) is met at every melt composition in a certain temperature range, the liquid solution may be termed "ideal" or "perfect".

## Ideal Temkin Activities

The classical ionic structure model for $NaF-AlF_3$ melts

$$AlF_6^{3-} = AlF_4^- + 2F^- \qquad (3)$$

may be used to illustrate the main feature of an ideal Temkin model [13]. The Temkin model is based on the comprehension that the melt consists of an anion lattice and a cation lattice, where the concentration measure is the individual ion fractions $(N)$, e.g.,

$$N_{Na^+} = \frac{n_{Na^+}}{\sum n_+} \quad \text{and} \quad N_{AlF_6^{3-}} = \frac{n_{AlF_6^{3-}}}{\sum n_-} \qquad (4)$$

where $n$ is the number of ions and the subscripts "+" and "-" represent cations and anions, respectively. The activity of $Na_3AlF_6$ is then calculated by

$$a_{Na_3AlF_6} = N_{Na^+}^3 \cdot N_{AlF_6^{3-}} \qquad (5)$$

It follows from Eq. (4) that the $Na^+$ ion fraction is unity at every composition, since $Na^+$ is supposed to be the only cation present. The anion fractions can be accurately computed from anticipated

equilibrium constants for Eqs. (3) and (4), combined with the obvious criterion that the sum of anion fractions is unity at all compositions.

If a real melt system containing a single cation is well described by an ideal Temkin model, it will also be well described by a thermodynamic model including neutral compounds as described above. Vice versa, a Temkin model can be derived using the results from the thermodynamic model. The formal activities of NaF and $AlF_3$ are easily computed from equations like

$$a_{NaF} = N_{F^-} \quad \text{and} \quad a_{AlF_3} = \frac{N_{AlF_4^-}}{N_F^-} = \frac{N_{AlF_6^{3-}}}{N_{F^-}^3} \qquad (6)$$

The cathodic concentration overvoltage (which is formally negative) is given by

$$\eta_c = \frac{RT}{3F} \cdot \ln\left(\frac{a_{AlF_3}^*}{(a_{NaF}^*)^3} \cdot \frac{(a_{NaF}^\infty)^3}{a_{AlF_3}^\infty}\right) \qquad (7)$$

where R is the universal gas constant [8.3143 $Jmol^{-1}$] and the superscripts "*" and "∞" represent the cathode and the bulk of the electrolyte, respectively. Using the ideal Temkin activity model the activities of $AlF_3$ and NaF can be represented by the assumed ionic species (see Eq. (6)), which gives

$$\eta_c = \frac{RT}{3F} \cdot \ln\left(\frac{N_{AlF_6^{3-}}^*}{(N_{F^-}^*)^6} \cdot \frac{(N_{F^-}^\infty)^6}{N_{AlF_6^{3-}}^\infty}\right) \qquad (8)$$

## Characterisation of the Chosen Model

In the previous work [7] the equilibrium constants C in Eq. (1) were fitted in the temperature range 900-1100 °C,

$$\ln C = A + B \cdot \frac{10^3}{T} \qquad (9)$$

where T is the temperature [K]. The parameters A and B as well as the equilibrium constants at 960 °C are given in Table II.

Table II. Equilibrium constants derived for the chosen model (see text).

|  | $Na_3AlF_6$ | $Na_2AlF_5$ | $NaAlF_4$ | $NaAl_2F_7$ |
|---|---|---|---|---|
| A | 3.136 | 3.516 | 8.781 | 15.007 |
| B | 7.718 | 5.526 | -3.433 | -13.722 |
| C (960 °C) | $1.203 \cdot 10^4$ | $2.974 \cdot 10^3$ | $4.021 \cdot 10^2$ | $4.833 \cdot 10^1$ |

In the Temkin model, there will be three equilibrium constants (K) between the four anion complexes. Those can be calculated from the formal activities of NaF and $AlF_3$ [11, 12] and the data in Table II, remembering that $Na^+$ is the only cation. At 960 °C,

$$AlF_6^{3-} = AlF_5^{2-} + F^-; \qquad K_1 = 0.2630 \qquad (10a)$$

$$AlF_5^{2-} = AlF_4^- + F^-; \qquad K_2 = 0.1675 \qquad (10b)$$

$$2\,AlF_4^- = Al_2F_7^- + F^-; \qquad K_3 = 0.0003561 \qquad (10c)$$

The structure model for the melt is illustrated in Figure 1. As can be observed, the thermodynamic model shows only minor deviations from the "unit sum of activities" criterion. In the corresponding Temkin model, the sum of activities is unity by definition. The following treatment was based on the Temkin model.
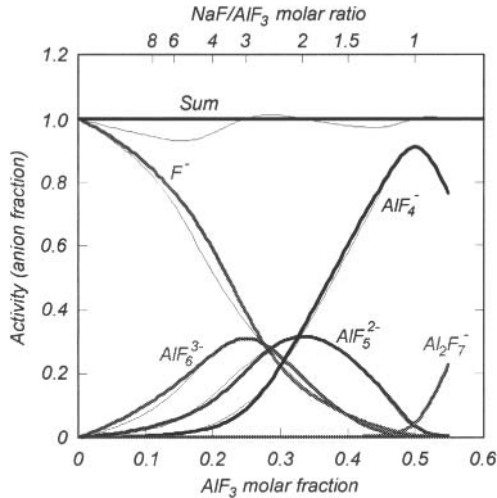


Figure 1. Activities of the different compounds assumed in the system NaF-AlF₃. Thin lines – thermodynamic model derived by Solheim and Sterten [10], thick lines – Temkin model with equilibrium constants derived from the thermodynamic model (see text).

**Theory of Diffusion in a Multi-Component System**

Diffusion in a multi-component system can only be accurately described using the Stefan-Maxwell equations [14]

$$\nabla x_i = \sum_{j=1}^{n} \frac{1}{c_{tot} D_{ij}} \cdot \left( x_i J_j - x_j J_i \right) \tag{11}$$

where $x_i$ is the molar fraction of component $i$, $c_{tot}$ is the total molar concentration [mol m$^{-3}$], $D_{ij}$ ($= D_{ji}$) is the binary diffusion coefficient for the system i-j [m$^2$s$^{-1}$], and J is the molar flux [mol m$^{-2}$s$^{-1}$].

In the bulk of the electrolyte, mass transport depends exclusively on convection. Within the boundary layer at the cathode, the convection decreases gradually and finally becomes zero at the cathode, at which point the transport depends only on chemical diffusion. Following the treatment in previous papers [14, 15], this can be described by using turbulent diffusion coefficients,

$$D_{ij(tot)} = D_{ij} + D_t \tag{12}$$

where $D_{ij(tot)}$ is the total diffusion coefficient for the binary pair i-j, $D_{ij}$ is the chemical diffusion coefficient, and $D_t$ is the turbulent diffusion coefficient. The turbulent diffusion coefficient is zero at the cathode and increases with increasing distance from the cathode (y). Close to the surface, it can be shown from boundary layer theory that

$$D_t = \alpha \cdot y^3 \tag{13}$$

where $\alpha$ is a constant depending only on the degree of convection (i.e, a function of the Reynolds number).

For numerical solution in a system with five components, Eq. (11) turns into five equations on the form

$$\Delta x_1 = \frac{\Delta y}{c_{tot}} \cdot \left( \frac{\overline{x_1} J_2 - \overline{x_2} J_1}{D_{12} + \overline{D_t}} + \frac{\overline{x_1} J_3 - \overline{x_3} J_1}{D_{13} + \overline{D_t}} + \frac{\overline{x_1} J_4 - \overline{x_4} J_1}{D_{14} + \overline{D_t}} + \frac{\overline{x_1} J_5 - \overline{x_5} J_1}{D_{15} + \overline{D_t}} \right) \tag{14}$$

where "$\Delta$" represents the difference between neighbouring elements and overlining represents the average of neighbouring elements. The terms within the parentheses in the five equations cancel, which means that the sum of changes in molar fractions becomes zero. With given molar fluxes and diffusion coefficients, the numerical solution involves using "old" molar fractions to calculate "new" molar fractions by Eq. (14), and the latter are again used as "old" molar fractions in a new iteration. The computation converges after only about five iterations.

**Solution of Transport in the Cathode Boundary Layer**

Criteria to be Fulfilled

There are three criteria that must be fulfilled in the cathode boundary layer. Those are,

• Electroneutrality

• Correct fluxes

• Ionic fractions at equilibrium according to Eqs. (10a-10c)

Electroneutrality. The anions can be described as "floating islands in an ocean of cations" (Na$^+$). The electroneutrality criterion will always be fulfilled when diffusion is regarded as motion of neutral substances (e.g., Na₂AlF₅ and NaF instead of AlF₅$^{2-}$ and F$^-$).

Fluxes. The only element that passes through the boundary layer at the cathode is aluminium; using the cathode surface as reference, the fluxes of all other elements are zero. At 100 percent current efficiency the flux of Al becomes

$$J_{Al} = -\frac{i}{3F} \quad [\text{mol m}^{-2}\text{s}^{-1}] \tag{15}$$

where i is the current density [Am$^{-2}$], F is Faraday's constant [96485 Asmol$^{-1}$], and the positive direction is defined as away from the cathode.

The transport number for Na$^+$ in cryolite is about 0.99, but it is lower in acidic melts [16]. Still, in the present work, it was assumed that the entire electric current in the electrolyte is transported by migration of the Na$^+$ ion,

$$J_{Mig(Na)} = -\frac{i}{F} = 3 J_{Al} \tag{16}$$

For the sake of simplicity we use the following notation in the following,

1 = NaF; 2 = Na₃AlF₆; 3 = Na₂AlF₅; 4 = NaAlF₄; 5 = Na₂AlF₇

The fluxes are related by the element balances,

$$J_{Al} = J_2 + J_3 + J_4 + 2J_5 \tag{17}$$

$$J_F = J_1 + 6J_2 + 5J_3 + 4J_4 + 7J_5 = 0 \tag{18}$$

$$J_{Na} = J_1 + 3J_2 + 2J_3 + J_4 + J_5 + 3J_{Al} = 0 \tag{19}$$

The diffusion fluxes of NaF and $Na_3AlF_6$ can then be expressed by $J_{Al}$, $J_3$, $J_4$, and $J_5$,

$$J_1 = -6J_{Al} + J_3 + 2J_4 + 5J_5 \tag{20}$$

$$J_2 = J_{Al} - J_3 - J_4 - 2J_5 \tag{21}$$

Equilibria. Not only diffusion and migration are taking place within the cathode boundary layer; there will also be transformations between the different complexes according to Eqs. (10a-10c). It was assumed that the reactions are very rapid, resulting in equilibrium between the species at any location within the boundary layer. Reactions between the species give fluxes that vary with the distance from the cathode.

Input Data and Method of Solution

The total concentration (Eq. (12)) was calculated as the sum of the concentrations of the five neutral substances, taking into consideration the variable density within the boundary layer [17].

The current density was assumed to be 8000 $Am^{-2}$, corresponding to $J_{Al} = -0.02764$ $molm^{-2}s^{-1}$ at 100 percent current efficiency.

It is known that small and light compounds have higher diffusion coefficients than more bulky substances, but measurements are scarce in the present system. It was assumed that the binary diffusion coefficients for the four sub-systems containing NaF was $2 \cdot 10^{-9}$ $m^2s^{-1}$, while the six binary sub-systems without NaF had a diffusion coefficient of $1 \cdot 10^{-9}$ $m^2s^{-1}$.

The turbulent diffusivity was calculated from Eq. (11) using $\alpha = 12000$ $m^{-1}s^{-1}$; it can be shown that this gives a mass transfer coefficient of $3.01 \cdot 10^{-5}$ $ms^{-1}$ for a species with $D = 2 \cdot 10^{-9}$ $m^2s^{-1}$.

The calculation domain, which ranged from the cathode and up to 10 mm away from the cathode, was subdivided into 0.015 mm elements. The element at y = 10 mm was assumed to have bulk properties. In the numerical treatment, the fluxes $J_3$, $J_4$, and $J_5$ in Eqs. (18) and (19) were varied systematically until the equilibria between the complex ions described in Eq. (9a-c) were fulfilled in the entire domain. The numerical procedure applied converged very slowly, mainly because there is a very weak dependency between ionic concentrations and fluxes at large y, where convection dominates. The calculation was regarded as finished when the maximum deviation between the calculated equilibrium constants and the predetermined equilibrium constants were less than 0.001 percent.

Four calculations were performed, using $NaF/AlF_3$ molar ratios of 3.0, 2.5, 2.0, and 1.5.

**Results and Discussion**

The computed concentration gradients and fluxes are shown in Figs. 2-5 in the following, while Figure 6 sums up the concentration differences between the bulk and the cathode.

Generally, the cathode reaction leads to a less acid bath close to the cathode; i.e., smaller amounts of excess $AlF_3$. The $NaF/AlF_3$

ratios at the cathode and in the bulk of the bath, as well as the concentration overvoltages calculated from Eq. (8), are shown in Table II. As can be observed, the difference in the molar ratio between the bulk and the cathode increases with increasing molar ratio in the bulk. Still, the overvoltage decreases with increasing molar ratio. This is related to the fact that a given difference in molar ratio brings about larger activity changes in acid baths.

Table II. Calculated cathodic concentration overvoltages and $NaF/AlF_3$ molar ratios in the bulk and at the cathode.

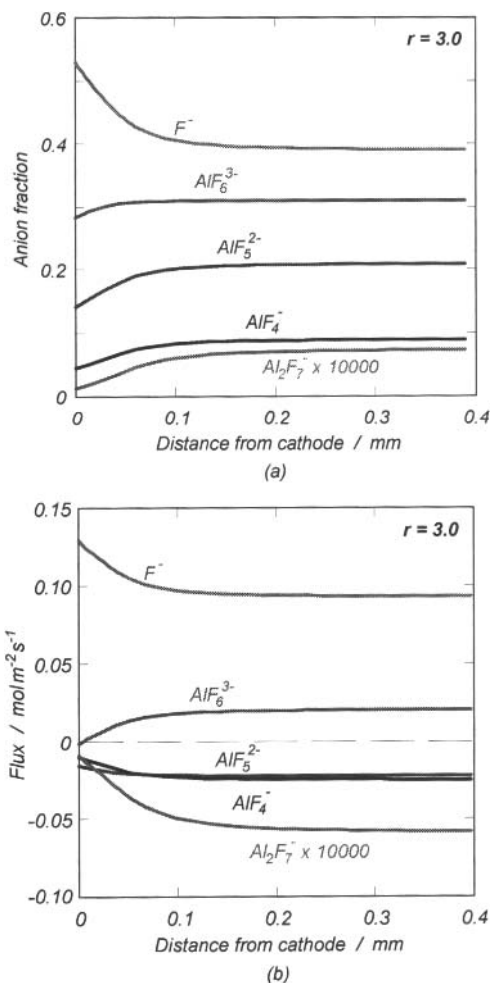| NaF/AlF$_3$ molar ratio | | | Overvoltage |
|---|---|---|---|
| Bulk | Cathode | Difference | mV |
| 3.000 | 3.637 | 0.637 | 68.4 |
| 2.500 | 3.063 | 0.563 | 87.1 |
| 2.000 | 2.515 | 0.515 | 101.4 |
| 1.500 | 1.972 | 0.472 | 123.8 |



Figure 2. a) – Calculated concentration gradients and b) – calculated fluxes as a function of the distance from the cathode at a $NaF/AlF_3$ molar ratio (r) of 3.0.

In Figure 2a, one observes that the concentrations of all other species than $F^-$ decrease when approaching the cathode. This is in accordance with what one would expect from the data in Figure 1, which shows that all concentrations other than $F^-$ decrease when starting at the cryolite composition and moving towards NaF. From Figure 2 b it can be observed that $F^-$ and $AlF_6^{3-}$ move away from the cathode, while the other species move towards it. Apparently, the cathode can be regarded as a site for conversion of acid compounds ($Na_2AlF_5$, $NaAlF_4$, $NaAl_2F_7$) into basic or less acid compounds ($NaF$, $Na_3AlF_6$). The fluxes shown in Figure 2 b are constant throughout the bulk of the bath, and there will be a corresponding consumption of basic compounds and production of acid compounds at the anode, so the bath composition will not change with time.

Although the results for the different $NaF/AlF_3$ molar ratios look very different at first glance, the patterns are, in fact, very similar. As a rule of thumb, compounds that are more acid than the bulk

composition move towards the cathode, while compounds less acid than the bulk composition diffuse away from the cathode. As an example, $AlF_5^{2-}$, which has a maximum concentration at $r = 2$, moves towards the cathode at electrolyte compositions corresponding to $r = 3$ and $r = 2.5$, it moves very slowly at $r = 2$, while it moves away from the cathode at $r = 1.5$.

A normal Hall-Héroult bath often has a $NaF/AlF_3$ molar ratio close to 2.3. At this composition (see Figures 3 and 4), it appears that the transport of aluminium towards the cathode mainly takes place by the $AlF_4^-$ ion. This does not necessarily imply that this ion is the primarily reactant in the cathode reaction.

**Concluding Remarks**

As mentioned earlier, there are several other structure models that can not be ruled out. Although it would be interesting to carry out similar calculations involving other structure models, it may be
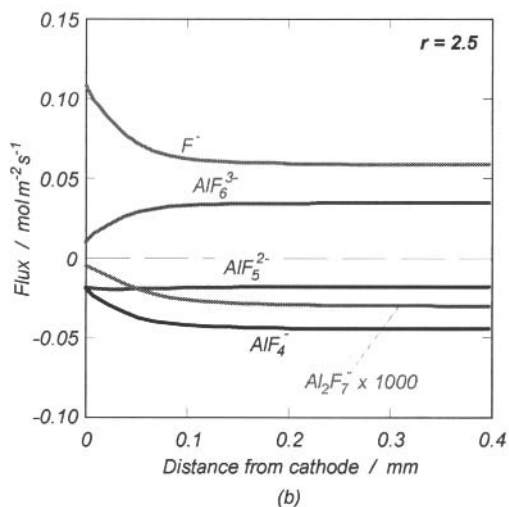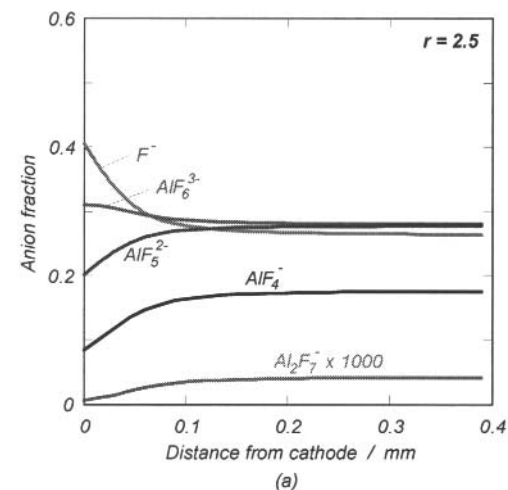
Figure 3. a) – Calculated concentration gradients and b) – calculated fluxes as a function of the distance from the cathode at a $NaF/AlF_3$ molar ratio (r) of 2.5.
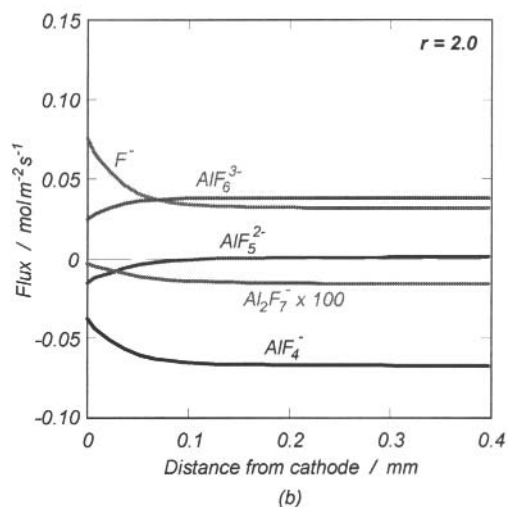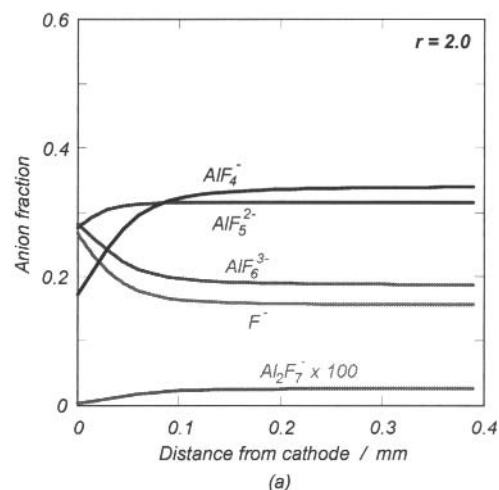
Figure 4. a) – Calculated concentration gradients and b) – calculated fluxes as a function of the distance from the cathode at a $NaF/AlF_3$ molar ratio (r) of 2.0.
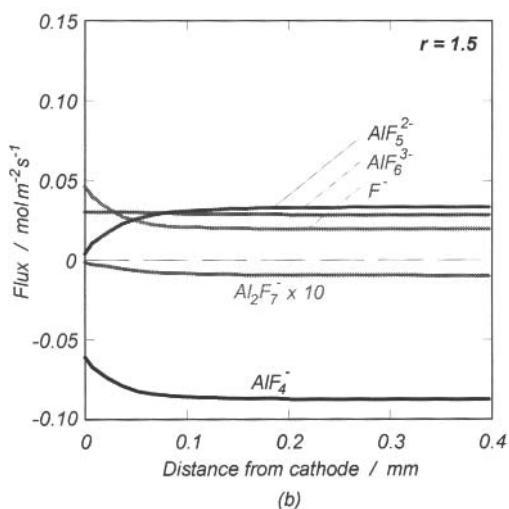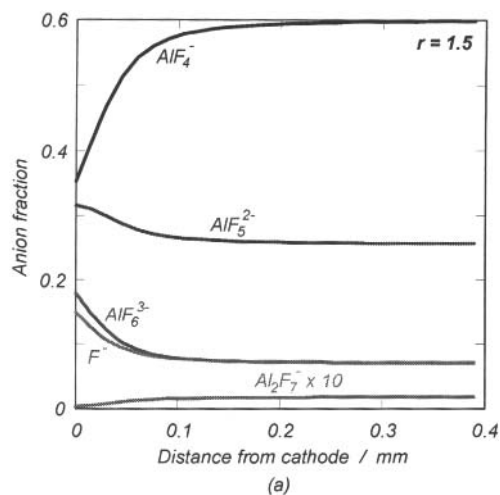
Figure 5. a) – Calculated concentration gradients and b) – calculated fluxes as a function of the distance from the cathode at a NaF/AlF$_3$ molar ratio (r) of 1.5.
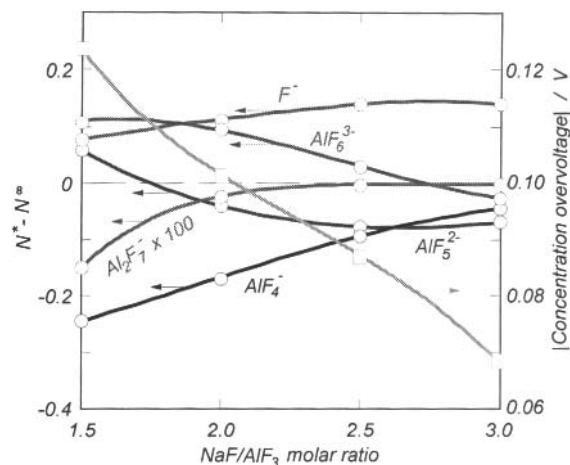


Figure 6. Difference in ionic fraction between the cathode and the bulk of the electrolyte (left hand scale) and cathodic overvoltage (right hand scale) as a function of the NaF/AlF$_3$ molar ratio.

more useful to investigate the effect of variable transport numbers. The present model could, eventually, be used as one of the tools necessary to develop a better current efficiency model.

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