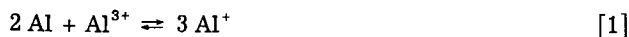


# The Solubility of Aluminum in Cryolite-Alumina Melts and the Mechanism of Metal Loss

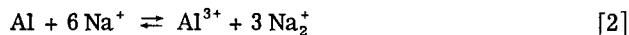
A. M. ARTHUR

The solubility of aluminum in cryolite-alumina melts has been determined in laboratory experiments by analyzing rapidly-quenched samples of the melt after equilibration with metal at temperatures between 960 and 1060°C. The solubility in pure cryolite increases from 0.085 at 1020°C to 0.12 wt pct Al at 1060°C. The addition of alumina decreases the solubility at 1020°C to 0.081 with 5 pct Al<sub>2</sub>O<sub>3</sub> and to 0.073 wt pct Al in melts saturated with alumina. Quenched samples have been taken from operating 130 kA prebake cells at different heights above the metal pad, both in the center channel and beneath the anodes. Within about 10 mm of the cathode the metal content is close to the equilibrium value obtained in the laboratory but above this level it decreases rapidly. It is suggested that oxidation occurs in a central zone of the electrolyte. Mechanisms of metal loss and implications for current efficiency are discussed.

THE dissolution of aluminum in cryolite-alumina melts and its subsequent oxidation by the anode gas is the major cause of the loss of current efficiency during the electrolytic production of aluminum. However, there are still differences of opinion regarding the exact nature of the dissolution process and the mechanism by which the metal is lost. Several investigators<sup>1-8</sup> support the hypothesis in which the dissolution process may be summarized by the following two reactions:



and



It has also been suggested that sodium may occur as uncharged metal atoms. Very little is known however about the occurrence of subvalent sodium, and in the presence of Na and Na<sup>+</sup> the stability of Na<sub>2</sub><sup>+</sup> may be questioned.

Yoshida and Dewing<sup>9</sup> rule out the formation of AlF or Al<sup>+</sup> as a product of dissolution and suggest that the solution may be partly as sodium in some form and partly colloidal. The differences of opinion may be due to the differences in experimental approach, and this is evident from the great discrepancies in published data (illustrated in Table I). It is apparent that there is a need for an improved experimental and analytical approach and this has been the prime objective of the present work.

Two different mechanisms of metal loss have previously been considered: in one CO<sub>2</sub> dissolves and oxidizes the dissolved metal either within the electrolyte or near the cathode; in the other the dissolved metal diffuses to the anode and is oxidized by CO<sub>2</sub> at the surface of the gas bubbles. The first mechanism is often dismissed because the solubility of CO<sub>2</sub> in cryolite is very low, of the order of 10<sup>-5</sup> to 10<sup>-6</sup> moles/cm<sup>3</sup>.<sup>15,18</sup> For the second mechanism four stages have been proposed:<sup>8,11,18</sup>

- 1) Interaction at the metal-electrolyte interface.
- 2) Diffusion of the reaction products through a thin boundary layer.
- 3) Transport of the products through the bulk of the electrolyte.
- 4) Oxidation of the cathodic products by CO<sub>2</sub> bubbles near the anode.

There are differences of opinion regarding which of the four stages is the rate-determining step. Stages 1 and 4 are chemical reactions and have high activation energies compared with the purely physical transport processes in stages 2 and 3. With increasing temperature, the rates of reactions 1 and 4 will be greatly enhanced and are unlikely to be rate-determining. Due to the vigorous agitation of the electrolyte in the commercial cell, stage 3 will be relatively fast, and the rate-determining step is thus probably stage 2, the initial diffusion of the dissolved species through the catholyte diffusion layer.<sup>12-14</sup> Thonstad and Solbu<sup>18</sup> consider stage 1 to be rate-determining when there is convection in the cell, but in the absence of convection the rate of the recombination reaction is determined by mass transport of dissolved metal and gas.

Although in practice features of cell operation affecting metal loss have been recognized and techniques have been applied which have improved current efficiency, the rate-determining step in the metal loss process has not been fully identified. Is it sited in a thin layer at the cathode or does it extend throughout the inter-electrode gap? With more precise knowledge further improvements in current efficiency should be possible.

Table I. Comparison of Some Published Solubility Values

Author	System	Temp, °C	Solubility Wt Pct Al
Hauptin <sup>1</sup>	Na <sub>3</sub> AlF <sub>6</sub> + 5 pct Al <sub>2</sub> O <sub>3</sub> + 8 pct CaF <sub>2</sub>	980	0.10
Thonstad <sup>7</sup>	Na <sub>3</sub> AlF <sub>6</sub> + Al <sub>2</sub> O <sub>3</sub> (sat.)	1000	0.10
Yoshida and Dewing <sup>9</sup>	Na <sub>3</sub> AlF <sub>6</sub> + Al <sub>2</sub> O <sub>3</sub> (sat.)	1000	0.05
Gerlach <i>et al.</i> <sup>10</sup>	Na <sub>3</sub> AlF <sub>6</sub> + Al <sub>2</sub> O <sub>3</sub> (sat.)	1000	0.70
Yoshida <i>et al.</i> <sup>2</sup>	Na <sub>3</sub> AlF <sub>6</sub> + Al <sub>2</sub> O <sub>3</sub> (sat.)	1000	1.80

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## EXPERIMENTAL

### Laboratory Measurements

**Apparatus.** The experimental cell is shown in Fig. 1. In essence it consists of a closed reaction crucible within a steel pot which itself is within a gas tight Inconel container. It was important to choose a crucible material which would be as unreactive as possible with all the components of the electrolyte and with molten aluminum. The crucibles were therefore made of titanium boride/titanium carbide (90 pct  $TiB_2$  and 10 pct  $TiC$  w/w mixture). In industrial tests this material was shown to be almost completely unattacked by the electrolyte for several weeks.<sup>16</sup> Due to the hardness of the material the crucibles were machined from 50 mm diam rods using a spark erosion technique. In order to prevent changes in the composition of the electrolyte due to the escape of volatile species, the crucible top and the lid were ground together to produce a tight seal.

**Materials.** Synthetic cryolite was prepared from aluminum fluoride and sodium fluoride. "Analar" grade  $AlF_3$  was purified by vacuum sublimation and "Analar"  $NaF$  was slowly heated in vacuum until molten and cooled in argon. This removed traces of moisture and other volatile matter. High purity  $Al_2O_3$  was calcined at  $1050^\circ C$  for 3 h. Super purity aluminum (99.997 pct Al) was used in all the experiments. All purified materials were stored and subsequently handled in a dry box with a nitrogen atmosphere.

**Procedure.** The crucible was charged with 4 to 5 g of metal—sufficient to form a pool covering the bottom of the left-hand well—and 43 g of salt. This was enough to cover the crucible partition when molten. The assembled cell was placed in a wire wound resistance furnace so that the crucible was positioned within the constant temperature zone of the furnace. The cell was then evacuated to 0.05 torr, and flushed with inert gas, a high purity (oxygen-free) mixture of 90 pct  $N_2$  and 10 pct  $H_2$  previously dried over molecular sieve. High purity argon or nitrogen was used in preliminary ex-

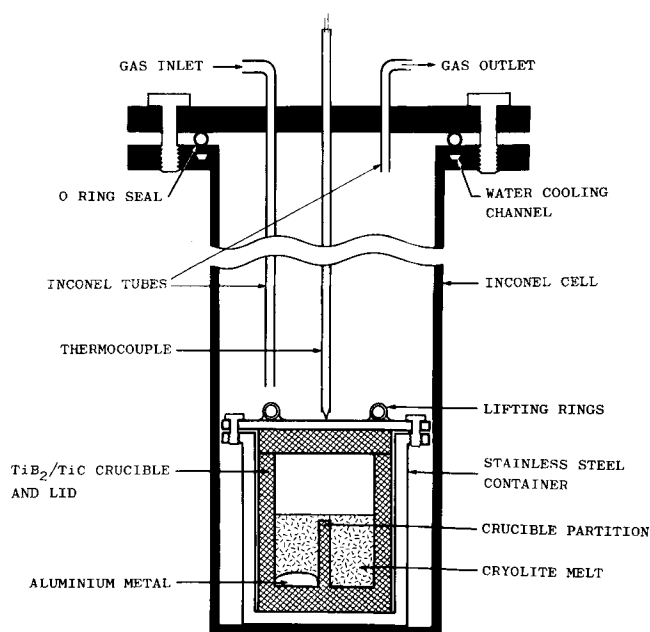


Fig. 1—Experimental cell.

periments but metal was observed to creep up the walls of the crucible from one well to the other. The  $N_2/H_2$  mixture prevented the metal creep probably because of its effect on the metal/crucible interfacial tension. The evacuation and flushing cycle was repeated three or four times while the temperature was gradually raised to  $500^\circ C$ , after which the gas was allowed to flow continuously through the cell under a small positive pressure. Temperatures were measured immediately above the stainless steel container and monitored on a Honeywell potentiometric recorder with a chromel-alumel thermocouple. The temperatures were controlled to an accuracy of  $\pm 2^\circ C$ . The temperature difference between the measuring point and the interior of the melt (2 to  $3^\circ C$ ) was initially determined and all temperatures corrected accordingly. When the salt was molten the furnace was mechanically oscillated through 45 deg to produce a gentle stirring effect within the melt. Equilibrium between metal and melt was attained in 3 h (2 h oscillating and 1 h standing).

Rapid quenching was considered essential to preserve the equilibrium reached in the melt. After equilibration, the stainless steel container with the crucible was rapidly transferred to a bed of alumina fluidized by a stream of oxygen-free nitrogen. From subsidiary experiments in which a thermocouple had been inserted in the melt and connected to a fast response (U.V.) recorder it was found that the melt was quenched from 1050 to  $800^\circ C$  (the critical temperature range) within 20 to 25 s, a time substantially less than that of other workers.<sup>5,7</sup> The total content of the right-hand well of the crucible which had received no initial charge of metal was removed and crushed ready for analysis. Samples were taken from the other well for analysis for  $NaF/AlF_3$  ratio and content of  $Al_2O_3$ .

**Analysis.** Aluminum (reduced species) was determined by treating the quenched samples with hydrochloric acid and measuring the volume of hydrogen evolved. It was assumed that the acid reacted with all the reduced species and the hydrogen evolved represented the total solubility of aluminum and sodium. For convenience the solubility is expressed in terms of equivalent weight percentage aluminum (wt pct Al). Dilute hydrochloric acid, containing a few drops of chloroplatinic acid as a catalyst, was frozen in a glass reaction bulb with liquid nitrogen and evacuated to 0.002 torr. After the acid had been thoroughly degassed the bulb was opened to an atmospheric pressure of argon and the weighed sample added to the solid acid. The bulb was again evacuated and then isolated from the vacuum system. It was quickly warmed to room temperature and the reaction between the acid and the reduced species was complete within a few minutes. The acid was again frozen and the liberated gas was quantitatively transferred into a calibrated vessel by means of a Toepler pump. A palladium thimble attached to this vessel was then heated to  $600$  to  $700^\circ C$  at which temperatures it became permeable to hydrogen. The escape of  $H_2$ , which formed the bulk of the gas, from the calibrated chamber was complete within 15 to 20 min and the volume of the residual gas was measured.

The residual gas, comprising about 4 pct of the total, was passed through a gas chromatograph (Perkin Elmer F11 hot wire detector, with molecular sieve columns). The chromatographic analysis showed no traces of  $H_2$ ,

but quantities of methane between 0.3 and 2.1 pct of the total gas volume were found. Nitrogen formed the rest of the residual gas. The methane was probably formed from  $Al_4C_3$ , produced in small quantities from the TiC in the crucible. No correction factor was applied to the solubility values since the source of aluminum in the  $Al_4C_3$  was uncertain. In any case the quantities of methane were relatively small.

The results were reproducible to an accuracy of  $\pm 4$  pct between runs and to  $\pm 1.5$  pct for duplicate analyses. No hydrogen was found in samples from blank runs without an initial charge of aluminum.

#### Sampling from Operating Cells

It is acknowledged that it is difficult to devise techniques for taking electrolyte samples at precise depths from an operating cell. The simple method described below, although used with a considerable degree of success, still has room for refinement.

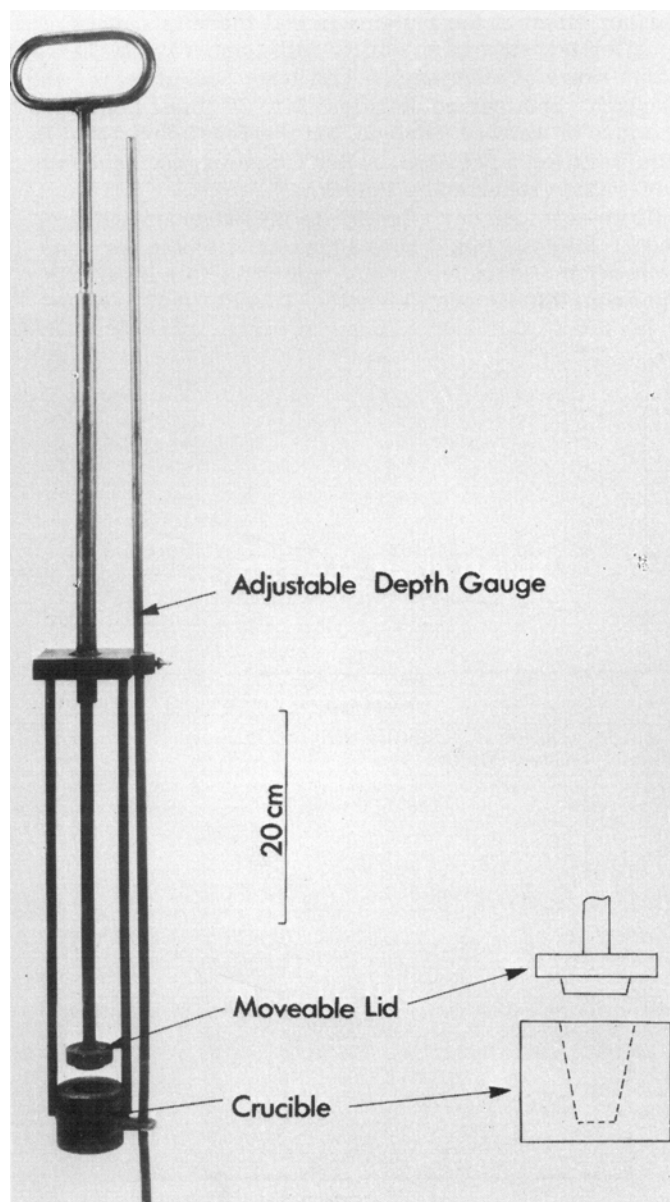


Fig. 2—Electrolyte sampling probe (center channel).

**Apparatus.** The apparatus for sampling electrolyte at different depths in prebake cells is shown in Figs. 2 and 3. The apparatus for sampling center and side channels (Fig. 2) was constructed of mild steel and comprised a vertically positioned crucible of 15 cm<sup>3</sup> capacity, a moveable lid attached to the handle forming a liquid-tight seal, and a variable depth gage. For taking samples beneath the anodes (Fig. 3) a horizontally positioned crucible of 25 cm<sup>2</sup> capacity was used. The lid, attached to the vertical handle by a flexible steel cable, sealed the crucible from the inside. The apparatus included a tripod for stability and a depth gage.

**Procedure.** Prior to sampling, bath temperature, metal and electrolyte depths and current in adjacent anodes were measured and all recent cell operations (breaking, alumina feed, metal tapping, salt additions and anode effects) were noted. The depth gage was set and the apparatus slowly lowered to touch the bottom of the cell. For samples from beneath the anode, the apparatus was lowered in the center channel and then turned to position the crucible about 40 cm from the edge of the block. After allowing a few seconds for the electrolyte to settle down, the handle was operated to open the lid and the crucible filled with electrolyte. On contact with the cold crucible the melt froze rapidly

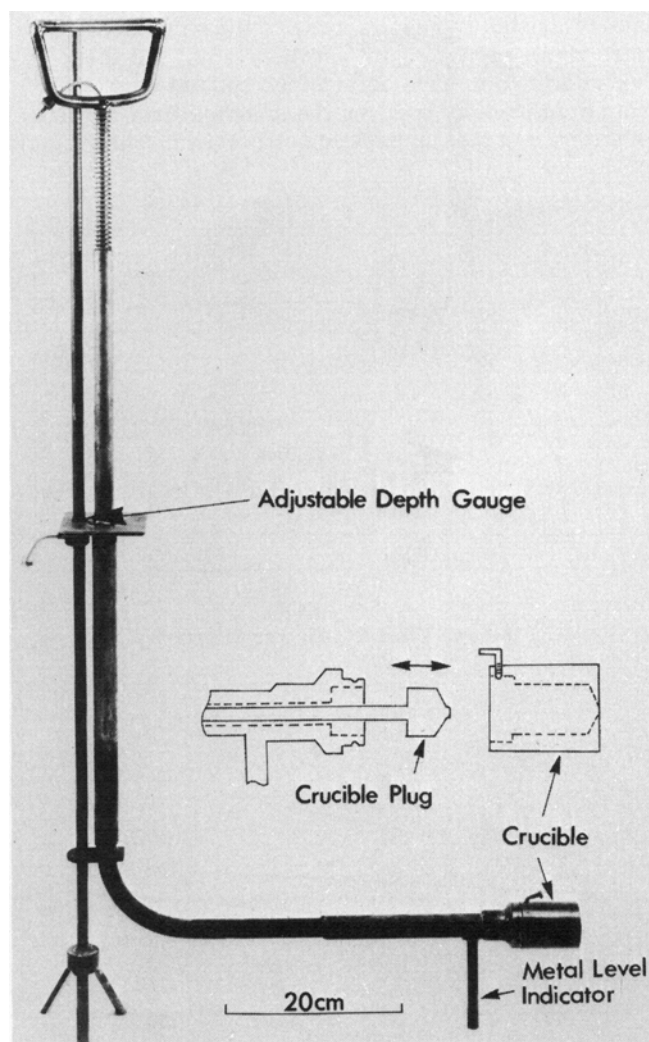


Fig. 3—Electrolyte sampling probe (beneath anode).

and the apparatus was quickly withdrawn from the cell. The sampling operation lasted less than 15 s. The depth positioning rod gave an indication of the metal pad level from the thickness of electrolyte frozen on to it.

Samples were taken at intervals of 12 mm above the metal pad. In this way, samples were collected at three different levels beneath anodes and at five levels in the center channel. Samples were also taken at three different points across the width of the center channel and between blocks in the side of the cell.

**Analysis.** The concentration of aluminum (reduced species) was determined by the method described in the previous section. Part of the sample was used to determine the cryolite ratio and the content of alumina and other additives.

## RESULTS

The results from the laboratory experiments are given in Figs. 4 to 6, and from operating cells in Fig. 7. Fig. 4 shows that equilibrium was attained in 3 h. After 6 h holding, there was no significant change in metal concentration and analyses also showed that the cryolite ratio was unchanged.

Fig. 5 shows the temperature dependence of the solubility of aluminum in cryolite melts saturated with alumina. The results are compared with two other sets of data. Thonstad's<sup>7</sup> results were of the same order as those obtained by Haupin<sup>1</sup> and Vetyukov.<sup>5</sup> All three authors claimed to have determined sodium separately from aluminum by treating the samples first in alcohol or water, and then in caustic soda or hydrochloric acid.

Their results are considerably lower than those obtained by the determination of loss of weight of aluminum,<sup>2,10,17</sup> but somewhat higher than values obtained in the present work.

Yoshida and Dewing<sup>9</sup> determined the concentration of aluminum by titrating the melts (without freezing them) with electrolytically generated oxygen. The portion of melt to be analyzed was "isolated" in an alumina tube, but it is not certain how successful this isolation had been. Fluctuations in the volume of the isolated melt could affect the accuracy of the analysis. The authors acknowledge other uncertainties in the analytical method. Their results are low and they report very high deviations. Nevertheless, it is a plausible technique which, when refined, could eliminate quenching and subsequent handling problems.

The solubility of aluminum in pure cryolite, and in cryolite containing 5, 10, and 15 pct alumina is shown in Fig. 6. In pure cryolite the solubility increases from 0.085 at 1020°C to 0.120 wt pct Al at 1060°C. The solubility is reduced by the addition of alumina but a further effect of the alumina is that there is a much smaller increase in solubility with temperature. In the same range of alumina concentration Yoshida *et al.*<sup>2</sup> and Gerlach<sup>10</sup> obtained solubilities 10 to 20 times higher by the loss of weight technique, but the results obtained in this work for 5 pct  $Al_2O_3$  at 980°C are in good agreement with values reported by Vetyukov.<sup>5</sup>

If we now turn our attention to measurements in an industrial cell, Fig. 7 shows the variations in the concentration of dissolved metal within the flux layer of operating 130 kA prebake cells. It is difficult to sam-

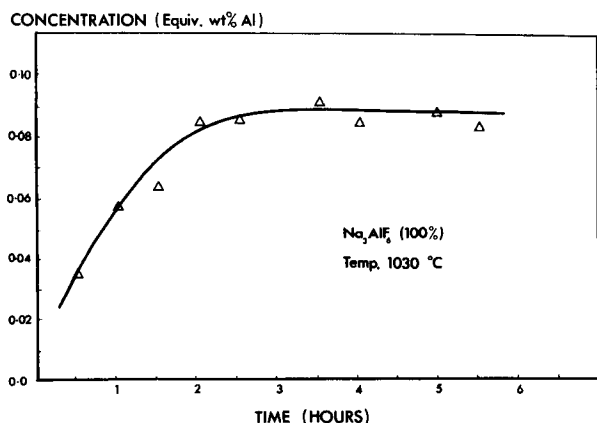


Fig. 4—Time to reach equilibrium.

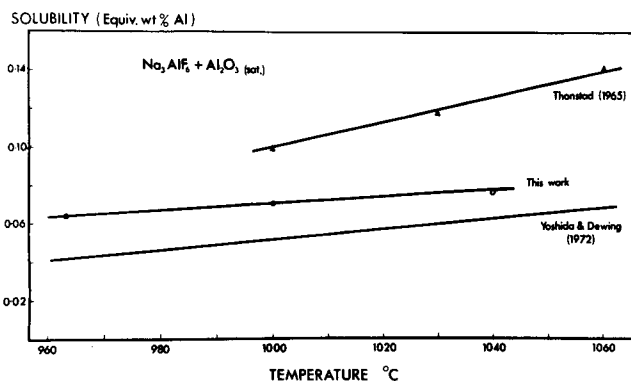


Fig. 5—Variation of solubility with temperature.

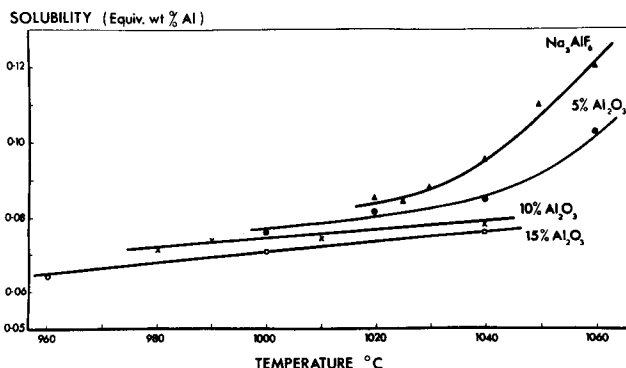


Fig. 6—Variation of solubility with temperature at different alumina concentrations.

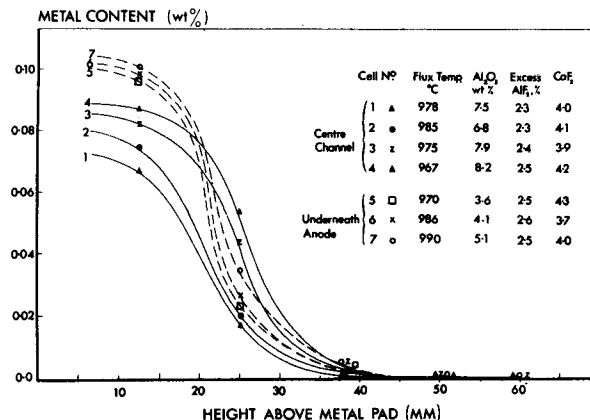


Fig. 7—Decrease in metal content within flux layer.

ple at precisely known distances above the metal pad because its contour is continually changing under the influence of electromagnetic forces, gas evolution and temperature gradients. Samples however, were taken from six different points around each of 7 cells, and also beneath anodes, thus certain generalizations are justifiable.

It is clear that there is a rapid fall in metal content between approximately 15 and 30 mm from the cathode. Below this region the metal content is close to the equilibrium value; above it there is little or not metal in solution.

## DISCUSSION

### Dissolution of Al

As shown in Fig. 6 the addition of alumina decrease the solubility of aluminum in cryolite melts, the decrease being more pronounced at higher temperatures.

Molten cryolite consists mainly of  $\text{Na}^+$ ,  $\text{AlF}_6^{3-}$ ,  $\text{AlF}_4^-$  and  $\text{F}^-$  ions. Aluminum, with its high polarizing power, is unlikely to exist to any appreciable extent as free  $\text{Al}^{3+}$  ions. With the introduction of  $\text{Al}_2\text{O}_3$  into the melt the added oxide ion  $\text{O}^{2-}$ , being doubly charged and with practically the same ionic radius, can replace part of the  $\text{F}^-$  ions in the  $\text{AlF}_6^{3-}$ ,  $\text{AlF}_4^-$  complexes with the subsequent formation of oxyfluoride complexes,<sup>15</sup> e.g.,



Stronger bonds will be formed between  $\text{Al}^{3+}$  and the anionic environment and the thermodynamic activity of the central aluminum ion will decrease accordingly. However, this decrease in cationic activity, which is difficult to evaluate, may be offset by the considerable increase in the overall concentration of aluminum containing ions resulting from the addition of  $\text{Al}_2\text{O}_3$ . As indicated by Yoshida and Dewing,<sup>19</sup> the measured activity of  $\text{AlF}_3$  is higher in melts saturated with alumina than in melts without.

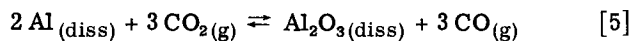
Thus, the observed decrease in metal solubility with increasing alumina concentration suggests that reaction 2 plays a more significant role in the dissolution process. However, on the basis of available data it might be premature to discount the occurrence of subvalent aluminum ions. With rising temperature the chemical reactivity of the species involved will be increased, hence the greater solubility at higher temperatures. The temperature effect is more pronounced in pure cryolite than in melts containing alumina.

### Mechanism of Metal Loss

The results from cell measurements (Fig. 7) show that even as far as 10 mm from the metal surface (interpolar distance  $\sim 50$  mm) the concentration of dissolved species is close to the equilibrium value obtained in laboratory experiments. This suggests that above the metal surface there is a layer of melt saturated with dissolved metal. Between 15 and 30 mm from the cathode the concentration of dissolved metal decreases rapidly, the level falling to zero at a point

10 to 12 mm beneath the anode. This shows that the reoxidation of dissolved metal occurs in a central zone within the bath.

As mentioned earlier, the solubility of  $\text{CO}_2$  in cryolite alumina melts is very low. It seems reasonable to assume therefore that the oxidation of the metal is predominantly by  $\text{CO}_2$  bubbles according to the reaction:



The contribution of dissolved carbon dioxide, if any, will be relatively small.

In order to understand the mechanism by which the metal is lost it is essential to understand the nature of convection in the bath. A schematic representation of different zones as now envisaged within the bath is shown in Fig. 8. In the vicinity of the cathode surface there is a measurable layer of bath with very low turbulence. In this zone, under the effect of the electromagnetic forces, the bath will move horizontally (laminar flow) along with the metal. The bath mixes horizontally but very little vertical mixing will occur. Near the anode the gases cause a vertical disturbance and a layer of very high turbulence is created. High vertical mixing will occur in this zone. As a result a diffuse layer with variable turbulence is created in the center of the bath where the dissolved metal is oxidized.

If this view is accepted, the mechanism of metal loss will therefore comprise the following stages: 1) Interaction at the metal-electrolyte interface. 2) Diffusion of reaction products through the layer of laminar flow. 3) Mechanical transport of gaseous  $\text{CO}_2$  into the oxidation zone. 4) Oxidation of dissolved metal in the middle of the bath.

The high concentration of dissolved metal within the layer of laminar flow indicates that stage 1 cannot be

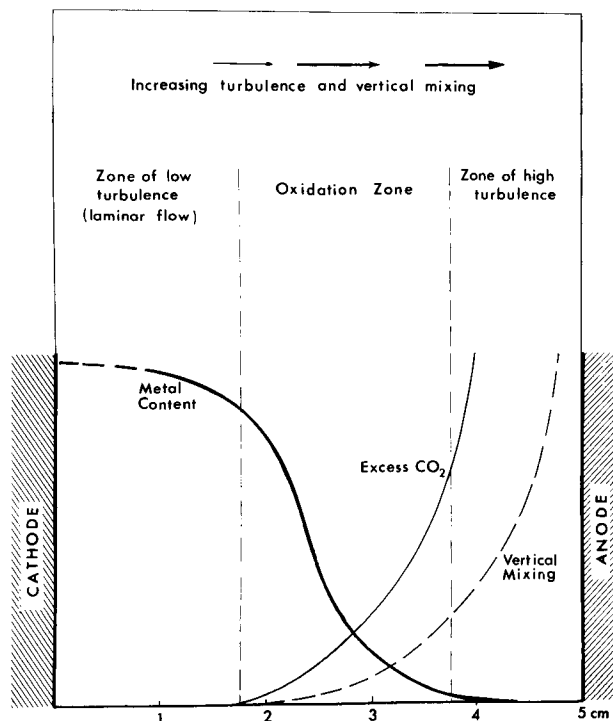


Fig. 8—Schematic representation of zones in the inter-electrode gap.

rate-determining. The extent of penetration of CO<sub>2</sub> bubbles, stage 3, will be governed by the turbulence in the bath and is unlikely to be rate-determining. Stage 4, the oxidation of the metal is also generally accepted to be fast. The diffusion of the dissolved metal into the oxidation zone, stage 2, thus seems to be the rate-determining step.

The rate of diffusion of the dissolved metal will depend on the viscosity of the melt and on the length of the path of diffusion. For a given anode-cathode distance the path of diffusion is determined by the extent of penetration of the gas bubbles.

It is known that at high alumina concentrations fine frothy bubbles are formed whereas at low alumina concentrations the gas bubbles tend to cling to the anode. One can imagine the fine bubbles penetrating deeper into the melt.

It has not been possible to take samples close to the metal surface by the present method, but there is probably a gradient of metal content within the laminar flow region leading to a higher concentration at the metal surface. The equilibrium concentrations in the laboratory experiments had been achieved under conditions of zero current, but in the commercial cell a higher equilibrium concentration at the metal surface may be established because of excess sodium ions at the cathode particularly at high current densities.

### CONCLUSIONS

It has been shown that alumina decreases the solubility of aluminum in cryolite melts particularly at high temperatures. It has also been shown that in the electrolyte of the commercial cell there is a layer of measurable thickness close to the cathode containing near-equilibrium concentration of dissolved metal. It is suggested that oxidation of the dissolved species occurs within a central zone in the bath and that metal loss is controlled by the rate of diffusion of the metal through a low turbulent zone.

The implications of these findings for current efficiency are that to improve the efficiency of the process, first it is essential to determine the optimum alumina concentrations for cell operation, particularly with respect to bubble formation and to the viscosity

of the melt, and second, turbulence in the bath must be reduced. In the latter case, some improvement may be achieved by modifying the method of running the cells but the long term solution may lie in modification of cell design to minimize the effect the electromagnetic forces and of the anode gases on convection within the bath.

The analytical and sampling techniques described open up possibilities for the detailed examination of the reoxidation process. For a complete interpretation of the findings it is essential to know the equilibrium concentration of dissolved metal at the surface of the cathode when the composition of the melt is changed by the flow of current.

### ACKNOWLEDGMENTS

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