

Light Metals

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BENCH SCALE ELECTROLYSIS OF ALUMINA IN

SODIUM FLUORIDE - ALUMINUM FLUORIDE MELTS BELOW 900°C

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Current efficiency as high as 92% was obtained in bench scale electrolysis of alumina in sodium fluoride - aluminum fluoride bath with weight ratios from 0.65 to 0.80 at temperatures from about 730 to 900°C. Special aluminas calcined at low temperatures had to be used to obtain rapid solution of the alumina at these temperatures. A solid cryolite layer slowly deposited on the cathode unless the bath temperature was maintained about 100°C above the liquidus temperature of the bulk sodium fluoride - aluminum fluoride composition. The carbon anodes were attacked during anode effect, sometimes swelling, dusting, and evolving larger than normal quantities of carbon tetrafluoride. Addition of 5 wt. % LiF to the bath gave more normal anode effects. Carbon consumption approached the theoretical 0.33 g C/g Al when the alumina content was maintained at high levels and moisture additions were made to the cell atmosphere.

Introduction

Most investigators have found that current efficiencies in electrolysis of alumina in sodium fluoride - aluminum fluoride melts increase as temperature and bath ratio decrease (1). Except for Hall's original patent, very little data has been published for temperatures below 900°C and at bath ratio (wt. % NaF/wt. % AlF₃) below 1.0. The relatively high alumina solubilities (3 to 4%) reported (2,3,4) for temperatures as low as 684°C at bath ratios below 1.0 dispelled the possibility that alumina solubilities would be impractically low, providing additional reasons for undertaking this investigation of the low temperature, low bath ratio region. Both benefits and problems found in electrolyzing alumina under these conditions will be discussed. Various efforts to solve the problems will be described and some of the tradeoffs considered.

Experimental

Tests were conducted in the cell shown in Figure 1. A one-liter sintered alumina crucible contained within a graphite crucible was packed in reduction grade alumina inside a nickel crucible

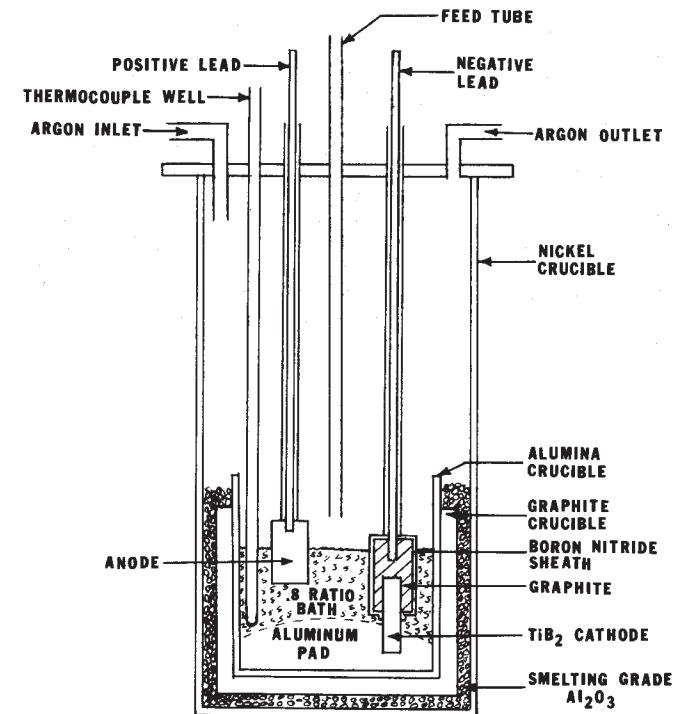


Figure 1. Bench Scale Electrolysis Cell

crucible. The cell was heated by a resistance furnace with temperatures controlled to within $\pm 1^\circ\text{C}$. Molten aluminum at the bottom of the alumina crucible served as the cathode. Protruding through a lid over the top of the nickel crucible were a tube to admit argon for sweeping the cell chamber, a chromel-alumel thermocouple well extending into the molten bath, a 3 mm diameter stainless steel rod threaded into a 50 mm long, 25 mm diameter anode, a feed tube for admitting alumina and bath materials, and a second 3 mm diameter stainless steel rod threaded into a carbon cylinder, which was sheathed in boron nitride over all exposed areas. A titanium diboride cylinder was seated in the bottom area of the carbon cylinder and projected through the boron nitride and into the molten aluminum cathode to complete the cathode connection. The sintered alumina crucible dissolved slowly enough in bath at these temperatures to always last the duration (up to 5 days) of these runs. Without the alumina liner to shield exposed areas of graphite at the cathode, low current efficiencies were obtained from formation of sodium intercalation compounds and/or aluminum carbide.

Handpicked crystals of natural Greenland cryolite and 92.6% pure aluminum fluoride (balance Al_2O_3) were used in the bath (~500 g). Carbon or graphite anodes (~6.4 cm^2 working areas) and graphite cathodes were employed with an anode-cathode spacing of about 25 mm. The anodes were normally immersed in bath and negatively polarized at the beginning of tests (in a treatment called "cathodizing") to promote wetting with bath for inhibiting air burning. Aluminas with surface areas of 30-40 m^2/g , 100 m^2/g , and 170-260 m^2/g (4 to 6% water) were employed in the tests as noted.

Alumina Solution Rate

Though alumina solubilities were adequate, alumina solution rates for reduction grade alumina (30-40 m^2/g) were much lower than at conventional smelting temperatures and bath compositions as shown in Table I. Aluminas of higher area (100 m^2/g and 170-260 m^2/g) did dissolve rapidly enough to keep up with electrolysis. Release of the 4-6% water content of the highest area alumina propelled alumina particles through the bath to further increase solution rates.

Table I. Effect of Temperature, Bath Ratio, and Alumina Surface Area on Solution Rates of Alumina in NaF-AlF₃ Melts

Alumina Surface Area m^2/g	Alumina Charge mg	Bath Volume ml	Bath Ratio	Temp. $^\circ\text{C}$	Solution Time, min.
40	100	50	1.5	980	5.5
100	"	"	1.5	"	0.8
170	"	"	1.5	"	0.1
40	"	"	0.65	740	14
100	"	"	"	"	6.8
170	"	"	"	"	0.2

Anode Attack

The voltage increases obtained when the alumina concentration was allowed to fall were much smaller than in anode effects with conventional bath. The bath continued to wet the anode, possibly aided by the initial "cathodizing" treatment. The gas at the lowest temperature contained 30-40% CF_4 and increased concentrations of CO. Both carbon and graphite anodes formed carbon dust during these times which reduced current efficiencies if air for oxidizing the dust was excluded. Graphite anodes swelled during anode effects at 740 $^\circ\text{C}$, sometimes doubling in diameter and taking a cruciform shape as shown in Figure 2. The deterioration of both carbon and graphite anodes increased with current density. More normal anode effects were obtained with LiF added to the bath.

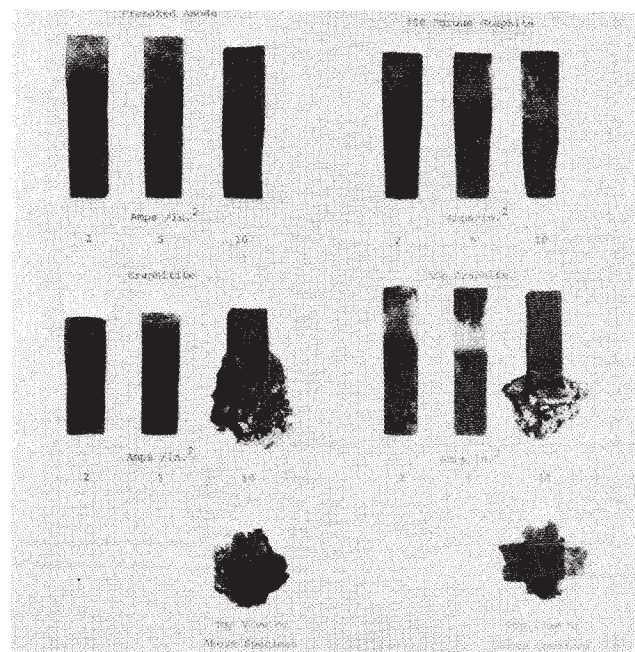


Figure 2. Appearance of Various Anodes After Electrolysis at 740 $^\circ\text{C}$

Anode Consumption

The cell atmosphere had strong effects on carbon consumption as shown in Table II. Consumption ran between 0.46 and 0.48 g carbon/g Al calculated on a 100% current efficiency. Either room air or moisture (4.6 torr) in argon decreased this to the range of 0.36 to 0.40 g/g Al. The atmosphere effect was even more pronounced with graphite anodes. Graphite consumption

which was greater than 0.70 g/g Al during periods of low alumina contents in argon or carbon dioxide atmospheres decreased to 0.40 to 0.44 g/g Al in argon with higher alumina contents. Room air - argon mixtures or moist argon lowered these values to the range of 0.33 to 0.37 g/g Al. Carbon scum formed on the bath surface in dry argon atmospheres (Figure 3a) using an AGR graphite anode in 0.8 ratio bath at 900°C but was absent in argon containing 5 mm water vapor (Figure 3b). These effects for carbon and graphite anodes were relatively independent of bath ratios between the limits of 0.65 and 0.82, temperatures between 760 and 900°C, current densities between 1 and 10 amps/cm² and the anode cathodizing treatment. The use of high surface area aluminas containing 4 to 6% water should supply sufficient water vapor to the cell atmosphere to obtain the beneficial effect of water. Any possible effects of the moisture on current efficiency were not determined.

To further investigate the effect of water vapor on graphite, separate samples of AGR graphite were suspended above and immersed in the 0.8 ratio bath at 900°C. No aluminum was present and atmospheres were employed consisting of dry argon and argon to which 22 torr of water vapor was added. As shown in Table III, the graphite lost 1.0 to 1.7% in weight by

Table III. Weight Change of AGR Graphite Samples Either Immersed in or Suspended Above 0.8 Ratio Bath at 900°C for 16 Hours With and Without Moisture Present. No Electrolysis, No Metal Pad Present.

	Percent Weight Change		
	Samples Above Bath		Immersed Samples
	Sample 1	Sample 2	
Dry Argon Blanket	-1.13	-0.97	-1.7
Wet Argon Blanket, 22 torr H ₂ O	0.00	0.00	+1.08

dusting in dry argon, the higher weight loss being obtained in the sample immersed in bath. With water vapor present, there were no weight changes for samples held in the vapor phase and a 1.1% weight gain for the immersed sample. It is proposed that the attack is due to NaAlF₄ which is the predominant vapor species over bath without electrolysis or the presence of aluminum. Thermodynamic calculations indicate NaAlF₄ can react with water vapor but not with carbon dioxide or oxygen which would explain the atmosphere effects described.

Current Efficiencies

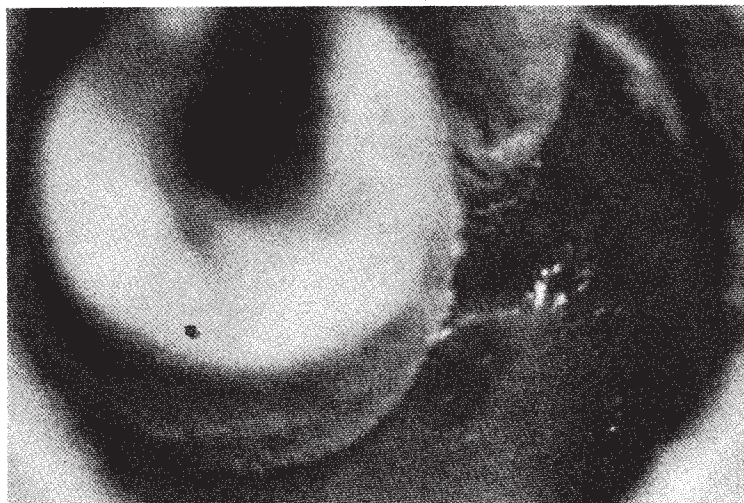
Current efficiencies calculated from the quantities of metal produced were commonly near 90% (92% in one run) in tests lasting a day or more. Lower efficiencies were often obtained with fresh bath in shorter duration runs because some hydrogen was generated from moisture in the fresh bath components during the early stages of the run. The use of an alumina crucible in

Table II. Effect of Cell Atmosphere on Anode Consumption

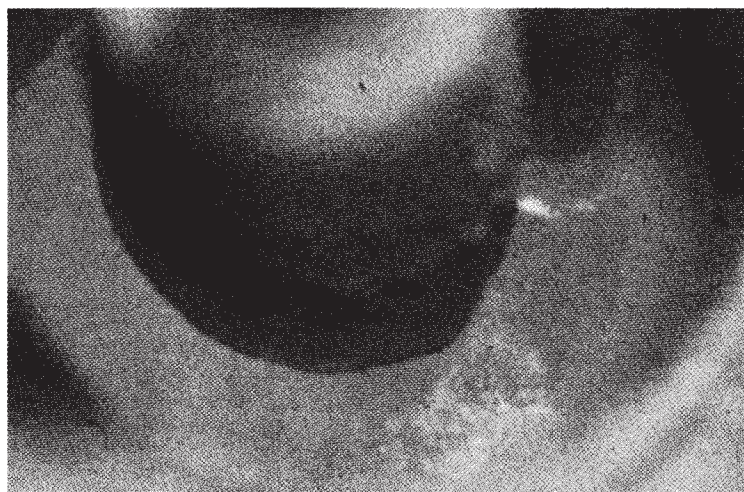
Temp. °C	Bath Ratio	Anode	Cell Atmosphere	Current Density amps/cm ²	Anode Consumption g C/g Al at 100% Current Efficiency
820-837	0.8	Prebake Carbon, Uncathodized	Argon	10	0.48
824-844	0.8	Prebake Carbon, Cathodized	Argon	10	0.47
824-844	0.8	Prebake Carbon, Uncathodized	CO ₂	10	0.46
832-844	0.8	Prebake Carbon, Cathodized	CO ₂	10	0.46
880-900	0.8	Prebake Carbon, Cathodized	Moist Argon*	10	0.40
900	0.8	Prebake Carbon, Cathodized	Moist Argon*	10	0.37
860	0.8	Prebake Carbon, Cathodized	Room Air - Argon	3.0	0.36-0.39
760-830	0.6-0.8	Graphite, Uncathodized	Argon	1-1.5	0.70
730	0.65	Graphite, Uncathodized	CO ₂	1.0	0.70
830-834	0.8	Graphite, Uncathodized	Argon	10	0.40-0.44
780	0.7	Graphite, Cathodized	Room Air - Argon	5.0	0.33-0.39
820	0.75	Graphite, Cathodized	Room Air - Argon	5.0	0.33
860	0.8	Graphite, Cathodized	Room Air - Argon	5.0	0.38
880-916	0.82	Graphite, Cathodized	Moist Argon*	5.0	0.33-0.36
900	0.8	Graphite, Uncathodized	Moist Argon*	5.0	0.33-0.37

} heavy graphite scum - low alumina contents

*4 to 32 torr of water vapor in 1 atmosphere of argon.



a - Note carbon scum on top of bath to right of anode in dry argon.



b - Carbon scum is absent on bath surface in argon containing 5-min. water vapor.

Figure 3. Effect of Moisture in Cell atmosphere on Carbon Scum Formation from an AGR Graphite Anode at 900°C in 0.8 Ratio Bath

place of the usual graphite crucible and the sheathing of graphite in the cathode connection with boron nitride avoided sodium intercalation and aluminum carbide formation in these runs. Without these provisions to eliminate sodium intercalation, the current efficiencies would have been much lower, and very much longer runs would have been required to minimize the effect of intercalation on current efficiency.

Cryolite Crusts at Cathode

In prolonged runs, a solid crust of cryolite often formed over the cathode. This was caused by depletion of aluminum-containing ions at the cathode to form aluminum and a consequent shift in the bath composition at the cathode interface to high NaF content. As can be seen from the phase diagram in Figure 4,

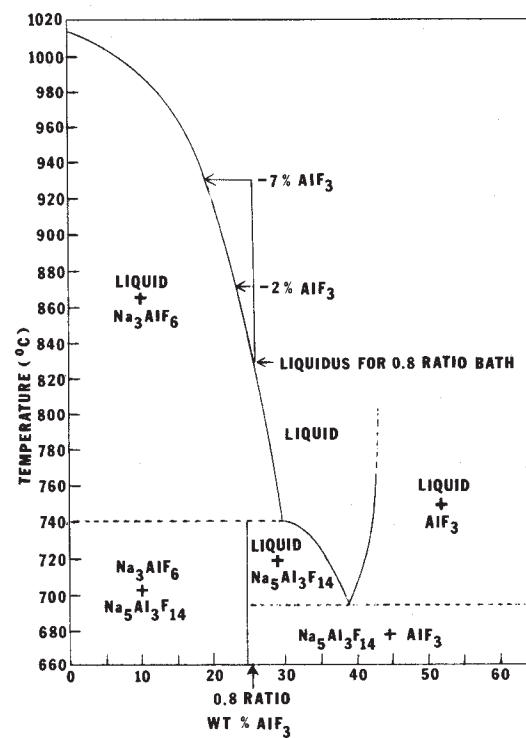


Figure 4. Phase Diagram for the System Na₃AlF₆-AlF₃ Illustrating the Effect of AlF₃ Depletion on Cryolite Deposition at the Cathode

the decrease in AlF₃ content need be only 2% at 860°C with an 0.8 ratio bath before cryolite will precipitate at the cathode. However, if the same bath is employed at 930°C, 100°C above the liquidus temperature, the local decrease in AlF₃ concentration has to be greater than 7% before cryolite precipitates. Higher

temperatures proved to be the practical way to control this problem although lower current densities, stirring, and lithium fluoride additions were somewhat helpful.

Fuming

With high aluminum fluoride contents in the bath, the tendency increases for NaAlF_4 vapor to be evolved and for hydrolysis of the bath to form HF. However, both can be partially offset by taking advantage of the lower operating temperatures possible with these compositions insofar as temperature adjustments to avoid crust formation at the cathode permit. The high surface area aluminas required for rapid solution rates in these baths should provide more than adequate capacity in alumina dry scrubbing systems for complete chemisorption of all the additional hydrogen fluoride in an efficient cell fume capture system.

Electrical Conductivity

Increasing the AlF_3 content and decreasing temperatures both decrease bath conductivity. The electrical conductivity of a 0.74 ratio bath at 775°C was estimated to be $1.3 \text{ ohm}^{-1} \text{ cm}^{-1}$ (Figure 5). Addition of 20% LiF raised this to $2.55 \text{ ohm}^{-1} \text{ cm}^{-1}$ as shown in Figure 6.

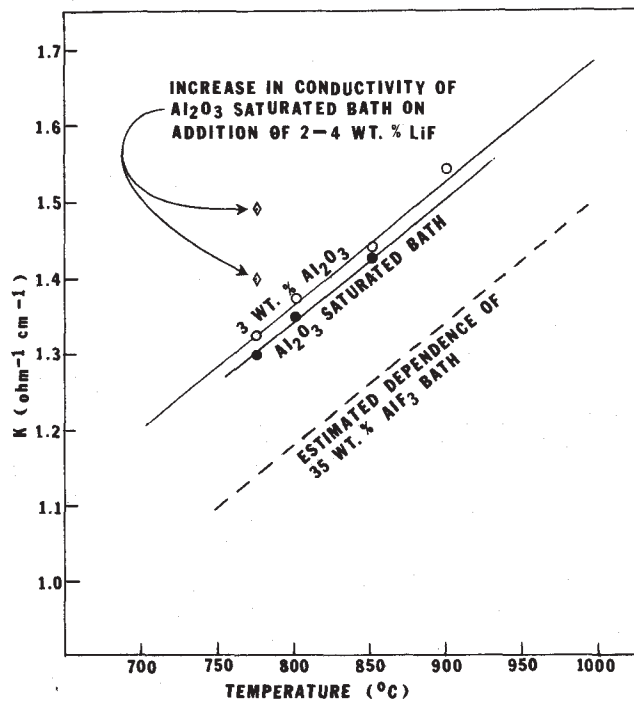


Figure 5. Temperature Dependence of Conductivity of Na_3AlF_6 - 29 Wt. % AlF_3 (0.74 Ratio) + 3% Al_2O_3

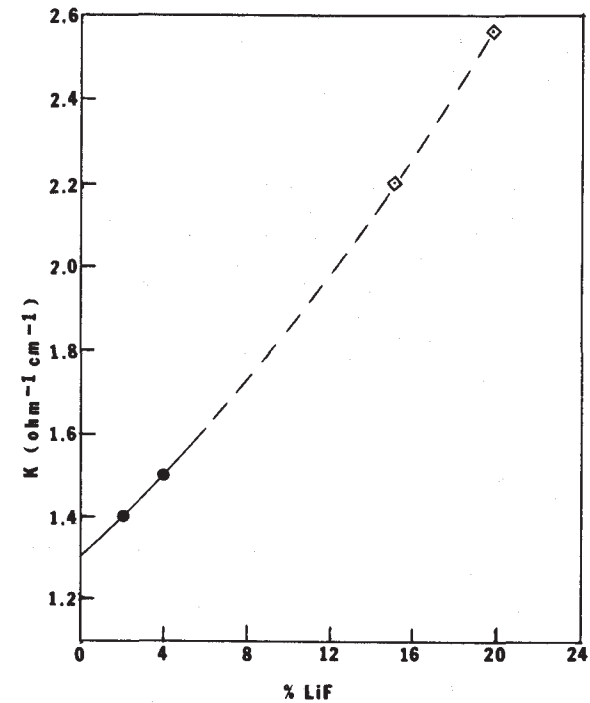


Figure 6. Specific Conductivity of Molten Na_3AlF_6 - 29 Wt. % AlF_3 (0.74 Ratio) + 3% Al_2O_3 as a Function of LiF Additions at 775°C

Conclusions

Methods have been found to successfully operate bench scale alumina electrolysis cells below 900°C in $\text{NaF}-\text{AlF}_3$ baths with ratios between 0.65 and 0.80. Operation in this region revealed both advantages and disadvantages. Benefits of higher current efficiency and lower carbon consumption were obtained at the expense of problems in lower solution rates and solubilities for alumina, carbon dusting at low alumina concentrations, and low moisture contents, higher fume evolution, deposition of a solid crust of cryolite at the cathode, and lower electrical conductivities. Operating the cell at temperatures 100°C above the liquidus temperature decreased crust formation at the cathode but traded away part of the advantageous lower temperatures. Use of higher surface area aluminas with water contents between 4-6% provided more rapid alumina solution rates while evolving water vapor to decrease carbon consumption. The water vapor may nullify some of the current efficiency gain and increase hydrolysis of bath to hydrogen fluoride. However, the high area alumina cell feed could provide more chemisorption capacity for recovering hydrogen fluoride in a closed loop, dry scrubbing system. Addition of lithium fluoride lessened anode attack at low alumina concentrations and improved electrical conductivity.

References

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