

# Alternative electrolyte compositions for aluminium electrolysis

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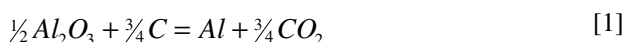
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The traditional electrolyte for aluminium electrolysis is based on molten cryolite ( $\text{Na}_3\text{AlF}_6$ ), acting as solvent for the raw material, alumina ( $\text{Al}_2\text{O}_3$ ). Over the years there has been a trend to increase the content of excess aluminium fluoride ( $\text{AlF}_3$ ) to the cryolite-based electrolyte, in order to enhance the current efficiency of the process. In most cases one has ended up at 11–13 wt% excess  $\text{AlF}_3$  because higher contents makes it difficult to control the heat balance of the process. This problem may be overcome if sensors are developed that will allow online control of electrolyte temperature and composition, and we may then see a surge towards still higher  $\text{AlF}_3$  contents. In the development of new anode materials to replace the carbon anode with inert, oxygen-evolving anodes, focus is on anode corrosion, and a low electrolyte temperature is then highly desirable. While the conventional process operates at around  $960^\circ\text{C}$ , electrolyte temperatures as low as  $750^\circ\text{C}$  are being tested. This is achieved by having large excess contents of  $\text{AlF}_3$  (40 wt%). The consequences of using such electrolyte compositions are discussed.

## Introduction

In the electrowinning of aluminium in so-called Hall-Heroult cells the raw material, alumina, is dissolved in a molten fluoride electrolyte and electrolyzed between a consumable carbon anode and a liquid pool of aluminium, serving as cathode; with the cell reaction,



The electrolyte is based on the solid compound cryolite,  $\text{Na}_3\text{AlF}_6$ , which in the molten state is a good solvent for alumina, and it also contains some excess aluminium fluoride,  $\text{AlF}_3$ , and a few per cent  $\text{CaF}_2$ .

The choice of an optimal electrolyte composition is a complicated matter, but two requirements are crucial:

- High alumina solubility

- The formation of a protective ledge of frozen electrolyte components on the cell walls.

Cryolite was chosen as electrolyte because of its high solubility of alumina. However, the electrolyte composition has been modified to meet other requirements, such as the highest possible current efficiency with respect to aluminium, as outlined below.

The second requirement of maintaining a frozen ledge stems from the fact that there is no lining material that is sufficiently resistant to the molten fluoride electrolyte. The traditional lining material is carbon, but in modern cells there is a trend to use silicon nitride-bonded silicon carbide instead. Both materials need to be protected by a frozen ledge most of the time in order to achieve a long lifetime for the cell. The presence of this ledge or ‘freeze’ is illustrated in Figure 1.

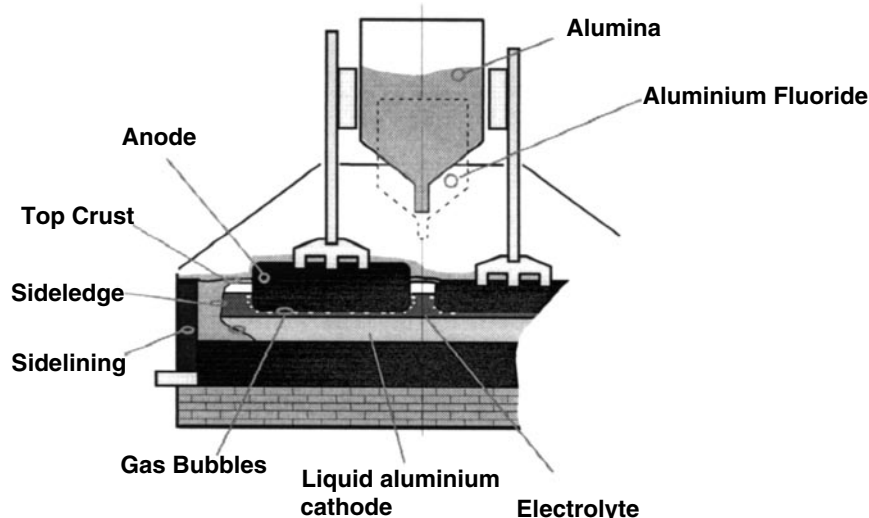


Figure 1. Sketch of an aluminium cell, showing the presence of a protective side-ledge

In order to maintain a frozen ledge, the electrolyte temperature must be kept rather close to its liquidus temperature, i.e. the so-called ‘super-heat’ must be low, typically 5–10°C. The heat flux ( $q$ ) through the side-lining is driven by a temperature gradient, and the temperature at the electrolyte/ledge interface will then be equal to the liquidus temperature of the electrolyte, in equilibrium with the frozen cryolite ledge. For uni-axial flux, the heat flux,  $q$ , is equal to the heat transfer coefficient,  $h$ , times the superheat, i.e.,

$$q = h(t - t_{liq}) \quad [2]$$

where  $t$  is the electrolyte temperature and  $t_{liq}$  is the liquidus temperature of the electrolyte. In a given cell the numerical values of  $q$  and  $h$  are more or less fixed, so obviously the superheat,  $(t - t_{liq})$ , plays a crucial role in stabilizing the ledge. At steady state, the ledge is stable, but if  $t$  rises and  $t_{liq}$  remains constant, the ledge will melt, while it will grow with decreasing  $t$ . If  $t_{liq}$  also varies, things get more complicated, as we shall see.

The NaF-AlF<sub>3</sub> phase diagram is shown in Figure 2. It is seen that around the cryolite composition (T<sub>2</sub>) the liquidus temperature varies little with variation in composition. This is a great advantage in stabilizing the ledge, because any drift in electrolyte composition has little influence on  $t_{liq}$  and thereby on Equation [2].

If we go 30–40 years back in time, this fact was a governing factor in the choice of electrolyte composition for Hall-Heroult cells. However, it was known that the current efficiency of the process could be improved substantially (from 80–85% to 90–95%) by applying more AlF<sub>3</sub>-rich electrolytes. This required improved cell control and improved alumina feeding, which gradually were achieved. From Figure 2 it can easily be seen that when increasing the excess AlF<sub>3</sub> content beyond the cryolite composition, the liquidus line becomes increasingly steep. By random variations in the electrolyte composition, there will then be substantial variations in superheat. As a result, electrolyte temperature and ledge thickness may fluctuate, and the system becomes unstable.

The answer to this problem was computer control of energy input and frequent determinations of electrolyte temperature and electrolyte composition. The problem of maintaining stability becomes more and more difficult with increasing AlF<sub>3</sub> content, and most plants have now settled

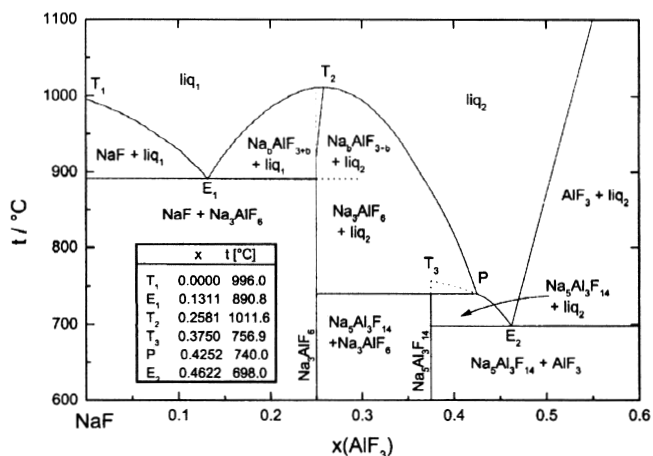


Figure 2. The NaF-AlF<sub>3</sub> phase diagram plotted versus the mol fraction of AlF<sub>3</sub><sup>1</sup>

at 10–13 wt% excess AlF<sub>3</sub> content ( $x_{AlF_3} = 0.3$ ). This can be regarded as a compromise between the advantage of higher current efficiency and the problem of maintaining stability.

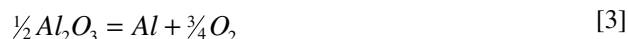
As will be shown in the following, the alumina solubility decreases with increasing AlF<sub>3</sub> content, making it increasingly difficult to keep sufficient alumina in solution.

The current efficiency in modern Hall-Heroult cells is normally 91–95%. A typical electrolyte composition is Na<sub>3</sub>AlF<sub>6</sub> with 11 wt% AlF<sub>3</sub>, 5 wt% CaF<sub>2</sub>, 2–4 wt% Al<sub>2</sub>O<sub>3</sub>.

**Sensors.** As mentioned above, the selected electrolyte composition can be regarded as a compromise between conflicting requirements. If online sensors can be developed for continuous monitoring of electrolyte composition (AlF<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>) and temperature, one will have much better tools for cell control. It should then be possible to raise the AlF<sub>3</sub> content further to achieve still higher current efficiency and more trouble-free operation.

## Inert anodes

The Hall-Heroult process has some inherent weaknesses, the most obvious being the consumable carbon anode, which needs to be changed frequently, and which causes emissions of the greenhouse gases CO<sub>2</sub>, CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> and the sulphur gases SO<sub>2</sub>, COS, and H<sub>2</sub>S. On the other hand, the fact that carbon contributes energy to the cell reaction (see Equation [1]), the theoretical decomposition voltage comes out one volt lower for Reaction [1] than for the cell reaction with inert anodes:



During the last 30 years great efforts have been made to develop a so-called inert anode, i.e. a non-consumable, oxygen-evolving anode. Apart from saving carbon and being more environmentally friendly, inert anodes might also allow for a more compact cell design, with possible savings in capital and energy.

The main challenge is to find an anode material that is sufficiently resistant to the aggressive fluoride electrolyte and to nascent oxygen. A moderate corrosion (e.g. 1–2 cm per year) of the anode material may be tolerated, as long as the integrity of the anode is sustained and the corrosion products do not contaminate the metal produced to such an extent that purity specifications are exceeded.

Candidate anode materials are:

- ceramics
- cermets
- metals.

It is beyond the scope of this paper to discuss properties of prospective inert anode materials, so only three examples will be given.

A much tested ceramic material is tin oxide, SnO<sub>2</sub>, doped with Sb<sub>2</sub>O<sub>3</sub> + CuO. Contamination of the aluminium with tin is a problem with this anode material.

The cermet material that has been tested the most is based on nickel ferrite, NiFe<sub>2</sub>O<sub>4</sub>, with about 20% metal phase, predominantly consisting of copper.

The metal anodes that have been tested have mostly been alloys of Ni-Fe-Cu and Ni-Fe.

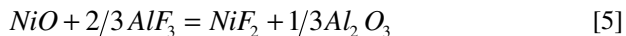
More information about inert anodes, problems and advantages, has been described elsewhere<sup>2–8</sup>.

**The Corrosion Problem:** It will be appreciated that the metal phase in cermets and metal anodes will be subject to oxidation, e.g.



The rate of oxidation has to be limited in order to have a workable system. Regardless of the nature of the anode substrate, the electroactive anode surface must be an oxide material.

Furthermore, it is so that all oxide materials have a finite solubility in the electrolyte. In the case of NiO, the dissolution reaction can be written:



The reaction product, in this case NiF<sub>2</sub> dissolved in the electrolyte, will subsequently be reduced at the cathode, ending up in the metal produced. In order to achieve metal of acceptable purity, it is essential that the solubility of the anode components in the electrolyte is low, or that the dissolution process is impeded in some way. Hence, it is important to select anode materials that exhibit low solubility in the electrolyte, or to modify the electrolysis conditions so as to reduce the corrosion rate.

In both cases, i.e. in the oxidation of metals and the dissolution of oxides in the electrolyte (Equations [4] and [5]), it is generally beneficial to lower the temperature. Particularly in the case of metal substrates, a low temperature can have a profound effect in reducing the rate of oxidation. Typically the rate of oxidation of metals may be reduced by an order of magnitude when the temperature is lowered by 100°C.

In the patent literature concerning inert anodes, temperatures as low as 750–800°C are being recommended in some cases. A look at the phase diagram in Figure 2 tells us that the concept of maintaining a frozen ledge can hardly work in this case, due to the steepness of the liquidus curve. This fact demonstrates the need for a new approach to the problem of cell lining.

**Low-melting electrolytes.** The electrolyte of choice is still the NaF-AlF<sub>3</sub> system, or possibly KF-AlF<sub>3</sub>, because of the high solubility of alumina in these systems. However, the alumina solubility decreases with increasing excess AlF<sub>3</sub> content. In the NaF-AlF<sub>3</sub> system it decreases from more than 10 wt% at the cryolite composition to about 3 wt% at the eutectic, as indicated in Figure 3. Better ways of feeding alumina may be required for the low-melting electrolytes,

because of the reduced alumina solubility.

The need for new lining materials is still an open question, which apparently has not been seriously addressed, at least not in the open literature, and there is no obvious solution to this problem. Since the anode gas is oxygen, the lining material should probably be an oxide material, e.g. an alumina-rich material. Provided that the electrolyte can be kept close to alumina saturation at all times, such a solution might work. A metal lining with an oxide skin is another solution.

One example of the use of a metal lining and low-melting electrolyte (750°C) can be given. The cell has an assembly of vertical anodes and cathodes, connected in parallel, as shown in Figure 4. Since the alumina solubility is so low in this temperature range, Beck<sup>10</sup> has suggested to use an

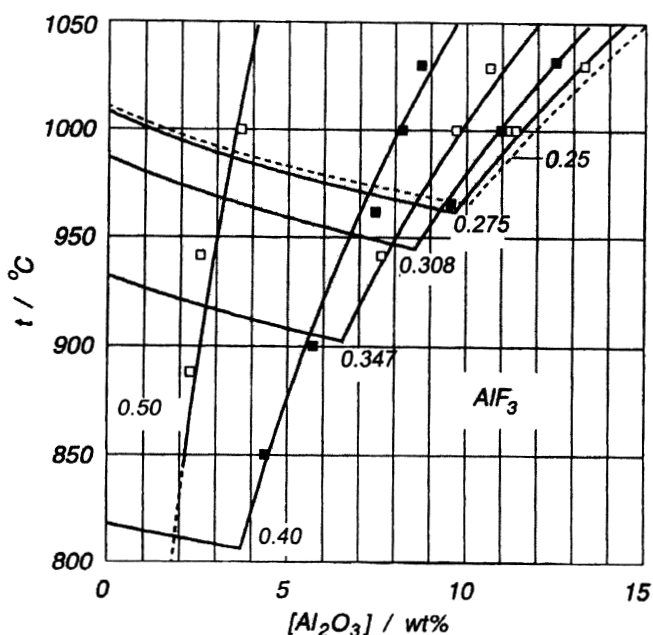


Figure 3. The solubility of alumina in the system NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. The dotted line represents the cryolite composition, while melts with excess AlF<sub>3</sub> (indicated in mol fraction AlF<sub>3</sub> as in Figure 2) are shown as solid lines. Modified from reference<sup>9</sup>

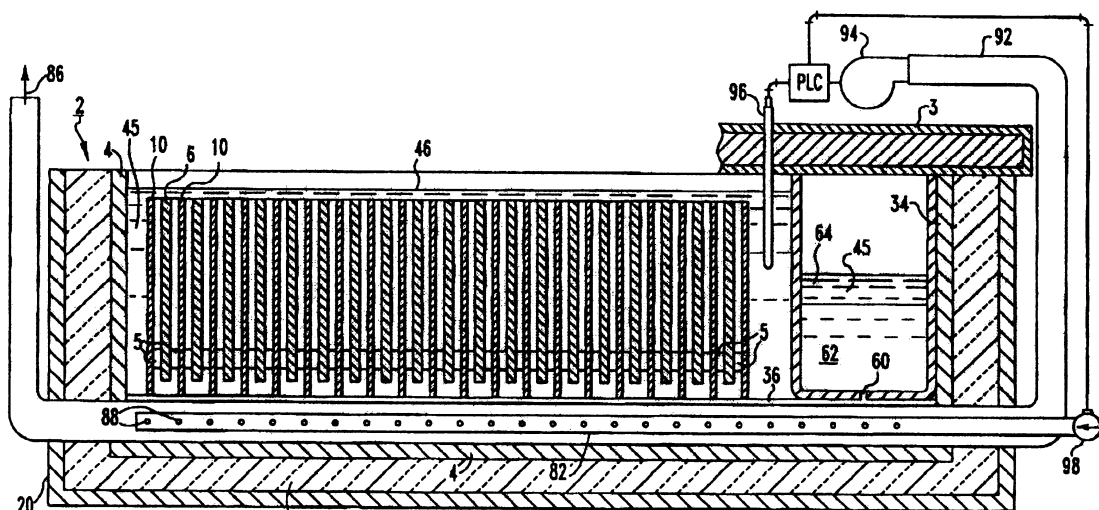


Figure 4. Low temperature reduction cell with vertical electrode, from reference<sup>10</sup>. The cell liner (4) consist of the same material as the inert anodes (6). Anodes and cell liner are connected in parallel. Cathodes (10) are positioned on either side of the anodes

alumina slurry, by keeping a suspension of solid alumina particles in the electrolyte at all times. To prevent the alumina from settling, the cell container is made from the anode material, serving as an auxiliary anode. In this way the lining problem is solved at the same time as securing the supply of dispersed alumina, since oxygen is evolved from the bottom of the cell as well as from the vertical anodes. The collection of the liquid aluminium coming from the titanium diboride ( $\text{TiB}_2$ ) cathodes, may be a problem with this cell design.

### Conclusion

- Although the Hall-Heroult process has settled at a more or less fixed electrolyte composition, i.e. at around 11 wt% excess  $\text{AlF}_3$  content, a possible development of online sensors may allow the use of still higher contents, yielding enhanced current efficiency
- For the use of inert anodes several electrolytes have been proposed, including the one presently used in the Hall-Heroult process. However, in many cases more low-melting electrolytes are favoured, some with very high contents of  $\text{AlF}_3$ , creating so far unsolved problems regarding lining materials.

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