

The Cathode Process and the Back Reaction in Aluminium Reduction Cells

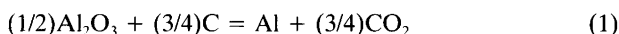
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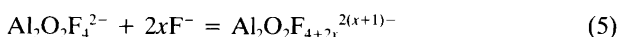
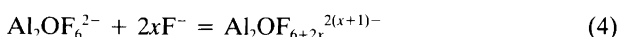
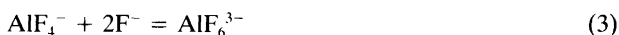
The cathode process for the manufacture of aluminium in industrial cells is discussed with reference to the nature of the dissolved metal in the system NaF–AlF₃–Al₂O₃–CaF₂–Al. A new mechanism for the so-called back reaction is outlined, mainly based on a literature review and some other relevant data. The rate-limiting step for the back reaction in commercial cells is normally mass-transfer controlled and located within the cathode electrolyte boundary layer, where the dissolved metal is being oxidized by polyvalent impurities entering the boundary layer from the bulk phase of the electrolyte. This means that the concentration of dissolved metal species during normal operation of commercial cells decreases from equilibrium values at the aluminium surface to a value equal to zero within the cathode electrolyte boundary layer, while polyvalent impurities will be involved in cyclic redox reactions in the cathode and the anode/gas electrolyte boundary layers. The rate of the back reaction must be expected to be influenced by the impurity level of reducible polyvalent impurities in the electrolyte.

In the Hall–Heroult process, liquid aluminium is deposited on the aluminium cathode with a current efficiency in the range 85 to 95 %. The main overall reaction may be written as reaction (1).



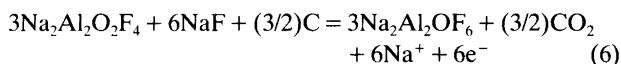
A consumable carbon anode liberates CO₂ with a current efficiency close to 100 %.¹ The electrolyte in industrial cells can be considered to be constituted of the components NaF, AlF₃, Al₂O₃ and CaF₂, besides a number of impurities.

An ionic structure model of NaF–AlF₃ melts containing alumina was derived in a previous work,² and can be described by equilibria (2)–(5).

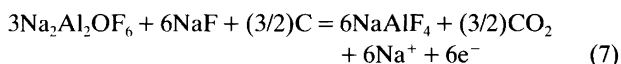


The only cation of importance was proposed to be Na⁺. The predominant ions in the region of industrial importance containing oxygen were found to be Al₂OF₆²⁻ and Al₂O₂F₄²⁻, with an increasing importance for Al₂OF₆²⁻ as the alumina concentration decreases.

At high alumina concentrations it is reasonable to propose the overall anode reaction given by reaction (6),



which with decreasing oxide concentrations will be followed by reaction (7). The relative importance of eqn. (7)



compared to eqn. (6) will also increase with increasing AlF₃ content of the melt.²

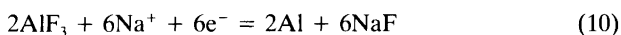
On a component basis these equations reduce to reaction (8).



The overall cathode reaction may be formulated as reaction (9), which will be followed by a corresponding



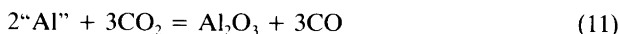
displacement of reaction (3). On a component basis the reaction may alternatively be written as reaction (10).



All electrode reactions, eqns. (6)–(10), are balanced by 6F (or 6e⁻, passing through the outer circuit) and 6Na⁺. The latter quantity corresponds roughly to the migration flux, since it is well established that the Na⁺ ions carry more than 95 % of the current in melts ordinarily used in com-

mercial cells.³⁻⁵ Writing the overall electrode reactions in this manner, it is possible to show directly which types of concentration gradients are set up in the diffusion layers at the interfaces of the electrodes.

It is commonly accepted⁶⁻⁹ that the lowering of the cathodic current efficiency below 100 % is mainly caused by the so-called back reaction between CO₂ and dissolved metal ("Al") according to reaction (11). The amount of CO



formed corresponds roughly to the loss in the cathodic current efficiency.¹⁰

The present paper discusses various aspects concerning the cathode process in industrial cells and the corresponding back reaction (11), mainly in view of literature data. The nature of the dissolved metal, which may be a key to an improved understanding of the cathode process, is briefly discussed. A process analysis to be carried out shows that certain impurities in the electrolyte will be involved in redox reactions and that they will greatly enhance the rate of the reoxidation reaction.

Nature of the dissolved metal

Aluminium reacts to a certain degree with cryolitic melts. The equilibrium solubility of aluminium, or more precisely of each reduced species formed, is an important property of the melt. Some careful studies in this field are described in recent publications of Ødegård *et al.*^{11,12} Quenched samples from NaF–AlF₃–Al₂O₃ melts equilibrated with aluminium were treated with HCl, and the amounts of H₂ evolved were determined in order to evaluate the equilibrium content of "metal" in each sample. With the use of literature data for the activities of NaF and AlF₃ in cryolitic melts,^{5,13} three structure models were found to give a good fit to the experimental solubility data. The model calculations showed definitely that ionic species like Al⁺ and Na₂⁺ can be ruled out as important reduced entities in the system. The calculations showed clearly that in NaF-rich melts, aluminium will dominantly dissolve as sodium, while in melts used in aluminium electro-winning AlF₂⁻ is most probably the predominant dissolved metal species, although a minor contribution of the dimer Al₂F₄²⁻ cannot completely be ruled out. Calculated equilibrium concentrations of the major species Na and NaAlF₂ at unit activity of aluminium in the NaF–AlF₃–Al system at 1273 K are given in Fig. 1. Some of the basic equilibria in this system are discussed below. The exact nature of dissolved sodium in cryolitic melts has so far not been completely clarified.^{9,11,12}

It is also well established that the electrolyte in industrial cells sometimes contains minor amounts of dispersed aluminium particles, probably formed under extreme convective mass-transfer conditions. Such conditions give rise to a reduced current efficiency, although the droplets themselves may play a minor role in this connection.

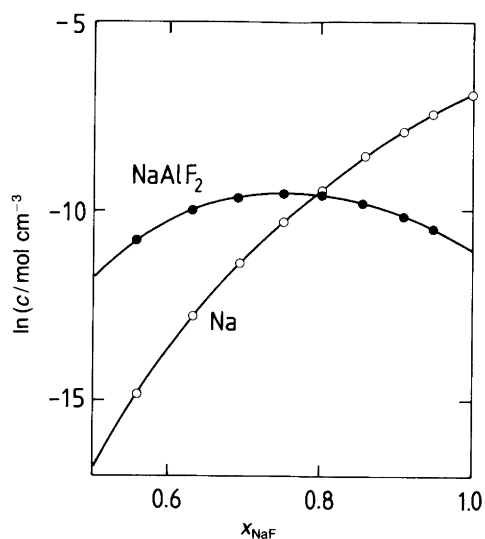


Fig. 1. The natural logarithm of the concentrations of Na and NaAlF₂ in the closed system NaF–AlF₃–Al as a function of the molar fraction x_{NaF} at 1273 K.

The cathode process

The formalistic view that reaction (9) or (10) proceeds with a current efficiency of 100 %, and that reaction (11) is responsible for the major reduction in the current efficiency, is somewhat confusing and is not a good starting point for a detailed discussion of the process. The model eqn. (11) predicts that the lower limit for the current efficiency should be 50 %, corresponding to a complete consumption of all CO₂ formed by reaction (6) or (7). In laboratory cells it is found that the current efficiency drops to values below 50 % and even below zero with diminishing cathodic current densities.^{9,14} This means that a critical cathodic current density exists at which the rate of aluminium production is exactly balanced by the rate loss of reduced species diffusing away from the aluminium surface. For current densities below the critical one the net production of aluminium will be negative, with a corresponding negative current efficiency. The back reaction for current efficiencies below 50 % has so far not been thoroughly investigated, and there is a certain lack of understanding of the process.

The main cathode reaction in a pure NaF melt will be reaction (12).



The sodium metal formed will continuously dissolve in the electrolyte when the electrolysis is carried out at a current density that is not too high, and if there is a rapid convective mass flow in the bulk phase of the electrolyte. On adding small amounts of AlF₃ (or Al₂O₃) to the NaF melt, the main electrode reaction on an inert cathode will still be the same. On adding more AlF₃ to the melt, the cathodic formation of aluminium as a separate phase will take place

as a competing reaction at a NaF/AlF₃ molar ratio of about 10 at 1273 K.⁵ Adding even more AlF₃ to the electrolyte gradually increases the relative amount of aluminium formed, compared to that of sodium, finally reaching the conditions in industrial cells. As discussed below, the cathode process proceeds with only a negligible reaction resistance during normal operations of industrial cells. This means that the formation of sodium on the aluminium cathode should preferably be written as a direct formation reaction according to eqn. (12). Even if the cell current is shut down the formation of sodium will continue as an electrochemical corrosion reaction according to eqn. (12) together with a corresponding anodic dissolution reaction of aluminium, so that reaction (9) or (10) will proceed to the left.

Experimental data from Piontelli and co-workers,¹⁵⁻¹⁷ Thonstad and Rolseth¹⁸ and Sum and Skyllas-Kazacos¹⁹ indicate clearly that the cathode process, including the back reactions discussed below, proceeds without any charge transfer or reaction overvoltage for current densities at least below about 10 A cm⁻². There is thus *no need* for splitting up reaction (9) or (10) into a chemical reaction following or preceding the electron transfer reactions. The results show clearly that the kinetics of the aluminium deposition reaction proceeds so fast that it safely can be considered as a three-electron transfer reaction without any reaction resistance.

The simultaneous net production of reduced species (Na, NaAlF₂, etc.) at the cathode surface corresponds exactly to the net fluxes of the reduced species diffusing into the cathode electrolyte boundary layers. The formation reaction of NaAlF₂ may be written as reaction (13), or alternatively as reaction (14).

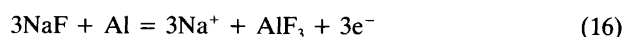


Since there is no measurable activation overvoltage related to the processes going on at the aluminium surface, it means that the overall side reactions (12)–(14) also proceed without any reaction resistance. Reaction (13) or (14) can of course be considered as an intermediate step in the overall deposition reaction of aluminium, reaction (9) or (10).⁹ This follows from the fact that the charge number of aluminium in the NaAlF₂ compound is +1. Since reaction (13) or (14) proceeds with only a minor reaction resistance, it may be extremely difficult to detect NaAlF₂ by standard electrochemical measuring techniques. The rate of formation of NaAlF₂ will have its maximum value when the melt composition at the aluminium surface corresponds to a NaF/AlF₃ molar ratio of 3.⁹

In the literature it is often proposed that the aluminium cathode during electrolysis reacts with the melt, producing the reduced species present in the melt, e.g. reaction (15).



However, this is a redox reaction which may be separated into reactions (16) and (17), where reaction (17) is



equivalent to eqn. (12) and reaction (16) is equivalent to the main cathode reaction proceeding to the left during the operation of commercial cells. The reaction scheme (15)–(17) is formally correct. However, this way of writing the back reaction may create confusion and should probably be avoided, since it is self-evident that reaction (16) is not a necessary preceding reaction for the formation of sodium, reaction (17). The simplest way of describing the formation of dissolved metal or reduced species in cryolitic melts is by the electrode reactions, eqns. (12)–(14). One important conclusion to be drawn from literature data is that both chemical and electrochemical equilibria are established between the cathode metal and the melt adjacent to its surface in all types of cells with current densities in the range 0–10 A cm⁻², which means that eqn. (15) adequately describes the equilibrium concentration/activities even on the aluminium cathode surface.

The cathode boundary layer

Interface concentrations and overvoltage. The equilibrium concentrations of dissolved metal species on the Al cathode surface in NaF–AlF₃–Al₂O₃ melts depend on several factors. Since Na⁺ is the current carrier in the electrolyte it means that the concentration of NaF increases and the concentration of AlF₃ decreases at the cathode surface with increasing current densities. Some concentration gradients are illustrated in Fig. 2. The convective mass transfer in the

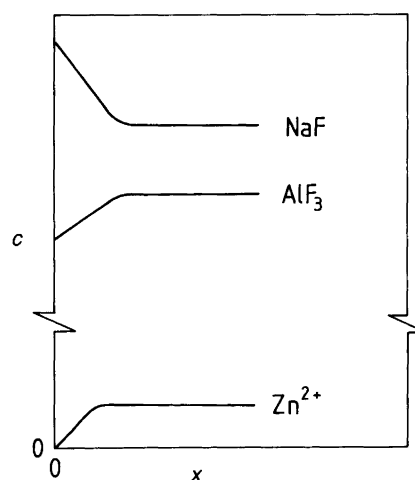


Fig. 2. Some schematic concentration gradients of NaF, AlF₃ and Zn²⁺ in the diffusion layer on the electrolyte side of the aluminium cathode surface. *x* is the distance from the metal surface.

bulk of the electrolyte in industrial cells is obviously very rapid and will be ignored as a rate-limiting factor in the present context. This means that all the gradients in the cathode diffusion layers depend not only on the electrolyte bulk phase composition, but to a strong degree on the cathodic current density and to factors determining the thickness of the cathode diffusion layers. The NaF/AlF₃ gradients determine the aluminium production, while the gradients set up by the dissolved metal species determine the loss in current efficiency.^{9,20} The gradients determining aluminium production and the loss are intimately inter-linked, although a forced convective change in the hydrodynamics of the system will effect all the gradients in a way that is not easily predicted. This means also that a current efficiency model should not only be based on the rate of the loss reactions, but also on the rate of the metal production.⁹

The concentrations describing the NaF and AlF₃ gradients are interlinked to the concentration overvoltage, η , for reaction (10), referred to an Al electrode with unit activity as in eqn. (18), where * refers to activities/concen-

$$\eta = \frac{RT}{F} \ln \frac{a_{\text{NaF}}}{a_{\text{NaF}}^*} + \frac{RT}{3F} \ln \frac{a_{\text{AlF}_3}}{a_{\text{AlF}_3}^*} \quad (18)$$

trations at the Al electrode surface. These concentrations can be estimated from measured overvoltage data and the bulk phase composition of the electrolyte.^{5,13} This means that the overvoltage is a key parameter in describing the electrochemistry in the cathode boundary layers.

The concentrations of reduced entities at the cathode surface can be deduced from equilibria such as eqns. (19) and (20).



The reduced entity having the highest saturation concentration in melts commonly used in industrial cells is NaAlF₂. However, Na may even be more important than NaAlF₂ in the mass transfer of reduced species through the diffusion layers because of its electronic nature. It is well established that dissolved Na in molten salts gives rise to a certain electronic contribution to the total conductivity.^{21,22} Since Na (or its electron) diffuses much faster than the other ionic entities there will be a continuous homogeneous transformation of reduced species to Na throughout the cathode boundary layer, e.g. eqn. (21). This means that



the rate of diffusion of reduced species will be enhanced by reactions of this type.

Reduced species and impurities: current efficiency. As pointed out above, it has been commonly accepted that

Table 1. Typical concentrations in wt % of some trace elements in the electrolyte of industrial aluminium reduction cells.

Atom	Concentration
Zn	0.006
Ni	0.008
Fe	0.030
Si	0.002
Cr	0.006
B	0.070
P	0.015

dissolved metal ("Al") is transported through the electrolyte of industrial aluminium cells reacting with CO₂ in the boundary layer at the electrolyte/gas interface in accordance with reaction (11). This explanation will be rejected in the following discussion.

The concentration of reduced entities at the aluminium surface depends on the concentration overvoltage and not upon the impurity level in the electrolyte of industrial cells. However, the rate of transport of reduced species through the cathode boundary layer is greatly influenced by the impurity level, as discussed below. Since the ionic structures of impurities dissolved in cryolitic melts are largely unknown, we will simply describe them as simple uncomplexed ions.

Table 1 shows some typical data for the concentration of some trace elements in the electrolyte of industrial aluminium reduction cells. The impurities in such cells may be divided into several groups. The main group of interest is the one which can be reduced at the cathode surface. All the elements in Table 1 belong to this group, which should be further split into subgroups. The first subgroup can be exemplified by the reduction reaction (22), characterized



by an impurity with a single oxidation state and which in the reduced state is insoluble in the electrolyte, but soluble in the cathode metal. The reaction is heterogeneous and may not take place in the homogeneous electrolyte phase. It is believed that the reaction is mainly localized at the aluminium cathode surface. If so, there will be an impurity gradient as schematically illustrated in Fig. 2. The net result will be that impurities of this kind partly enter the cathode metal, with only a corresponding minor decrease in the current efficiency with respect to aluminium.

As an example of the next subgroup reactions (23) and (24)



can be chosen. The characteristic features of this group are that the impurities have at least two stable oxidation states in the melt and that the final product is soluble in

the aluminium phase, but insoluble in the electrolyte. Several impurities belong to this group, e.g. $\text{Cr}^{6+}/\text{Cr}^{3+}/\text{Cr}$, $\text{V}^{5+}/\text{V}^{4+}/\text{V}^{3+}/\text{V}$, $\text{Ti}^{4+}/\text{Ti}^{3+}/\text{Ti}^{2+}/\text{Ti}$ and $\text{Si}^{4+}/\text{Si}^{2+}/\text{Si}$.

The next subgroup can be illustrated by the reaction sequence (25) and (26) characterized by a cathode product



with a very low solubility in aluminium, but dissolving in the electrolyte. Phosphorus may be dissolved either directly or it may be released in the gaseous state. In either case it must be expected that phosphorus will be reoxidized by impurities in the cathode diffusion layer. Such a redox cycle within the diffusion layer may greatly enhance the rate of the back reaction and reduce the current efficiency with respect to aluminium.

The magnitude of the total concentrations of impurities with more than one oxidation state, as indicated in Table 1, is in the same order as the equilibrium concentration of reduced aluminium species (Na and AlF_2^-) on the cathode surface. This means that in industrial cells the convective flux density of polyvalent impurities from the bulk phase towards the cathode boundary layer is usually high enough to oxidize all the reduced aluminium species diffusing from the metal surface into the boundary layer. The net result will be a series of redox reactions within the cathode boundary layer. A reaction scheme for iron impurities with concentration gradients is illustrated in Fig. 3. At point B reactions like reaction (27) will take place. Such



homogeneous reactions at temperatures around 1000°C are expected to proceed extremely rapidly, which means that

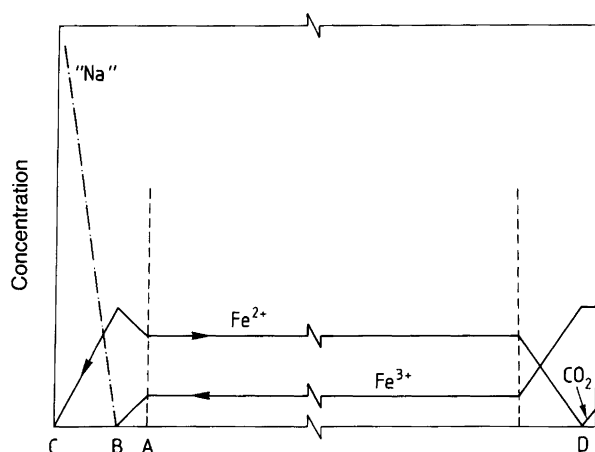
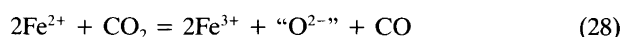


Fig. 3. Schematic concentration profiles of iron ions in the diffusion layer at the cathode surface (C-A) and at the melt/ CO_2 interface. The CO_2 concentration profile at the melt/ CO_2 interface is also indicated (D), while the concentration gradient of reduced aluminium species is denoted "Na".

the rate of the reaction does not limit the rate of the process. At the cathode surface, point C in Fig. 3, a normal cathode reaction, eqn. (24), is expected to take place. It should be noted that there are both an inward and an outward diffusion flux of Fe^{2+} in the diffusion layer, as illustrated in Fig. 3. The concentration profiles in the outer diffusion layer at the melt/gas interface are also included in Fig. 3, where at point D an oxidation of iron ions take place according to reaction (28). " O^{2-} " reacts further to



one or the other of the complexes indicated in eqns. (4) and (5). A direct oxidation reaction like reaction (29) must



also be expected to take place on the anode carbon surface. In commercial cells it must be expected that reactions of this type will be the dominating ones at anode current densities below about 0.05 A cm^{-2} , which means that there is only a very limited evolution of CO_2 or CO at the anode surface. The relative importance of reaction (28) compared to reaction (29) will increase with increasing anodic current densities. If there is a gradual reduction in the cathodic current density then the current yield of aluminium will drop below 50% and finally towards zero and negative values.

Other impurities with two or more oxidation states will have similar or even more complicated concentration profiles in the electrolyte boundary layers than shown in Fig. 3. This means that the so-called back reaction in aluminium reduction cells is rather complicated. However, the net effect of the impurities participating in the back reaction will clearly be an increased rate of that reaction, with a corresponding decrease in the current efficiency with respect to aluminium.

During normal operation of industrial cells the fluid velocities in the interelectrode gap are typically in the range $2\text{--}20 \text{ cm s}^{-1}$.²³ Then it must be expected that the total diffusion flux of reduced aluminium species in the cathode boundary layer is considerably smaller than the convective fluxes of impurities towards the cathode boundary layer. This means that the convective bulk phase of the electrolyte will not contain any reduced aluminium species during normal cell operations.

Careful analysis of electrolyte samples from industrial cells²⁴ showed that the iron content was composed of about 70% divalent and about 30% trivalent iron ions. This result clearly supports the idea that there is no dissolved metal present in the bulk electrolyte of industrial cells, since it must be expected that dissolved metal and trivalent iron ions cannot coexist in the same liquid phase. The results also support the idea that there is no CO_2 dissolved in the molten salt mixture, since it may be expected that CO_2 and divalent iron ions cannot coexist in the mixture. The valence distribution of impurities in the electrolyte of

industrial cells should be further investigated, since it may throw some light on the back reaction and the relative importance of various impurities.

Samples taken from the electrolyte of industrial cells often contain dispersed globules of aluminium of varying size, the formation of which may be related to extreme magnetic and gas-induced disturbances at the bath/metal interface, especially outside the vertical projection of the outer side of the anode.²³ Arthur²⁵ found a concentration gradient of dissolved metal in the bulk of the interelectrode gap, which hardly can be related to normal cell operation with high convective mass transfer in the bulk phase of the electrolyte.²³ The content of metal was determined by the volume of H₂ evolved when a crushed sample of electrolyte was treated with HCl. Rolseth and Thonstad²⁶ carried out similar measurements and found a constant concentration of dissolved metal in the order of 0.01 wt % "Al" throughout the bulk of the electrolyte. However, the amount of H₂ evolved may equally well be explained by impurity reactions like reaction (30). Limiting current measurements in

$$M^{2+} + HCl = M^{3+} + (1/2)H_2 + Cl^- \quad (30)$$

commercial cells will obviously be influenced by the impurities in the melt.

It may be expected that phosphorus, through eqns. (25) and (26), and impurities like titanium with several oxidation states will especially be involved in cyclic redox reactions imposing a detrimental effect to the current efficiency with respect to aluminium. Results presented by Deininger and Gerlach²⁷ from a laboratory cell study seem to support this idea, although the convective patterns in such a cell may be completely different from those in commercial cells. Anufrieva *et al.*²⁸ found that minor additions of V₂O₅ and Ga₂O₅ to the electrolyte greatly reduced the current efficiency with respect to aluminium in a 6 kA pilot cell, supporting the idea that the rate-limiting step is located in the diffusion layer at the cathode surface and that cyclic redox reactions of impurities greatly enhance the back reaction.

The proposed mechanism for the back reaction rules out a direct reduction in current efficiency by electronic conduction through the bulk of the electrolyte. However, an extremely high value of the mass transfer coefficient of dissolved metal in the cathode diffusion layer⁹ may at least partly be explained by a contribution of electronic conduction.

It can be noted that the proposed cyclic reoxidation mechanism may not be valid in laboratory cells, since both the impurity level and the convective pattern may be completely different from those in industrial cells. On the other hand the proposed model equations describing the current yield in alumina reduction cells⁹ should still be valid.

If the impurity level in industrial cells is increased it means that the mass-transfer coefficient of dissolved sodium is increased, giving rise to a reduction in the current efficiency of aluminium. This means that purification of dry scrubber alumina should be seriously considered.

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