

Solubility of alumina in three-layer aluminium-refining cell electrolytes

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*Dedicated to Associate Professor K. Matiašovský, DrSc.,
in honour of his 60th birthday*

The solubility of alumina was determined in electrolytes used in aluminium three-layer refining, based on the mass loss of a rotating alumina disk. Solubilities at 750 °C were 0.97 mass % Al_2O_3 and 1.49 mass % Al_2O_3 for the so-called Pechiney and Alusuisse electrolytes, respectively, while other proposed electrolyte compositions showed lower solubilities.

The predominant process for production of high-purity aluminium (99.99 % +) is electrolytic refining in the three-layer process which is conducted in the so-called Hoopes cells. Commercial grade metal (99.7 %) is dissolved in a liquid Cu—Al alloy which serves as a high-density (3.3 g cm^{-3}) anode, resting at the bottom of the cell. The electrolyte which has a lower density (2.7 g cm^{-3}) makes up the second liquid layer, and on top of that rests the pure aluminium cathode ($\rho = 2.3 \text{ g cm}^{-3}$). A further description of the process can be found in the literature [1].

The electrolyte serves as a highly selective carrier of aluminium from the anode to the cathode in the form of aluminium-containing ions. Apart from selectivity, other electrolyte properties of concern are density, electrolytic conductivity [2], hygroscopicity, and alumina solubility. In commercial refining cells the deposition of a crust along the sidewalls takes place gradually. The crust consists of alumina together with some electrolyte. As the crust grows it obstructs the passage of current, so it must be removed periodically.

The reason for the crust formation is not clear. In spite of the fact that the electrolyte is protected from exposure to the atmosphere by the thick ($\approx 20 \text{ cm}$) cathode metal pad, it somehow picks up alumina, and this alumina is deposited on the walls when the saturation limit is reached. Possible sources of alumina are hydrolysis of the electrolyte due to moisture coming from the raw materials

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or from atmospheric exposure of electrolyte creeping to the surface, or alumina formed by oxidation of the cathode metal which dissolves in the electrolyte and subsequently deposits at the coldest spot, *i.e.* at the walls where there are nucleation sites. Regardless of the mechanism of the build-up of the alumina crust, the solubility of alumina in the electrolyte may be of importance for the rate with which it grows.

Three different electrolytes are being used commercially. They are usually named after the companies which once introduced them. The names and approximate compositions are given in Table 1. The present study was concentrated on the two most commonly used, the Pechiney (Gadpau) and the Alusuisse electrolytes, but a spot test was also made of the Sumitomo electrolyte. Finally, three other compositions which have been proposed in the patent literature [3] were tested. The compositions of these electrolytes are given in Table 2.

Table 1

Compositions (w/%) of commercial refining cell electrolytes

Components	Electrolyte		
	Pechiney	Alusuisse	Sumitomo
NaF	17	18	10
AlF ₃	23	48	41.4
BaF ₂	—	18	35
BaCl ₂	60	—	—
CaF ₂	—	16	13.6

Table 2

Compositions (w/%) of three electrolytes proposed in literature [2]

Components	Electrolyte		
	1	2	3
AlF ₃	22	24.5	27
BaF ₂	46	51	56
NaCl	32	24.5	17

Literature data on alumina solubility in aluminium-refining electrolytes are very scarce. *Moskvitin et al.* [4] reported a solubility of 0.5 mass % in the Pechiney electrolyte, based on voltammetric measurement.

In the present work the alumina solubility was determined from the mass loss of a rotating alumina disk immersed in the melt. This experimental technique

was originally developed to determine alumina solubility in cryolite-based melts used in aluminium electrowinning [5]. Extensive testing showed that the method yielded reliable results. A sintercorundum disk of 40 mm diameter and 6 mm thick is immersed in the melt and rotated at 300 revolutions per min for a given time (hours) whereafter the mass loss of the disk is determined. Tests run in presaturated melts showed a negligible mass increase of the disk due to uptake of melt.

Previous works using sintered alumina disks in cryolite melts show that the dissolution process is mass-transfer controlled [6, 7]. Provided that the same is true for the present electrolytes, the time needed to achieve saturation can be estimated from the equation given by *Levich* [8]

$$\frac{dm}{dt} = 0.62 AD^{2/3} \nu^{-1/6} \omega^{1/2} \rho(w^* - w) \quad (1)$$

where dm/dt is the mass flux of dissolved alumina, A is the surface area of the disk, D is the diffusion coefficient of alumina, ν is the kinematic viscosity and ρ is the density of the melt, ω is the angular velocity of the disk, and w^* and w are the mass fractions of alumina in the melt at saturation and in the bulk of the solution, respectively. The term m can be replaced by $m = \rho V w$ where V is the volume of the solution, and eqn (1) can be integrated from time zero (0, 0) to time t (t, w)

$$t = \frac{-1.61 V \nu^{1/6}}{AD^{2/3} \omega^{1/2}} \ln(1 - w/w^*) \quad (2)$$

For cryolite systems, saturation ($w/w^* \rightarrow 1$) should be reached under the given condition (200 g melt, 970 °C) after ≈ 2 h, and this was confirmed by experiment [5]. For the present electrolytes and temperatures (750 °C) diffusivities and viscosities are not available, but by the use of estimated data and for the amount of bath chosen (43 cm³) the time comes out as 1–2 h also in this case. Hence, 3 h was used as the duration of the experiments, and it was confirmed that longer times had no effect on the results.

Experimental

The electrolyte was made up of high-purity salts as purchased except for AlF₃ which was prepared by vacuum sublimation of technical grade aluminium fluoride. The salts NaF, NaCl, and CaF₂ were dried at 400 °C overnight, and BaF₂ and BaCl₂ were dried at 200 °C overnight and for four days, respectively. Voltammetric measurements indicated that melts made from these salts had very low oxide contents, so the initial alumina content of the melts was taken to be zero.

After being prepared from the pure salts the electrolyte was placed in a nickel crucible to an amount of approximately 43 cm^3 at 750°C . The nickel crucible was placed inside a graphite crucible for support. An argon atmosphere was maintained in the furnace during the experiment. The sintercorundum disk ($w(\text{Al}_2\text{O}_3) > 99.7\%$, 40 mm diameter, 6 mm thick) was mounted on a stainless steel rod and immersed in the melt *ca.* 1 cm and rotated at 300 revolutions per min.

When the experiment was over, the disk was removed from the melt and transferred to an aqueous solution ($30\% \text{ AlCl}_3 \cdot 6\text{H}_2\text{O} + 8 \text{ cm}^3 \text{ 1 M-NaOH}$) at 65°C to remove the adhering salt. Rotation accelerated the cleaning process. The amount of alumina which was dissolved in the solution during this treatment was very low ($\approx 1 \text{ mg}$). The alumina solubility was derived as the ratio between the mass loss of the disk and the initial mass of the electrolyte. Evaporation losses of the electrolyte were found to be very small at this temperature (750°C).

Results and discussion

Repeated tests showed that the precision of the solubility determination was 10% (for higher alumina solubilities, like in cryolite melts, the precision is superior [5]). The experimental results are given in Table 3. The result obtained for the Sumitomo electrolyte was based on a single spot test, and it is not considered to be reliable, so it is given in parenthesis.

Table 3

Measured alumina solubilities at 750°C for the given electrolytes

Electrolyte	Pechiney	Alusuisse	Sumitomo	1	2	3
$w(\text{Al}_2\text{O}_3)/\%$	0.97	1.49	(0.25)	0.58	0.72	0.69

Hardly anything is known about the structure of these melts, so it is difficult to discuss the results in view of any dissolution model. The closest analogy is found in cryolite-based melts used in aluminium electrowinning. These systems have been investigated extensively, and the dissolved alumina is known to dissociate into various Al—O—F complexes, forming three new particles at low concentrations [9]. A similar behaviour may be expected in the present system.

In cryolite-rich melts near the melting point the highest alumina solubility is found in pure cryolite (13 mass %). Addition of aluminium fluoride lowers the solubility, at first slightly and then more rapidly until it tapers off at around 2 mass % Al_2O_3 for 35 mass % AlF_3 and higher (750°C) [5]. All the other additives in question lower the solubility.

Tentatively one could assume that for the refining electrolytes there are the contents of cryolite and aluminium fluoride which are responsible for the alumina solubility, while the other components either act as neutral diluents or they actively suppress the solubility. In the absence of any firm evidence, all the other components (BaF_2 , CaF_2 , BaCl_2 , NaCl) are regarded as mere diluents.

Table 4

Electrolyte compositions (x/%) of the components

Components	Electrolyte					
	Pechiney	Alusuisse	Sumitomo	1	2	3
Na_3AlF_6	21.7	16.1	9.1	32	23.8	14.8
AlF_3	22.4	49.9	47.8	16	26.7	35.9
BaF_2		11.7	23.1		13.7	26.9
CaF_2		23.3	20.0			
BaCl_2	55.9			48.3	35.9	22.4
NaCl				3.7		

In Table 4 the electrolyte compositions have been recalculated on a cryolite basis (in mole %). The NaCl in electrolytes 1—3 (Table 2) was converted into NaF (in Na_3AlF_6) and BaCl_2 . It is seen that all these melts are extremely acid (AlF_3 -rich) with respect to cryolite compared to the compositions used for electrowinning. If we assume that the ultimate solubility at 750 °C in the Na_3AlF_6 — AlF_3 fraction of the electrolyte is 2 mass % Al_2O_3 , and that this content is diluted by the other components, we arrive at estimated alumina solubilities of 0.88 mass % for the Pechiney and 1.32 mass % for the Alusuisse electrolytes. These values are not too far off from the measured solubilities. For the three proposed electrolytes (named 1—3) the estimated values are close to 1 mass % in all cases, which is considerably higher than the measured value. One might expect the chloride additives to suppress alumina solubility more than fluorides, but the results do not seem to substantiate such an assumption.

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