

FURTHER STUDIES OF ALUMINA DISSOLUTION UNDER CONDITIONS SIMILAR TO CELL OPERATION

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ABSTRACT

Previous studies (1) have highlighted that thermal effects, method of addition and the dispersion of alumina (which is aided by the release of volatiles, for example) are all important. However, those studies were unable to derive quantitative assessment of the relative importance of the various structural properties of alumina versus cell operating variables. The earlier apparatus has been modified by incorporating a fibre optic cable, variable feeder design and modified stirring for control of mass transfer thus increasing sensitivity. After determining the importance of electrolyte superheat, its velocity, the alumina concentration and method of addition, the experimental conditions could be adjusted for a fast dissolution regime for normal alumina. This has enabled the importance of selected physical or structural properties of alumina to be determined. The results show that the most important structural properties are those effecting the flowability (or flow funnel time), the particle size (favouring coarse material) and loss on ignition. The BET surface area is also important, but this is inter-related to loss on ignition generally. While structural properties can change the dissolution time, the magnitude of dissolution time is influenced more by operating conditions.

INTRODUCTION

Modern smelting technology utilizes a number of technological advances which are directly or indirectly related to either alumina quality or its feeding technology. All process control strategies employed rely on the alumina dispersing and dissolving readily in the cells if they are to give their peak performance. However, many of the design and operating changes made - such as reduced flow velocities through magnetic compensation, lowering the cell operating temperature, and using lower melting electrolytes - either reduce the saturation solubility of the alumina (and hence its capacity to dissolve) or alternatively lower the rate with which the alumina or sludge dissolves (2). Thus, nowadays, cells are more sensitive to problems arising from "sludge/muck" and "ridge" formation. As a flow-on from this, it is more desirable to ensure a smelter uses a "fast dissolving" alumina to the cells and therefore the properties and conditions that influence alumina dissolution have assumed greater importance.

Cross-comparing plant experience with different aluminas is a dangerous (but frequently used) practice because of the wide range of cell technologies feeding and operating strategies used. Similar criticisms can also be directed to comparisons between the more fundamental studies that have been made on alumina dissolution in

laboratories, since sample treatment, equipment design, processing conditions, and methods (whereby complete dissolution is assessed) have also varied. In the last 10 years this laboratory has performed a large number of dissolution measurements and the results of some of these have been reported elsewhere (3-5). During this period refinements in techniques have been made to the extent we are closer to quantifying the impact of relevant variables.

EXPERIMENTAL

As it is desirable to have a good basic understanding of how structural differences in smelter grade aluminas influence the dissolution behaviour, we have developed an apparatus that gives some form of cross-check on the measurements and reduces the effect of specific designs and techniques. The apparatus developed combines three different methods:

- electroanalytical measurement of the change in dissolved oxide concentration change
- thermal analysis of the electrolyte following alumina addition
- visual recordings of interactions of the alumina with the electrolyte.

The advantages of using a combination of techniques include:

- not having to rely on the results of one method alone
- providing an explanation/cross-check on apparent abnormalities from an individual test.

A large crucible (ID of 100 mm) was used so that up to 1 kg of electrolyte could be used if desired. The stirrer design was optimised from modelling tests and average electrolyte velocities could be adjusted by varying the stirrer speed (6). For most tests the electrolyte velocities were held in a narrow range with the average value similar to the average reported in the literature for operating cells.

The use of a video recording system (via a fibre optic cable) to record events, while simultaneously measuring the dissolved oxide concentration, had the advantage that the colour contrast could be subsequently varied to highlight features associated with the addition and dissolution phenomena.

Measurement of dissolved oxide concentrations could be carried out at approximately 1 second intervals using a modification of single sweep cyclic voltammetry. The analytical electrode is held an appropriate rest potential to ensure dissolved metals are always oxidised and do not interact with the electrode. This combined with a linear sweep rate of approximately 20 V per second in the forward direction, but much faster in the reverse direction, ensured the electrode could be reproducibly cycled every 1 second if desired. Because of superimposed electrode processes, it was found that using the area of the curve up until anode effect was the most sensitive and reproducible parameter measured, but even then variations of up to 10% were still observed between successive measurements. Since these variations were of a cyclical nature, due to the irreversibility of the system, they could be filtered out by performing a Fourier transform, thus generally improving the accuracy and improving the earlier procedures.

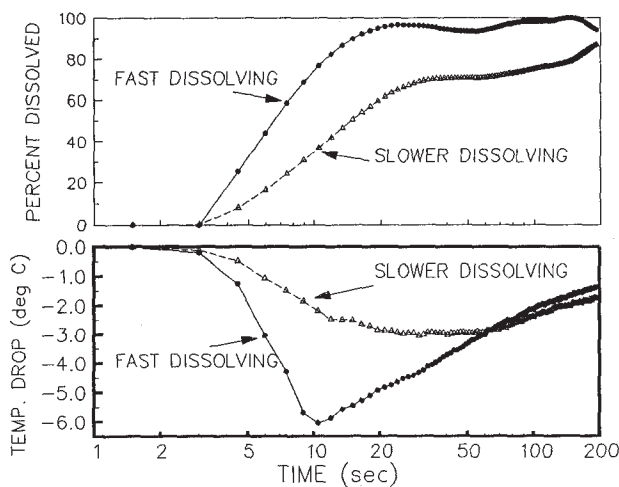


Figure 1: Dissolution Characteristics of Two Aluminas & Their Accompanying Thermal Effect.

Experimental Procedure

Before a dissolution measurement, the required electrolyte is synthesised, melted, its freezing point determined and it is then thermally equilibrated at the desired temperature. The dissolution characteristics are usually measured by addition of a charge of alumina sufficient to increase the concentration by between 0.7 and 1.5 wt%. Normally the alumina is added cold or with only a limited amount of preheat.

If alumina powder is added rapidly and uniformly, and disperses, each dissolving particle should be independent of the other. Thus, in the absence of secondary effects the dissolving time would be expected to be independent of the mass added. Accordingly, it was found to be convenient to express the dissolution of the material in terms of the percent of the charge added as is seen in the typical results are presented in Figure 1. The associated thermal response for these two curves is also presented. This set of data illustrates several key features including:

there is an initiation time before the alumina starts dissolving

- initial dissolution is fast with the process slowing down towards the end
- the thermal response associated with fast dissolution is characterized by a more rapid initial temperature decrease of between 4 and 6°C typically, with a slower thermal recovery after much of the alumina has dissolved.

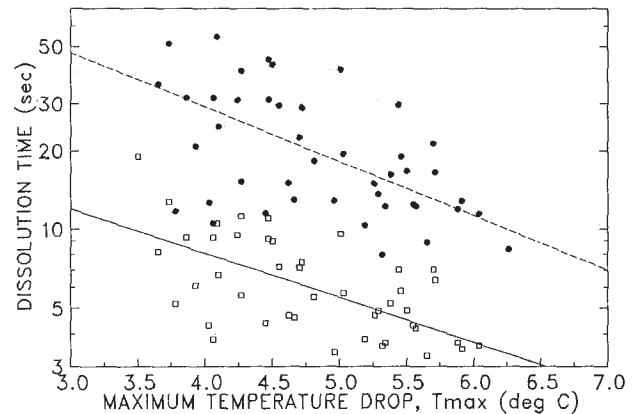


Figure 2: The Inter-relationship Between Dissolution Time & the Maximum Temperature Drop Following Addition.

The inter-relationship between two techniques is illustrated in Figure 2, where the magnitude of the initial thermal response is correlated with the dissolution time. Here it is seen that a definite correlation exists but there is considerable scatter. Some deviations can be explained by a combination of electrolyte freezing on the added alumina, and the occurrence of the exothermic transformation to alpha alumina prior to dissolution, while irregular break-up of aggregates and other effects also contribute. Unfortunately the thermal response of the thermocouples varies, making it difficult to precisely align the various techniques on a second to second basis. The video recording of the dissolution was useful for indicating the initial interaction of the bath with the powder alumina samples, the flow/dispersion behaviour, the release of volatiles and dusting, and as an aid to understanding abnormal results. The alumina was generally much colder than the bath because the powder was preheated to less than 200°C as a result of its fall through the feeder into the cell.

Table 1. Variables Studied	
Related to Operating Conditions and Design	Properties of Alumina
- Electrolyte Velocity (stirring)	- Particle Size & Distribution
- Superheating (heat transfer)	- Flow Characteristics (flow funnel time)
- Alumina Concentration	- Volatiles Content (L.O.I., M.O.I., reacted ore)
- Electrolyte Ratio	- Bulk Density (L.B.D., P.B.D.)
- Feeder Dispersion	- Alpha Content

Table 2. Selected Properties of Some Aluminas Studied

BET (m ² /g)	MOI (wt%)	LOI (wt%)	ALPHA (wt%)	FFT (min _{100g})	LBD (g/l)	PM (μm)
47	3.00	0.60	11	5.2	990	104
56	3.00	0.70	4	3.6	994	120
22.5	1.52	0.36	64	3.76	962.0	107.7
67.6	1.20	0.87	1	3.47	902.1	106.7
231.1	1.60	3.19	0	3.96	866.9	115.4
1.01	1.52	0.36	72.5	5.2	990	104
105	3.05	1.82	0	4.25	839	128
54	2.80	0.60	7	3.8	972	118
55.8	0.40	0.30	1	3.3	939	(244)
48.6	0.40	0.30	12	16	939	27
53	2.40	0.60	6	3.7	949	116
42.0	2.03	0.64	15	3.76	931.2	110.7
27.6	1.60	0.47	46	3.80	960.2	110.1
72.2	0.53	0.82	1	3.46	936.7	115.9
162.9	6.40	2.16	0	3.59	897.0	117.5
257.9	1.52	3.47	0	3.89	861.0	121.1
240.9	0.71	3.20	0	3.79	859.6	122.0
44	3.00	1.30	11	10	1027	113
86.3	2.80	1.20	0.2	7.5	875.0	53.5
88.9	3.00	0.90	0.3	6.7	894.4	63.7
73.9	1.33	0.90	1	3.27	919.4	126.6

As a result, some electrolyte froze on to the underside of the alumina as it spread across the surface, holding it into definite rafts that were visible on the melt surface. Movement of the alumina raft could be observed and breakup and penetration of some of the charge into the electrolyte was continually occurring.

Scope of Study

Of the many variables associated with either the properties of the alumina or the process conditions that may affect dissolution, the variables studied in this investigation are summarized in Table 1.

Whilst it is not possible to independently vary all properties (recognising links between surface area, alpha content and volatiles content, for example) a wide range of aluminas was studied. These are summarized in Table 2 where BET refers to the traditional BET surface area, MOI and LOI are the moisture on ignition and loss on ignition respectively, and the alpha content has been determined via traditional methods, as has the loose bulk density (LBD). The flow characteristics of the alumina are represented by the flow funnel time (FFT) which is essentially based on the method described by Hsieh, (7). Although only the 50 percentile particle size diameter (PM) is listed, the distributions for each sample has also been characterized by the 10th and 90th percentiles.

THE EFFECT OF OPERATING CONDITIONS ON DISSOLUTION

This sequence of experiments was carried out using a well characterized typical commercial alumina and except for the variable being measured, the same operating conditions were maintained. In each instance the dissolution was measured at four discreet alumina concentrations which encompassed the full range encountered in operating cells. This range varying from 0.7 to 3.5 wt% alumina. Generally dissolutions were measured in

approximately 600 g of electrolyte with the following experimental conditions:

- constant stirring rate
- superheat = 10 °C
- cryolite ratio = 1.20
- calcium fluoride content = 5.0 wt%

By using tracer studies and modelling, it was found the electrolyte velocities varied between 5 and 15 cm per second for the mass of electrolyte and stirring speed used. This is comparable to the range seen for typical gas induced electrolyte flow velocities in actual operating cells. Within this phase of the study a large variation in dissolution times was observed, varying from 15 to more than 500 seconds for all the added charge to dissolve.

Table 3. Effect of Electrolyte Velocity

RPM	Flow Rate	Range for Dissolution Time
200	15 cm/s	20 - 35 seconds
0	<3 cm/s	120 - 500 seconds

The effect of electrolyte velocity

The flow rate could be varied by changing the speed of the stirrer or alternatively by changing the mass of the electrolyte. Results given in Table 3 are for dissolution times at an average alumina concentration of 1.5 wt% in an electrolyte with a cryolite ratio of 1.20. Using electrolyte flow conditions similar to that encountered in smelting cells (velocity ≈15 cm/s⁻¹) it was found that the dissolution was fairly fast typically being between 20 and 35 seconds. However, the situation changed dramatically with no

stirring (other than the natural convection of the experimental arrangement) where the dissolution time increased to over 500 seconds in some instances.

Electrolyte superheat

As shown in the following table (Table 4) superheat becomes more important for conditions where the electrolyte flow velocities are low. Based on comparison with the equivalent conditions of electrolyte flow, decreasing the superheat below 5°C gave at least a 35% increase in dissolution time. In some instances the dissolution time more than doubled.

Superheat	Flow rate	Range for Dissolution Time
>10°C	>10cm/s	20 - 35 sec
2-10°C	>10cm/s	20 - 50 sec
0-10°C	< 5cm/s	180 - 500 sec

Method of addition

Only limited variations in feeder design can be made in a laboratory cell. Earlier work by Bagshaw and Welch (3) showed the method of addition clearly influenced the results. In this work there was a 40% variation in the results for the two different addition methods used despite other conditions, remained the same.

Electrolyte composition

As seen in Table 5, increasing the excess aluminium fluoride content by lowering cryolite ratio from 1.20 to 1.08 almost doubled the dissolution time.

Ratio	1.20	1.08
Average Time	25 secs	48 secs
% Increase over CR=1.20	0	90%

Influence of alumina concentration

Figure 3 presents the trends for dissolution time as a function of alumina concentration for a large number of measurements made with alumina from a common source. Because of the scatter an accurate correlation equation cannot be derived. Different curve fitting techniques all gave correlations that indicated the dissolution time increased with alumina concentration. The data shows 10-20% increase in dissolution time when the alumina concentration is increased from 1.5 to 3.5 wt%. However, it should be noted that at higher concentrations, larger alumina additions were made. Based on the assumption that dispersed powder should act as discrete grains this difference should be negligible.

However, both the video's and the thermal effects suggest some freezing and aggregation occurs. Since this would be worse for larger additions, extended dissolution times are more likely. Thus the concentration effect is likely to be magnified. In another study involving equal sized additions (8) there has been no discernable concentration effect. However, this other study only involves a limited number of data points.

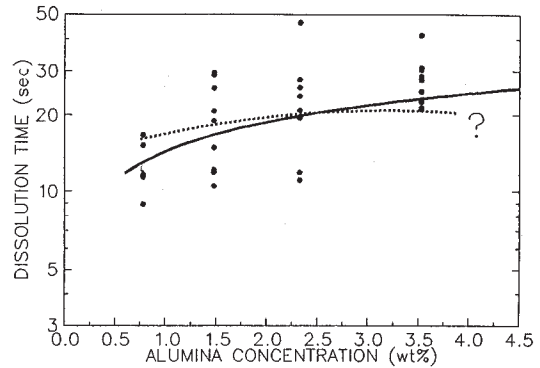


Figure 3: Alumina Dissolution Times at Different Concentrations (but for different sized additions).

INFLUENCE OF ALUMINA PROPERTIES ON ITS DISSOLUTION

As has already been noted, many of the properties of alumina derived from a given source are somewhat inter-related. Therefore, each specimen will have several varying properties and accurate correlation becomes difficult. (This is especially so since variations through very minor deviations in experimental conditions have been demonstrated above.) Consequently plots were performed for both 50% of the sample dissolving as well as complete dissolution and consistency of trends for both curves becomes a basic requirement. All the following figures encompass both curves.

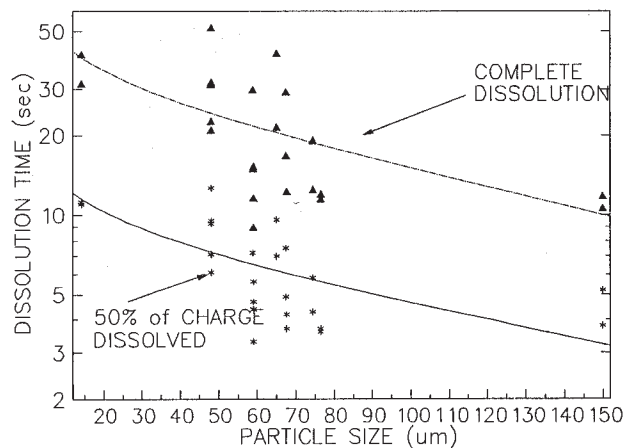


Figure 4: Effect of Particle Size on Dissolution Time.

Particle size

When discrete size fractions are removed, we have changes in bulk properties. For the data presented in Figure 4, the particle sizes in the medium range have a wider span than the two extremes. The figure shows that dissolution time decreases with increasing particle size. This finding makes one wonder why there is an upper limit on the particle size of alumina in many of the smelters' specifications. Whilst fines led to slightly lower dissolution rates, a greater problem observed was their tendency to blow-back as dust during addition to the alumina.

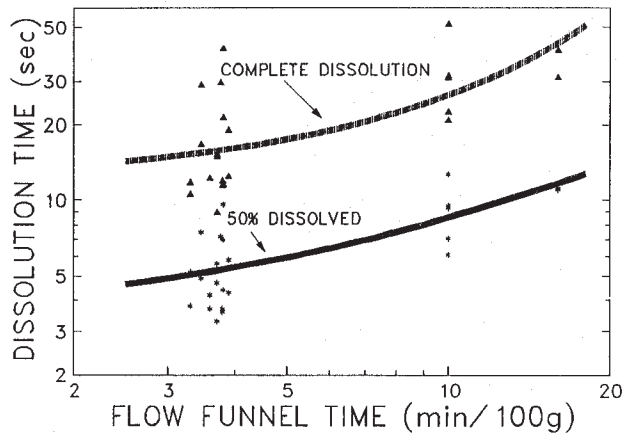


Figure 5: Relationship between Flow Funnel Time & Dissolution Times.

Flow funnel time

The correlation between flow funnel time and dissolution time is seen in Figure 5. This effect is probably indirectly related to uniformity of the addition and mixing. Both the time for 50% of the charge to dissolve and the time for it all to dissolve increase as the flow funnel time increases.

Volatiles content

Whilst we were unable to ascertain reliable correlations for moisture on ignition, the loss on ignition plays an important role - generally the higher the loss on ignition the shorter the dissolution time (Figure 6). This is consistent with earlier observations by Bagshaw and Welch (1). At low LOI's (below 1 wt%), it is possible that an increase in dissolution time up to 30% might be observed if the volatile content is reduced too much. The influence of volatiles is not restricted to water as absorbed hydrogen fluoride also increases the rate. Despite this, some reacted alumina dissolved slowly but those samples invariably had long flow funnel times.

BET surface area / Alpha content

Since these are so closely inter-related they are discussed together. Correlation of BET data established a trend for shorter dissolution times for aluminas with high surface areas. Aluminas with a low alpha content also had shorter dissolution times. However, the high BET/low alpha aluminas had high LOI's and therefore one cannot positively ascribe the trend to BET surface area or alpha content. Within the operating range of BET surface area the change is small.

THE IMPORTANCE OF VARIOUS VARIABLES

Results show a greater variation in dissolution time results from varying conditions related to operation or design than by varying the specific properties of alumina. Both heat and mass transfer play important roles as can be seen from the following summary of conditions that impart fast dissolution:

- high electrolyte velocity

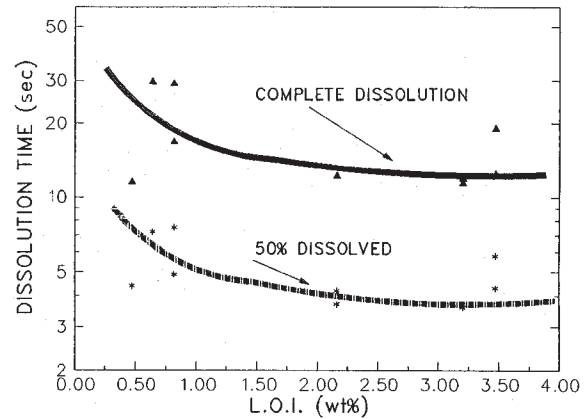


Figure 6: Effect of L.O.I. on Dissolution Time.

- good feeder dispersion
- high superheat
- high volatile content of the alumina
- low flow funnel time (high flowability) of the alumina

The effect of particle size reinforces the flow funnel time observations since the coarse material tended to flow better as did the aluminium with higher volatiles content generally. Observations on feeder dispersion and electrolyte are also consistent with heat and mass transfer being important. In the case of electrolyte ratio at low values, the saturation solubility is reduced significantly and therefore the mass transfer becomes more important.

Although the coefficients associated with each variable are not accurately defined, the impact of various changes in alumina quality can be assessed from the above data.

Expected variation through alumina quality

Different refineries produce aluminas with differing properties and this makes it unrealistic to compare dissolution times on properties alone. For example, different calcination conditions give different alpha and LOI and flow funnel times, all of which have a bearing on dissolution but not in a simple manner. Accordingly we have monitored the variations and properties of aluminas from two quite different refineries over a 12 month period.

The dissolution rates of these aluminas have also been measured. The variations observed are summarised in Table 6. The difference in dissolution times measured for this range of aluminas illustrates the inherent difference between the two aluminas, although typical dissolution rates for each are within 30% of each other. For both alumina sources, the percent variation observed from the average over the year was within 50% when identical conditions (alumina concentration super heat, electrolyte composition and addition technique) were used.

As seen in Table 6 the effect of no single property would have changed the dissolution by more than 25% whilst, because of inter-relationship of effects, the overall percentage expected would be less than 55%.

TABLE 6. Shipment Variations and the Impact on Alumina Dissolution Times

PROPERTY	UNITS	REFINERY A		REFINERY B		% CHANGE IN DISS. TIME
		RANGE	TYPICAL	RANGE	TYPICAL	
DISSOLUTION TIME	s	27 - 48	35	20 - 40	26	<50%
ALPHA*	wt%	14.0 - 17.5	16.0	5 - 10	6	<15%*
L.O.I.*	wt%	0.67 - 1.25	0.95	0.5 - 0.9	0.6	<20%*
B.E.T. AREA*	m ² /g	76 - 82	80	55 - 65	55	<15%*
BULK DENSITY	kg/m ³	928 - 1004	950	950 - 990	950	<8%
-45 MICRON**	wt%	6.7 - 11.5	8.5	4.5 - 9	6.0	<5%
F.F.T.**	s/100g			3.6 - 7	4	<25%

It is noted in Table 6 that alpha content, loss on ignition, and BET surface area are inter-related. So too are the particle size distribution (as reflected by the -45 micron fraction) and the flow funnel time.

The data presented in Table 6 clearly demonstrate the importance of alumina quality consistency for dissolution time since a 50% variation can occur.

Cell dynamics and alumina dissolution

In recent years, more attention has been given to the dynamics of cell operation and it has been demonstrated that there is a significant range of operating conditions within a cell. Variations in operating procedures also aggravate this. The magnitude of swings as well as modelling of the impact has recently been presented (9-11).

Thus, for a typical cell we can summarise the range of process conditions that can occur through cell dynamics. Some of these will occur over a short time and others over a longer time. Table 6 gives the impact of the change in key variable on the overall dissolution time, and it is seen that for extreme conditions the impact can be dramatic.

Whereas alumina quality can cause a 50% increase in the time required to dissolve it, we now see more than a twenty-fold or >2000% increase is predicted (and also observed in laboratory tests) if the cell conditions fluctuate through the extremes that give both good and bad dissolution. These data do not take into account design variations that also can occur influencing the dissolution time.

GENERAL DISCUSSION

When the dissolution time increases significantly there is a strong risk of sludge formation, and consequently the adverse operating cycle (11) can be readily encountered. Based on the results presented here and our understanding of the impact of sludge formation, there are several checks that can be made to reduce the likelihood of alumina problems occurring in the cell.

Quality checks on alumina that give an indication as to whether an operating problem is likely to be encountered, include the following:

- measuring flow funnel time/flowability of alumina
- monitoring the particle size distribution of the alumina being fed to the cell (especially in the fines fraction).
- determining the volatiles content of the alumina.

Within an operating cell there are several parameters that indicate alumina dissolution problems and these include:

- changes in sludge level and metal heights
- cell temperature variations (especially if cross-linked to a lower average alumina)
- an apparent increase in current efficiency.

The warming trend is related to a lower average alumina concentration because of it not dissolving whilst the displacement of the metal pad by the sludge formed can give false security on the current efficiency.

TABLE 7. Influence of Cell Dynamics on Alumina Dissolution Times

PROPERTY	UNITS	RANGE	TYPICAL	% CHANGE IN DISSOLUTION TIME
ELECTROLYTE VELOCITY	cm s ⁻¹	4 - 25	15	-100 to +500%
BATH RATIO	wt	1.25 - 1.08	1.20	-20 to +80%
SUPER-HEAT	°C	5 - 15	10	-15 to +300%
ALUMINA CONCENTRATION	wt%	1.6 - 4.5	2.0	<20%
DISSOLUTION TIME	s	13 - <500	26	-50 to +3000%

When operating problems are detected, the results also give a clear guide as to possible changes that can be made to operating conditions to eliminate the trouble. Some of these changes are not totally acceptable to people in potrooms operation since they may have a short term adverse effect on current efficiency (even though the long term effect probably outweighs this. The changes that can be made include:

- altering bath chemistry by increasing the ratio, or lowering excess aluminium fluoride
- increasing the cell superheat
- reducing the alumina dump sizes, especially when extinguishing anode effects.

The operational changes that can be made to reduce alumina dissolution times and hence operating problems have a greater impact than normal fluctuations in alumina quality, although it is obviously desirable to maintain a consistent alumina.

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REFERENCES

1. A.N. Bagshaw and B.J. Welch, "The Influence of Alumina Properties on its Dissolution in Smelting Electrolyte" AIME Light Metals 1986, pp. 35-39.
2. K.Grjotheim and B.J.Welch, "Technological Developments for Aluminium Smelting as the Industry Enters the 21st Century" J. of Metals 41 (11), pp12-19, 1989.
3. R.K. Jain, S.B. Tricklebank, B.J. Welch and D.J. Williams, "Interaction of Aluminas with Aluminium Smelting Electrolytes", A.I.M.E. Light Metals 1983, ed. C.J. McMin.
4. R.K. Jain, S.B. Tricklebank and B.J. Welch, "A Study of the Relationship between the Properties of Alumina and its interaction with Aluminium Smelting Electrolytes". Proc. 1st Int. Conf. on Molten Salt, Chem. Tech., Kyota (1983).
5. A.N. Bagshaw, G. Kuschel, M.P. Taylor, S.B. Tricklebank and B.J. Welch, "Effect of Operating Conditions on the Dissolution of Primary and Secondary (Reacted) Alumina Powders in Electrolytes". AIME Light Metals 85, pp. 549-659, 1985.
6. S.R. Brandtzaeg, G.I. Kuschel, S.B. Tricklebank and B.J. Welch, "Studies of Selected Secondary Phenomena that Affect the Performance of Aluminium Smelting Cells", Proc. RACI Int. Electrochem Conf. Sydney, February 1988 pp. 174-178.
7. H.P. Hsieh, "Measurement of Flowability & Dustiness of Alumina", AIME Light Metals 1987, pp.139-149
8. R. Haverkamp (University of Auckland) private communication 1990.
9. K. Grjotheim, B.J. Welch and M.P. Taylor, "Relating Operating Strategy and Performance in Aluminium Smelting Cells - an Overview" AIME Light Metals, 1989, pp 255-260.
10. B.J. Welch, G.I. Kuschel, X. Lui & M.P. Taylor, "Phase equilibria dynamics in aluminium reduction cells: A thermochemical view" Metals Materials & Processes 2 (1990) at press.
11. M.P. Taylor, X. Liu, K.J. Fraser & B.J. Welch, "The dynamics and performance of reduction cell electrolytes" AIME Light Metals 1990 pp259-266.