

THE INFLUENCE OF ALUMINA PROPERTIES
ON ITS DISSOLUTION IN SMELTING ELECTROLYTE

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The dissolution of a wide range of commercially produced aluminas in modified cryolite bath was studied on a laboratory scale. Most of the aluminas were products of conventional refineries and smelter dry scrubbing systems; a few were produced in laboratory and pilot calciners, enabling greater flexibility in the calcination process and the final properties. The mode of alumina feeding and the size of addition approximated to the point feeder situation. Alpha-alumina content, B.E.T. surface area and median particle size had little impact on dissolution behaviour. The volatiles content, expressed as L.O.I., the morphology of the original hydrate and the mode of calcination had the most influence. Discrete intermediate oxide phases were identified in all samples; delta-alumina content impacted most on dissolution. The flow properties of an alumina affected its overall dissolution.

INTRODUCTION

The literature contains a wide range of reports relating to alumina dissolution in smelting bath; most studies have been conducted on a laboratory scale with few systematic studies arising from full-scale smelting operations. The latter situation often includes subjective comments from operating personnel that "this alumina performs better than that" without identifying the important contributing factors. Such cases reflect the complexity of successfully presenting an alumina to, and interacting it with, molten bath.

Invariably each investigator has found that dissolution behaviour depends to a greater or lesser extent on a range of alumina physical properties. Thus statements are made that increased surface area aids dissolution, increased alpha-alumina content hinders it, particle size plays a significant role and primary aluminas perform better than secondary (reacted) aluminas. Some physical properties are closely interlinked: an increase in surface area involves increasing L.O.I. content and there is an inverse relation with alpha-alumina content. Different modes of calcination, such as through kilns or fluid bed systems, impart particular characteristics to the resultant alumina. In addition, the properties vary with the particle size distribution of each alumina as do the handling properties such as flowability.

The objective of the present work was to correlate a wide range of physical properties of a diverse group of commercially produced smelting

grade aluminas with their dissolution behaviour. The study, carried out on a laboratory scale, did not investigate the impact of alumina impurities nor cover any aspects of crusting properties. It was limited at this stage to smelting technologies employing point feeders. The more widespread use of such feeding places greater emphasis on the speed with which the alumina dissolves in the bath. The experimental procedure adopted in the study was designed to equate as closely as possible to the practical operating conditions in point-fed pots.

EXPERIMENTAL PROCEDURE

Aluminas Studied

Some thirty-four individual aluminas were investigated to determine their dissolution behaviour. Thirty of these were products of operating refineries; eight resulted from kiln calcination, the remainder from fluid bed calcination. In addition five of the thirty had been reacted in dry scrubbing systems at smelting plants. Three aluminas were produced from hydrate under laboratory or pilot scale calcination conditions. The final alumina was a chemical grade material with high alpha-alumina content; an additional test involved saturating this with water vapour so that the influence of increased moisture content on dissolution behaviour could be studied.

The range of surface areas and alpha-alumina contents for these aluminas is evident from the data in Table I. Median particle size (PM from Microtrac analysis) ranged from 67 to 106 μm , M.O.I. content (moisture on ignition: to 300C) from 0.4 to 8.3 wt.percent and L.O.I. content from zero to 4.8 wt. percent.

A detailed study of the X-ray diffraction traces from all aluminas enabled an estimate of the amounts of intermediate (transition) aluminas present. A sample of pure gamma-alumina was employed as a reference to determine gamma contents using the 0.197nm peak in the traces; this procedure slightly overestimates this content since delta- and chi-alumina also contribute to this peak, but the error is small. The proportions of theta-, delta- and chi-aluminas were determined using the diffraction peaks at 0.280, 0.271 and 0.231nm, respectively, the last being corrected for the previously determined gamma content. No suitable peak was found to determine kappa-alumina content. The resultant values, listed in Table I, are not

Table I. Surface Area and Phase Composition of Aluminas Studied

Alumina	Surface Area (m ² /g)	Phase (wt.%)					Note
		Gamma	Delta	Theta	Chi	Alpha	
1	55	65	4	14	6	11	
2	46	66	5	11	5	13	
3	51	67	4	14	5	10	
4	51	75	5	11	3	6	
5	50	69	7	13	5	6	
6	47	64	6	14	6	10	
7	47	69	5	12	7	7	
8	44	66	4	13	7	10	
9	43	74	3	13	4	6	2
10	49	75	3	13	6	3	2
11	53	70	4	13	7	6	
12	63	78	5	11	4	2	
13	98	73	3	19	4	1	
14	55	69	3	15	7	6	
15	52	47	2	17	8	26	1
16	7	7	-	4	-	89	1
17	104	58	9	20	9	4	
18	75	83	2	11	3	1	
19	73	62	5	22	7	4	2
20	59	81	3	10	4	2	
21	35	59	5	11	5	20	
22	72	88	2	8	2	-	3
23	46	63	2	10	3	22	1
24	67	63	3	11	3	20	1
25	65	64	2	10	3	21	1
26	53	64	3	9	2	22	1
27	67	72	2	9	2	15	1
28	72	71	5	16	6	2	
29	68	73	6	13	5	3	2
30	71	76	3	14	2	5	3
31	130	68	2	19	5	6	3
32	13	14	2	7	-	77	4
33	64	47	3	19	6	25	1
34	54	45	6	18	7	24	2

Note 1: kiln-calcined

2: reacted alumina

3: laboratory- or pilot-calcined hydrate

4: chemical-grade alumina, subsequently saturated with water vapour

fully quantitative but do indicate trends in these contents which is the relevant point for the present work.

To obtain an indication of the relative flowabilities of the aluminas a funnel with 15° cone and 2mm diameter orifice was set up and times recorded for 10g of each alumina to flow out of the funnel. Four runs were carried out on every sample to yield an averaged flow funnel time.

Dissolution Technique

Rapid linear sweep voltammetry was used to monitor changes in dissolved alumina concentration in molten bath. The technique, with the advantages of fast data acquisition and simultaneous monitoring of bath and crucible wall temperatures, has been previously described in detail (1,2); it provides a reproducible means of determining the dissolution profile of an alumina.

Test conditions were chosen such as to simulate the point-feeder situation for alumina addition. Alumina was added from room temperature direct to

the bath in an amount sufficient to increase the dissolved concentration by one wt.percent, assuming it dissolved completely. Analysis of bath samples subsequent to dissolution runs confirmed that this was so.

All dissolution runs used a constant bath composition of five wt.percent calcium fluoride and ratio 1.20. Such bath had a liquidus of 982°C prior to alumina addition; to ensure minimisation of bath freezing on addition of alumina, all dissolution runs were carried out at bath temperatures around 992-994°C, giving a bath superheat of at least 10 degrees.

Early runs used an open tube feeder for adding alumina. Problems with bath freezing and sludging, reported previously (2), prompted a change to a feeder with an inverted cone at its base to ensure lateral dispersion of alumina over the bath surface. Such style of addition resulted in substantially improved reproducibility in the total dissolution times (+10 seconds in the range 250 to 410 seconds) and bath temperature drops (+0.3°C in the range 5 to 9°C).

Visual observation of the bath surface following alumina addition provided some interesting subjective information. Initial attempts to video-record these events were unsuccessful; further work is being undertaken.

RESULTS

Dissolution Behaviour

The data presented in Figure 1 relate total dissolution time to alumina surface area. This plot illustrates several points:

- for all aluminas studied there is a lack of correlation between these parameters
- the alumina with the lowest surface area and highest alpha-alumina content (No.16 in Table I) had a total dissolution time towards the faster end of the range whereas that with the highest surface area (No.31) was at the slower end
- the alumina with a medium surface area and essentially zero alpha-alumina content (No.22) had the longest total dissolution time
- there is a strong correlation between parameters for families of primary aluminas arising from common hydrate sources but subjected to a range of heat treatments (for both kiln and fluid bed calcination); the

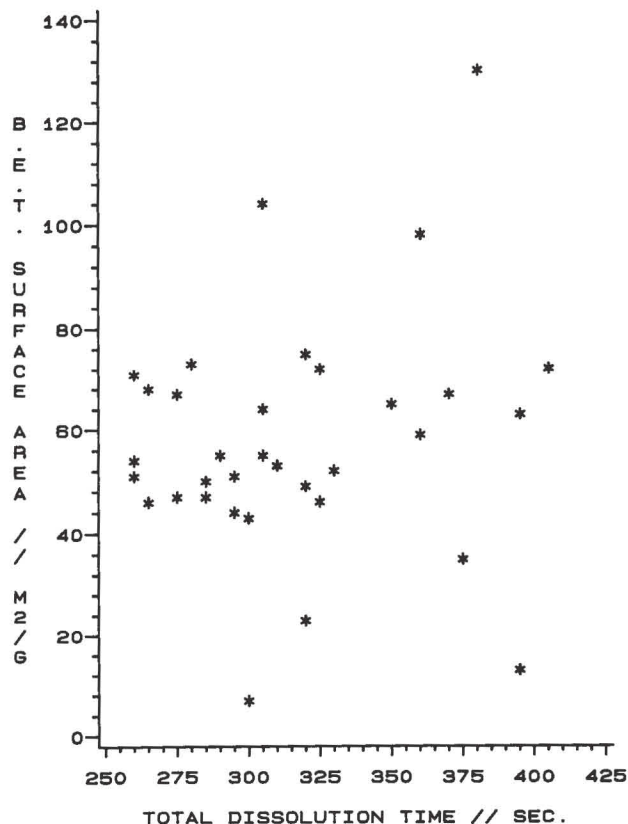


Figure 1 - The B.E.T. surface areas of the aluminas studied plotted against their total dissolution times.

appropriate data are replotted in Figure 2 and the families identified as KC, FC1 and FC2.

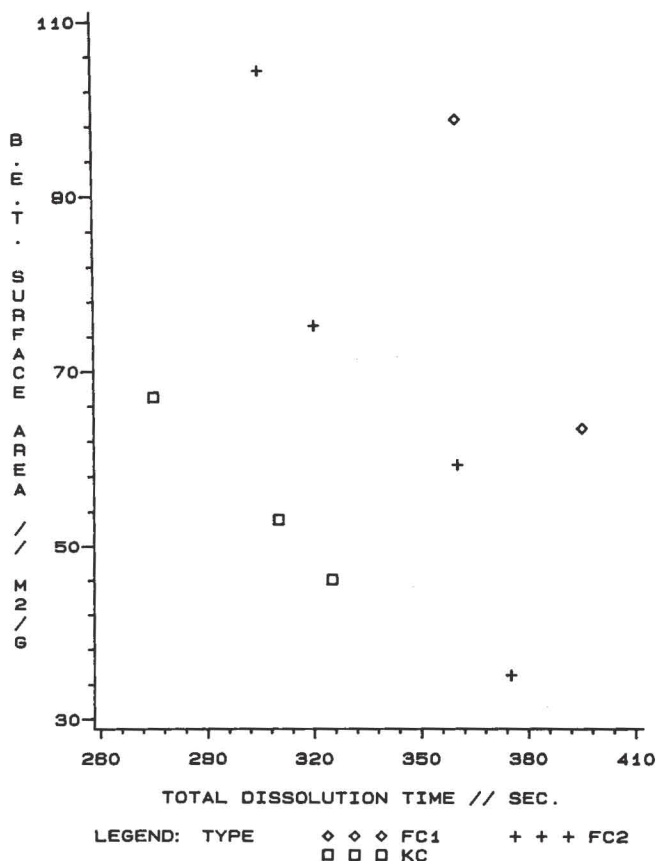
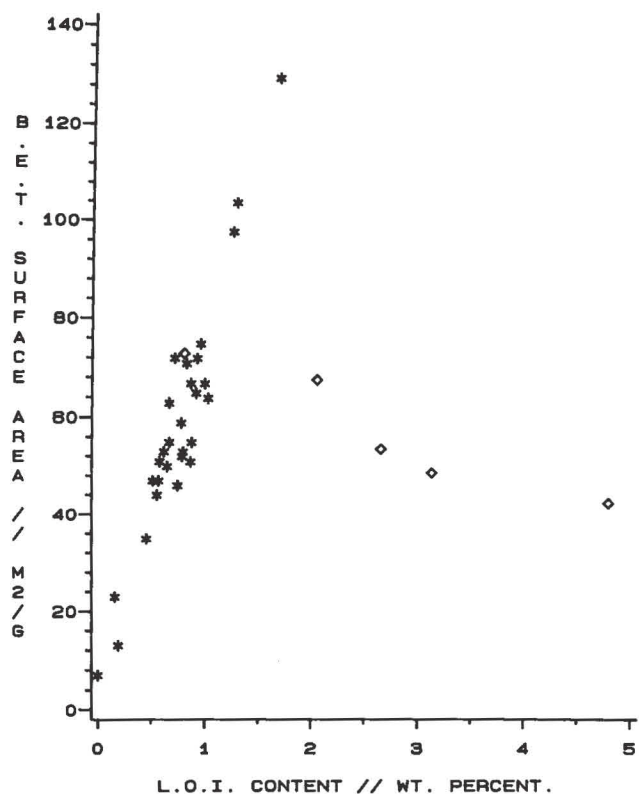


Figure 2 - The influence of B.E.T. surface area on total dissolution time for aluminas from common hydrate sources.

Similar plots for other physical properties such as alpha-alumina content, median particle size, M.O.I. and L.O.I. contents again show a lack of correlation with total dissolution time, for all the aluminas examined. In some cases a particular change is interesting:

- the chemical grade alumina (No. 32 in Table I) showed a 20 percent decrease in total dissolution time following presaturation with water vapour which increased its M.O.I. content by 600 percent but with little change in its L.O.I. content
- in three instances both a primary alumina and its reacted counterpart were examined; in each case the total dissolution time was significantly reduced for the latter, corresponding to a substantial increase in L.O.I. content (as measured by the normal procedure: weight loss from 300 to 1200C) through reaction with pot off-gases.

This latter point is illustrated in Figure 3 which relates alumina surface area to L.O.I. content for all samples. There is a strong correlation between these parameters for the primary aluminas; reacted aluminas usually show an increased L.O.I. content for little change in surface area. Such behaviour for the former samples is again shown in



LEGEND: TYPE * * * PRIMARY ◊ ◊ ◊ REACTED

Figure 3 - The variation of B.E.T. surface area as a function of L.O.I. content for aluminas studied.

the significant relation between total dissolution time and L.O.I. content for the families of aluminas produced from common hydrate sources, as was illustrated in Figure 2 for the influence of surface area.

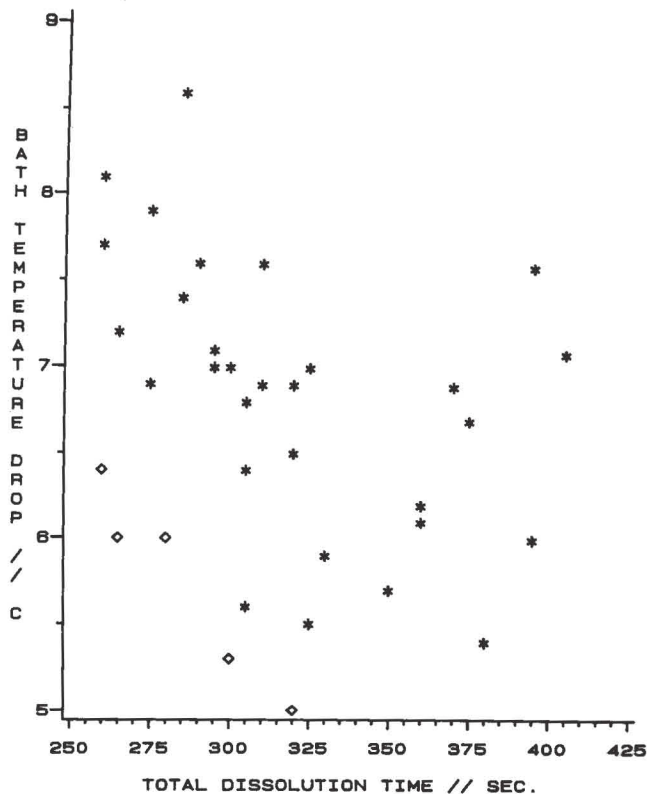
For the intermediate (transition) aluminas, delta-alumina content had the most influence on total dissolution time, followed by chi-alumina and theta-alumina; dissolution time decreased as those contents increased. There was essentially no influence of gamma-alumina content.

Alumina flowability, as measured by the flow funnel time, indicated that slower flowing aluminas dissolved faster overall.

Thermal Behaviour

Contrary to the situation with total dissolution time for all aluminas L.O.I. content and, to a lesser extent surface area, did impact on the magnitude of the bath temperature decrease, following addition of each alumina. As these parameters increased the temperature drop lessened. For the contents of intermediate (transition) aluminas theta-alumina, then chi-alumina, had the most influence; again, as content increased, the temperature drop became less. Flow funnel time had little effect.

The plot of temperature drop versus total dissolution time, shown in Figure 4, illustrates



LEGEND: TYPE * * * PRIMARY ◊ ◊ ◊ REACTED

Figure 4 - The bath temperature decrease observed on alumina addition related to the total dissolution time for each alumina.

again that the reacted aluminas present a distinct behaviour: faster overall dissolution with smaller bath temperature decreases. There also appears to be a similar trend with the other aluminas although the correlation is not as good.

DISCUSSION

The information resulting from the work described herein provides a means to relate the dissolution behaviour of an alumina to its various physical properties. Such behaviour embraces not only the dissolution step per se but includes aspects involving the feeding operation, dispersion of particles in bath, wetting of the alumina surface and possible encapsulation of individual particles and/or aggregates by frozen bath. The last aspect would involve heat transfer to remelt bath before dissolution could continue, thus influencing the overall dissolution time, and was a significant factor in earlier work (2) where the alumina feeding procedure limited effective dispersion in the bath. Thus it is inappropriate to relate the dissolution times reported here with those of other studies which concentrated on the kinetics of the dissolution process itself. However, the present results on a wide range of aluminas do indicate overall dissolution behaviour of relevance to smelters operating with point feeders.

An important conclusion of this work is that, for the aluminas studied, their principal physical

properties have little influence on overall dissolution behaviour. Thus surface area, alpha-alumina content, median particle size and M.O.I. and/or L.O.I. content individually play a minor role in determining the time taken for dissolution in smelting bath, when considering aluminas from many different commercial sources. Such a finding is supported by recent work (3) conducted in a similar fashion (but using visual estimates of total dissolution time) on some twenty-eight commercially produced aluminas.

Notwithstanding this conclusion closer examination of the data indicates some significant features. Figure 2 shows that for particular families of aluminas there is a strong correlation between total dissolution time and alumina surface area. A similar situation applies to L.O.I. content which is not unexpected since this parameter is closely related to surface area, as Figure 3 illustrates. This suggests that the parent hydrate structure (shape, nature of agglomeration, radial versus mosaic core) contributes significantly to the dissolution behaviour of its resultant alumina. Calcination (by kiln or fluid bed systems) to different extents will produce a range of surface areas, or more importantly, L.O.I. contents whilst maintaining to a large extent the original morphology.

The influence of particle structure may further explain the behaviour of particular aluminas such as those with very low (No.16 in Table I) and high (No. 31) surface areas as well as that (No. 22) with essentially no alpha-alumina content.

Reacting an alumina in a smelter dry-scrubbing system contributes to its L.O.I. content and leads to more rapid overall dissolution in the present work. Even presaturating a high alpha-alumina (low surface area) material with water vapour significantly decreased its total dissolution time. Such behaviour points to the influence of the volatiles content of an alumina on its dissolution profile. Particularly under the point-feeder conditions studied, with essentially no preheating of the alumina, these volatiles will be retained until contact with the bath is made. Subsequent release will provide buoyancy and dispersion, both of which will aid dissolution and limit bath freezing (with possible sludge formation). A further factor with the reacted aluminas is that the surface properties of the alumina may have been significantly altered with fluoride capture, leading to improved wettability by bath and reduced interfacial tension at the particle surface.

Limited comment can be made on the influence of the intermediate (transition) alumina contents on total dissolution time since published data on their transformation mechanisms in the presence of molten bath is sparse. The present work suggests that delta-alumina exerts the most influence with theta-alumina having a minor (positive) effect, contrary to a report (4) that this phase in fluid bed calcined aluminas is highly ordered and therefore not very soluble.

The observation that longer flow funnel times related to faster overall dissolution, that is, quicker flowing aluminas took longer to dissolve, may be due to an artifact of the particular feeding arrangement used, bearing in mind the amount of alumina added over a relatively short time span.

However, with the inverted cone feeder employed a fast flowing alumina would tend to empty out of the feeder more quickly, with possible slower dispersion in the bath and greater chance of clumping (and sludging) resulting from bath freezing. Based on such an argument one would expect the slower-flowing aluminas to contribute a greater bath temperature drop during more effective dissolution; the appropriate data did suggest this.

Alumina properties which impacted significantly on the bath thermal behaviour were the L.O.I. content and, concomitantly, the surface area. Such behaviour is to be anticipated if volatiles content contributes to good dispersion through the bath. This is further supported by the data in Figure 4, illustrating that the reacted aluminas, with increased L.O.I. contents, contributed smaller bath temperature decreases and faster total dissolution times than the majority of the aluminas studied.

CONCLUSIONS

From the present study on a wide range of aluminas the important alumina properties impacting on dissolution in smelting electrolyte are:

- the morphology of the original hydrate and the subsequent type of calcination treatment
- the volatiles content, especially in the form of pot off-gases present in reacted aluminas
- the presence of particular intermediate (transition) alumina contents, especially delta-alumina
- the flowability of the alumina in relation to the feeder design employed.

Clearly further study is warranted on the structures of alumina (and hydrate) particles by morphological analysis and alumina surface properties where surface area is too inadequate a descriptor. Work is continuing in both these areas.

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