Crust and Alumina Powder Dissolution in Aluminum Smelting Electrolytes

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Modern smelter potlines often undergo process excursions, which are attributed to "solubility problems" of the alumina used. Assigning the problem to a specific property is, however, a challenge, compounded by the fact that the alumina has usually undergone secondary treatments through a dry scrubbing system prior to arrival at the cell. With a better understanding there is the potential for avoiding some of the troubles experienced in these "alumina solubility" problems but there is a need to clarify what are the relevant chemical and physical properties of the alumina that are having the impact. Published and unpublished data are drawn together here to provide further insight into the alumina solubility issues.

INTRODUCTION

During the last 30 years there have been dramatic changes in both prebaked cell technology and the handling and use of the primary alumina supplied by the refineries prior to its addition to the electrolyte in the cell. Changes in cell technology include resistance-based feeding control to maintain the electrolyte alumina concentration within a target band; a move from massive irregular alumina additions to smaller aliquots via point feeders; a move toward more acidic (high excess aluminum fluoride or sodium tetrafluraluminate) concentrations in order to improve efficiency; partial compensation of the magnetic force fields that generate adverse distortion and high flow velocities; reduced electrolyte volume per operating kilo amperage; and operating the cells at lowest excess energy, and hence a minimum superheat of the electrolyte through relying on side freeze to protect the cell from leakage and corrosion.

Engineering and environmental control changes have also taken place. These include changed handling systems for the transport of the alumina, the hooding and collection of cell gases directing them to dry scrubbers, and the use of the primary alumina as an absorbent for recycling the fumes and gaseous emissions.

This range of changes impacts many of the conditions that have the potential to alter either the concentration and distribution of the alumina at the cell, or alternatively, the conditions for its dissolving that may impact its speed. Compounding this, while there has been a universal trend in the technology, subtle differences exist in almost all technologies, even in different generations of the same. This makes isolating the problems much more difficult.

Reported "alumina solubility" problems[1] from operating smelters include increases in operating temperature, anode effect frequency, and amount of sludge (and the associated control noise), as well as greater difficulty in controlling the chemistry at or near the optimum value.

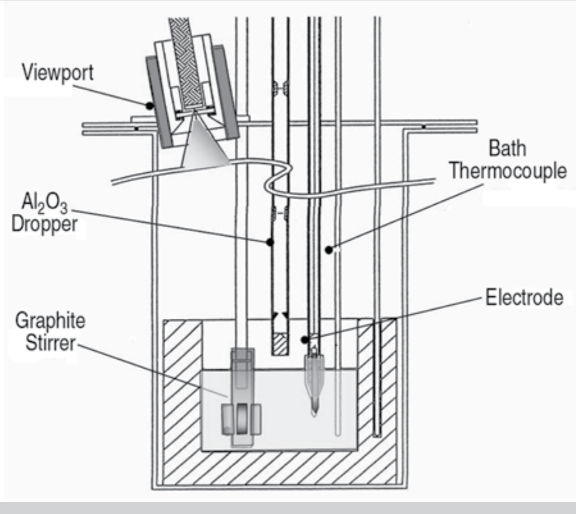

Figure 1. A schematic of apparatus to measure the solubility rates of alumina in electrolytes under controlled conditions.

ALUMINA SPECIFICATIONS

Historically, most of the alumina specifications revolved around purity requirements plus a comfort factor that ensured a supply of a material conformed with the one that a smelter found to be suitable. Subsequently with the universal introduction of dry scrubbing and the greater use of both point feeders and enclosed conveying systems for transport of the alumina, other properties have been expanded into the specifications. These properties include specific surface area, flow funnel tests for measuring flowability, and more recently, dustiness and attrition index.

What is meant by alumina solubility? In the industrial context it does not refer to the saturation solubility that can be predicted from phase equilibrium, but is more closely linked to the speed with which it dissolves. Practically, it refers to the tendency of all the alumina-containing material that is attempted to be or is actually introduced to the electrolyte from above its surface to dissolve and mix in the fluid before it can settle down beneath the metal pad, forming a resistive accumulation of a slurry containing alumina and cryolite-rich electrolyte.

The steps in the overall alumina dissolution and consumption are preheating of the alumina from its storage to the temperature of the dissolution process, transfer of heat to the alumina added from the electrolyte, reactive dissolution via the endothermic process, and the mixing of the dissolved product around the cell's inter-electrode gap prior to decomposition at the anode surface.

There are two accepted dissolution reactions,[2] both of which are endothermic. (See Equations 1 and 2 in the Equations table.)

Equations

$$Na_3AlF_{6\,(l)} + 2Al_2O_{3\,(s)} \rightarrow 3Na_2AlO_2F_{4\,(dissolved)} \tag{1}$$

$$4Na_3AlF_{6\,(l)} + Al_2O_{3\,(s)} \rightarrow 3Na_2Al_2OF_{6\,(dissolved)} + 6NaF_{(l)} \tag{2}$$

$$\text{Rate of Dissolution} = k\,(C_{Al2O3,\ saturated} - C_{Al2O3,\ electrolyte}) \tag{3}$$

Measurements of the energy required for the dissolution, $\Delta H_{(dissolving)}$, range from ~106 kJ/mol to 130 kJ/mol Al_2O_3; the required energy is higher at the lower alumina concentration. When the preheat energy required to lift the alumina temperature to that at which it dissolves (between 90 kJ/mol and 112 kJ/mol Al_2O_3) is added to the energy for dissolution, the heat required is enough to lower the electrolyte temperature by approximately 15°C for a 1 wt.% addition. For modern cell operation this value can be greater than the energy available purely by cooling the available electrolyte without some freezing and therefore heat transfer and heat flow have the potential of being important.

Based on the normal rate equations for heterogeneous processes such as the dissolution reaction, the following are key features that would maximize the speed with which the alumina dissolves:

- Having the maximum concentration of the cryolitic species in the electrolyte (and hence tending toward a neutral electrolyte)
- Having the lowest dissolved concentration of the reaction product within the electrolyte
- Having the maximum accessible interfacial area
- Having the maximum heat transfer rate to the surface
- Having the linked maximum mass transfer rate of the product away

This is supported by fundamental studies of sludge dissolution by J. Thonstad, P. Johansen, and E.W. Kristensen[3] where their studies reduced to an equation analogous to Equation 3. In this equation, in the operating electrolyte concentration range, the rate constant k is dependent on the electrolyte stirring or interfacial mass transfer rate. The saturation solubility, $C_{Al2O3,\ saturated}$, decreases as the AlF_3 concentration in the electrolyte is raised.

For the dissolution of sludge, alumina powder, and crust (which is essentially solidified sludge), defining the interfacial area for both heat transfer and dissolution is strongly dependent on both the tendency of the material to disperse and the associated agitation.

IMPACT OF SPECIFIC PROPERTIES ON THE DISSOLUTION PROCESS

Within a smelter cell it is not possible to control a particular parameter with the required precision to determine its impact on the solubility. Achieving an analogous simulation within a laboratory cell is almost equally difficult. The apparatus developed to help determine the standing of parameters approached pilot plant scale for the latter reason and is illustrated in Figure 1.

Key features of the apparatus were: use of a fiber optic cable interfaced to a video recorder to observe the behavior of the alumina powder added to the electrolyte; use of a specially designed stirrer to impart the required electrolyte flow velocities that are compatible with both measurements and models developed for smelting cells; use of a refined version of the fast alumina concentration analysis developed earlier; and use of simultaneous thermal analysis for following the energy flow of the fed alumina through the dissolution process.

A correlation was developed between mixer speed (rpm) and electrolyte flow velocities to simulate the range determined by analogous modeling and bath flow velocity measurements.

The analytical probe could measure alumina concentrations at approximately 2 s intervals with a precision of 10% of the analyzed value in the low alumina concentration range typically used today. For these studies between 0.2 kg and 0.6 kg of electrolyte were used, with the size of the alumina addition being equivalent to that mass needed to lift the alumina concentration by 1 wt.% or less. Full

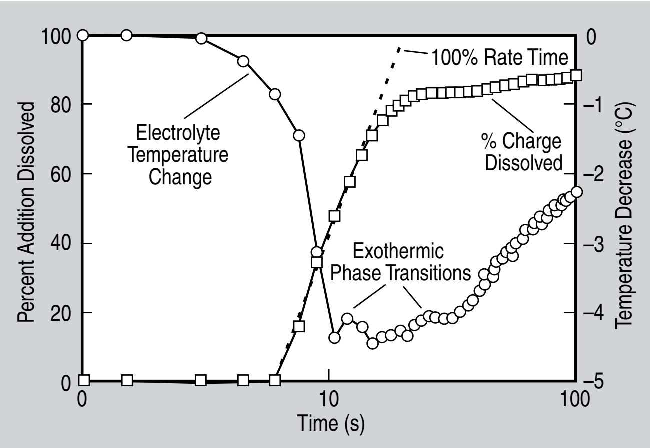

Figure 2. A typical dissolved concentration versus time curve for a sag alumina with the accompanying thermal impact on the electrolyte.

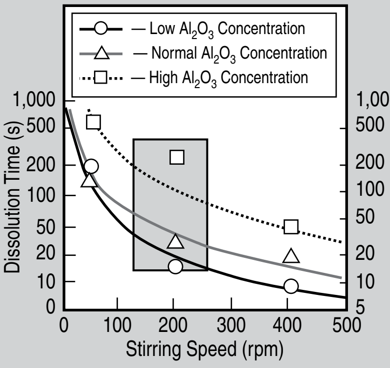

Figure 3. The impact of both mixing and pre-existing alumina concentration on the dissolution time.

Table I. Primary Alumina Properties Sometimes Included in the Specifications

Property Specified	Role / Importance of Property
Purity	Na and Ca for AlF_3 consumption, others metallic contaminants
Loss on Ignition	0°C to 300°C–adsorbed readily released volatiles (can form "volcanoes" for point feeders)
	300°C to 1,000°C–predominantly Al-O-H compounds that are major contributors to HF evolution
Bulk Density	Accuracy of correlation between volumetric feed and assumed mass
Angle of Repose	Covering quality if using only Al_2O_3, flow properties, ability to fill storage vessels, actual volumetric feed transfer
Particle Size Distribution	Consistency of properties, tendency to release dust (fines), cell performance perception of impact on solubility (coarse)
B.E.T. Surface Area	Potential capacity for gaseous HF absorption
Alpha content	Measure of the conversion of the precipitated $Al(OH)_3$ ("trihydrate") to the most stable alumina form; a secondary measure of surface area for a given calcination method; crusting tendency
Attrition Index	Tendency for the poly-granular material to degrade to a finer particle size range
Flow Funnel Test	The flowability of the alumina
Dust Index	Qualitative assessment of ability to become suspended in the cell environment and be transported away

details are given elsewhere.[4,5] A typical response curve is given in the Figure 2 where it is seen that there are various stages detectable—some of which required simultaneous thermal and video recording analysis as well. After a short initiation time the dispersed powder starts dissolving rapidly. However, during the dissolution process, some of the alumina that has aggregated also undergoes exothermic phase transitions. In other instances freezing and clump formation that retards the dissolution can be observed. The freezing and aggregation is variable, reducing the repeatability for a given set of conditions. However, trends could be discerned from repeat measurement. This highlights the importance of feeder design.

In interpreting these data on a rate basis, several parameters can be used including the total time to dissolve all the alumina added, the inherent rate for the specific alumina as indicated by the slope of the curve while the powder is dissolving (the 100% rate of Figure 2), and the time for a fixed fraction, such as about two-thirds of the alumina, added to dissolve.

Other indicators come from the thermal analysis, which provides an excellent cross-reference of the importance of variables.

The inherent rate and the time for a high fraction of the alumina to dissolve (typically more than two-thirds) gave comparable trends and were used in the various subsequent studies. The composite process of the powder and the aggregates was discerned through the video recordings and thermal analysis.

IMPACT OF CELL CONDITION AND ELECTROLYTE VARIABLES

The results summarized below are not only based on this core study[4,5] but also on other complementary studies using similarly scaled equipment and laboratory testing.[6–8] The base case was set to simulate typical operating conditions of 10% excess aluminum fluoride and an operating superheat of 10°C.

The effect of some of the variables that change within a point-fed operating cell are illustrated in Figures 3 and 4 and an overall summary of the sequence of studies for the impact of cell condition and electrolyte variables is given in Table I. The highlighted box in Figure 3 encompasses the normal operating range.

The simultaneous importance of heat transfer is illustrated in Figure 4 where faster dissolving alumina additions absorb heat from the electrolyte more quickly. However, in some instances the cooling is limited by the magnitude of the superheat and visual observations clearly associated that with freezing and clumping, causing a retardation of the dissolution rate.

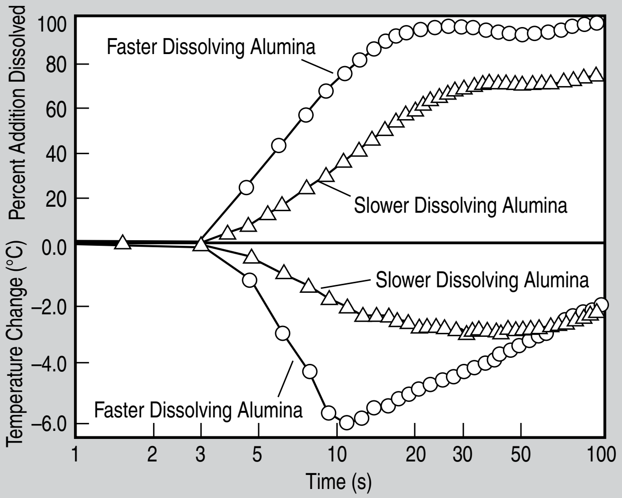

Figure 4. The slow dissolution through inhibited heat transfer associated with some freeze aggregation.

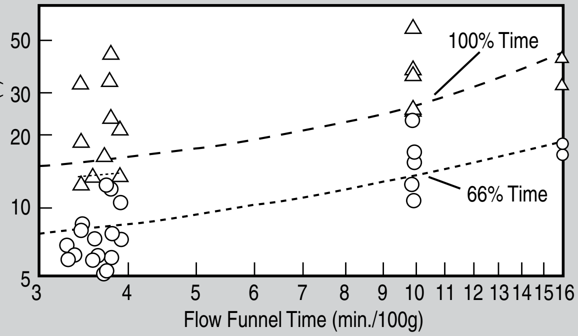

Figure 5. The correlation of flow funnel time with alumina solubility.

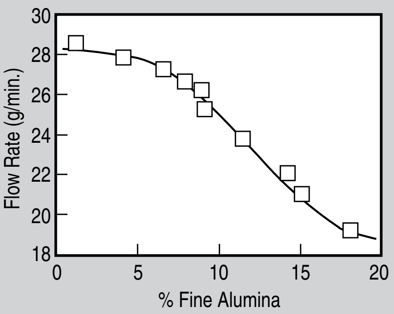

Figure 6. The impact of increasing the fines fraction on flow rate of alumina.

IMPACT OF ALUMINA QUALITY ON DISSOLUTION

By controlling conditions and many repeat measurements, the subtle effects of alumina could be determined.

The flow funnel time was found to have a significant impact for aluminas with high flow funnel times. These were usually also inconsistently flowing aluminas. Visually more flowable alumina tends to disperse better, leading to faster dissolution as is illustrated in Figure 5.

Among the alumina quality features that affect dissolution are fines content, moisture on ignition, gamma/alpha contents, and coarseness.

Fines content is inherently linked with flow funnel time as can be seen in Figure 6. At high fines content the alumina flow becomes both slow and inconsistent, leading to clumping and aggregation and subsequently poor dissolution.

Regarding moisture on ignition, as the concentration of readily releasable volatiles on the alumina increases, the dissolution time is found to reduce. Typically a 15% to 20% reduction can be achieved within the normal operating range. While this can be attributed to aiding dispersion and minimizing aggregation, it may also be linked with its impact on the tendency for alumina to flow more freely at higher moisture contents.[6]

The dissolution of high gamma alumina visually follows a different path with the phase transformation aiding the dissolution process. By contrast, the high alpha content alumina tended to dissolve less and clump and be more dependent on high superheats and stirring.[9]

Finally, when the speeds of the coarsest 50% of an alumina sample were compared with the finest 50% essentially no differences in dissolution times could be observed. However, in these aluminas the size fraction can have different impacts on the flowability of alumina and therefore the impact could be dependent on the specific source.

Linking Fundamental Data to the Dissolution of Alumina in Operating Cells

P. Homsi[1] has reported correlations between high fines content and changed bulk densities of the aluminas on the solubility, as for example reflected in a higher anode effect frequency (due to insufficiently dissolved alumina). This is consistent with the observations of the impact of flowability, mixing, and heat transfer on the dissolution process.

Figure 7 presents some operating data for a point-fed cell that undergoes the normal range of operating variability but has superimposed on it an alumina solubility problem. For modern control systems, when insufficient dissolved alumina in the electrolyte is automatically detected, extra additions are made. The amount of alumina being fed into the cells is in approximate balance when the aluminum fluoride concentration and temperature are within their target bands. However, for higher aluminum fluoride concentrations (and also low temperatures and superheats) there is an overfeeding of the cell because of the poor solubility. In such situations the excess alumina settles as sludge/muck underneath the metal pad. As particularly highlighted in days 75–81, where there was low superheat and high aluminum fluoride concentration, the solubility of the alumina was less with considerable sludge formation. The anode effect frequency (which is normally 0.06 anode effects per cell day) increased enough to double it for the period of the data presentation. These trends are consistent with the process conditions for good solubility: maintaining an adequate superheat (preferably greater than 8°C), keeping the excess aluminum fluoride concentration close to the target value, and keeping the alumina concentration in the target band.

The operating problems highlighted here are symptomatic of a typical operating cycle which also emphasizes the importance of heat balance (see Figure 8). The ultimate impact of the high-temperature, low aluminum fluoride concentrations is a poor cell performance as reflected by a low current efficiency.

Consequently, while alumina properties are important, keeping the cell operating conditions within the target band helps avoid serious difficulties (see Table II).

CONCLUSIONS

As shown in Figure 8, smelters have two approaches for minimizing alumina solubility problems. The first is preven-

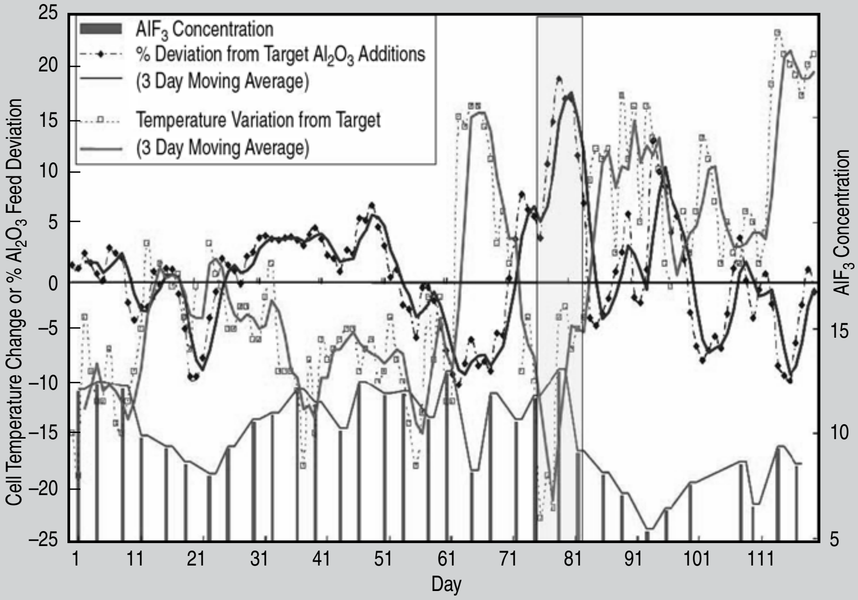

Figure 7. Fluctuations in cell conditions and automated alumina feeding as a consequence of changed alumina solubility.

Table II. The Impact of Conditions at the Cell on Alumina Dissolution

Mixing / Electrolyte Flow	More than a twofold impact on dissolution speed is observed by having good agitation that avoids aggregation.	Poor mixing gives poor heat transfer and, the combined effect gives extremely slow dissolution.
Alumina Concentration	Within the normal operating range, increasing the alumina concentration can give a 50% decrease in dissolution speed. At very low alumina concentrations, however, this impact is negligible.	This is consistent with the basic dissolution equation and localized interfacial conditions.
Aluminum Fluoride Concentration	In the normal operating window of smelter cells (6–14%), this has been found to have a 50% impact on the dissolution speed.	The combination of low operating temperature and high AlF_3 concentrations the worst.
Heat Transfer	Of similar importance to electrolyte agitation—poor heat transfer increases the tendency to form frozen aggregates. Worse for larger additions.	High superheat helps reduce the extent of freezing.
Feeder Design	For fast dissolution it is important to have a steady, dispersing flow rather than "rapid" which can clump.	Keeping feeder hole open aids dissolution.
Mass of Feed	For a given accessible electrolyte volume, the smaller the total mass of addition the faster the dissolution.	Linked with both mixing and heat transfer.

tion by having an alumina of such a quality that it maintains its critical properties at the target values until delivered to the cells. To achieve this the aluminum smelting industry would need to come to an agreement on, first, what the critical properties are for modern-day smelting and, indeed, what values of these properties (as well as tolerance bounds) are needed. With significantly different technologies operating this is a challenge and has not been possible to date.

The second approach may be one of adaptation at the smelter cells where alterations to operating and control parameters can be made when variations occur in incoming shipments of alumina. The smelting cells have been modified over the years with the objective of increasing productivity but less emphasis has been given to the alumina transport even though it is known that, for example, the degree of aeration introduced strongly influences the flow properties of alumina.

Immediate adaptation in operating and process control parameters can also be made when changes in bulk density and alumina purity occur. Rather than relying on the common built-in automated adaptation it is better to make step changes. P. Navarro[10] has demonstrated altering feed strategies to handle different arrival times and rates of the alumina at the electrolyte can be a valuable way of improving cell performance and reducing anode effect frequencies. Therefore there is probably considerable scope existing already.

Perhaps what is needed most is to move away from the blame syndrome toward a solution approach and to recognize that the magnitude of the alumina solubility problems can be reduced considerably with pre-planning and forethought.

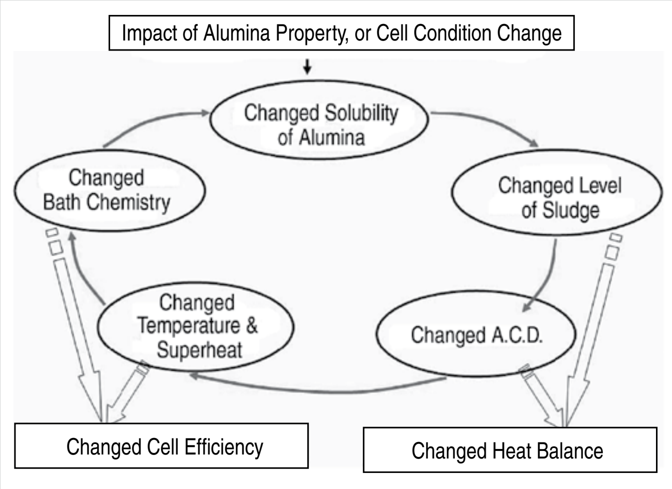

Figure 8. The cycle that occurs in operating cells through alumina solubility.

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