# The Crusting Behavior of Smelter Aluminas

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Aluminas having a wide range of physical characteristics were added in the laboratory to cryolite melts under different, controlled conditions of temperature and melt composition. Crusts were usually obtained, and their strengths, durability and solubility noted. It was shown that well-formed crusts are produced only by aluminas that are both sandy and relatively under-calcined. Such aluminas flow readily, and have a high surface area and a low $\alpha$-alumina content. The mechanism of crusting is postulated as an initial cooling and freezing of the melt following penetration into alumina on the surface; a strong crust is a consequence of the subsequent growth of a network of $\alpha$-alumina platelets. Aluminas initially of high $\alpha$ content do not form such a network. The difference between crusts formed by alumina additions and by simple freezing of a melt is considered. The effect of different aluminas on cell operation, as a consequence of their different crusting and solubility characteristics, is discussed.

IT has become more widely appreciated in recent years that the physical nature of the alumina used in aluminum reduction plants can greatly influence the operation of the cells. The use of a type of alumina for which the cell is not designed can lead to sludging, excessive open bath, poor current efficiency and general operational problems. The economic consequences may be serious.

The satisfactory operation of an aluminum reduction cell requires a crust to be maintained on the molten bath for as large a proportion of the time as possible. Without such cover heat losses, and evaporation of relatively volatile fluorides, will be unacceptably high.

A crust can form either by a simple freezing of the melt (which is normally maintained at a temperature close to the liquidus), or by the addition of alumina to the surface. Freezing is important in practice and occurs fairly readily; it is, however, impeded by the circulation of the melt and the agitation caused by gas evolution from the anodes. Under suitable conditions a crust will be formed by the addition of alumina, although this crust may break up through agitation or through its inherent weakness.

The stimulus for this work was the observation (at a smelter with prebake anodes and center channel alumina feed), that a change from sandy to floury alumina led to a considerable increase of open bath following routine two-hourly breaks and feeds. As open bath is a general symptom of a poorly operating cell, it was not certain that the crusting behavior of the alumina was the cause. It was therefore decided to observe, under controlled conditions in the laboratory, the addition of different types of alumina to molten cryolite, and to deduce the factors which determine the nature and persistence of crusts so formed.

Closely associated with crusting behavior is the problem of dispersion and dissolution of alumina in the melt. If, as a result of methods of feeding or of the inherent properties of the alumina, all the added alumina enters the bath over a short time period, a slurry will tend to accumulate on or under the metal pad and may lead to a persistent sludge. If, however, part of the added alumina forms a crust and is held on the surface, self-feeding over a long period can occur and the tendency to sludging will be reduced.

The solubilities of aluminas in cryolite melts have been discussed by several authors (*e.g.* Thonstad *et al*[1] and Kachanovskaya *et al*[2]). There seems to be agreement that $\gamma$-alumina dissolves more rapidly than $\alpha$-alumina, but that for both types dissolution is very rapid (a few seconds) if the alumina is well dispersed, and if the melt is not close to saturation. In practice, however, the alumina is unlikely to be well dispersed and may even be present as hard plates. Under these conditions dissolution may be a lengthy process.

## EXPERIMENTAL

In order to simulate the addition of alumina to an operating cell, a laboratory cryolite bath was required having a moderately large surface area, and a depth similar to that in a commercial cell. A slightly tapered graphite pot, 18.5 cm in diam at the liquid surface, was held in an open, deeper Inconel pot which rested in a 24 cm diam wire-wound furnace tube (Fig. 1). 8 kg of a mixture containing cryolite + $AlF_3$ + $CaF_2$ + $Li_2CO_3$ + MgO was added to the pot and heated slowly. The final liquid depth was 15 cm. The approximate composition of the melt was:

| | | | |
|---|---|---|---|
| $Al_2O_3$ | 2.5 pct | $CaF_2$ | 4.0 pct |
| Excess $AlF_3$ | 2.5 pct | $MgF_2$ | 2.0 pct |
| Li cryolite (LiF 2.0 pct) | 4.1 pct | Na cryolite | 84.9 pct. |

In order to reduce air-burning of the graphite pot, a cover was kept on the furnace while heating the melt, and at all times a stream of $N_2$ was passed into the vessel. Five or six runs were achieved with each graphite and each Inconel pot. The furnace temperature was controlled by a thermocouple placed close to the winding, and the melt temperature was meas-

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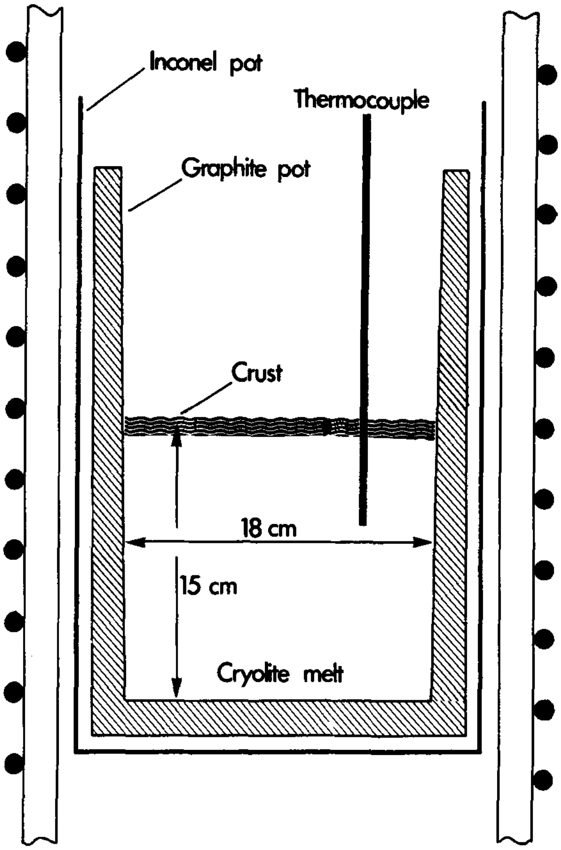


Fig. 1—Apparatus.

ured directly with an additional chromel-alumel thermocouple. There was less than 2°C temperature variation throughout the melt, which was located in the hot zone of the furnace. As a consequence there was little tendency to form a crust by freezing even when the pot was open to the atmosphere.

To perform a test the melt was heated overnight, and the liquidus was determined by reducing the temperature slowly until a slurry of primary cryolite started to form. This could be observed to within 1 or 2°C. The temperature was then raised 20°C above the liquidus and time allowed for the slurry to melt fully. 160 g of the alumina under test (2 pct of the flux weight) was placed in a small pot and after preheating in a separate furnace, it was poured evenly on to the liquid surface over a period of 10 to 15 s. The nature of the crust was observed, particularly its coherence, hardness, wettability and time taken to break up. If the crust remained unbroken after 10 min, it was pushed mechanically beneath the melt. Following natural or forced immersion, the nature of the solid on the bottom of the pot (*e.g.* slurry or hard plates) was observed, either directly (using strong illumination to penetrate the melt) or by feeling or removing a sample with Inconel or steel tools.

The solid was allowed to dissolve fully, assisted if necessary by stirring or by raising the temperature, and the new liquidus determined by cooling. A further 2 pct alumina addition could then be made. Normally only two additions could be given before the melt was almost saturated with alumina, unless some of the crust from a previous addition was removed (this was possible with well-formed crusts). After several runs it was found that the liquidus was predictable if no crust (containing alumina) had been removed, and separate liquidus measurements were not needed in each test.

## Definition of Crusting Behavior

Several characteristics of the crust were noted, both when it was on the surface and following immersion and it was possible to define crusts in one of five categories, listed in order of increasing strength or durability:

1) No coherent crust. Some floating "islands" usually sinking within 1 min. Slurry formed, dissolving rapidly.

2) Coherent but poorly formed, thin crust. Upper surface may remain powdery and not easily wetted by flux. Crust sinks within 1 min to give a slurry which dissolves rapidly.

3) Coherent and fairly well-formed crust but tending to break up. Upper surface may remain powdery and unwetted for up to 2 min. Crust sinks in 1 to 5 min. Slurry formed, dissolving fairly rapidly.

4) Coherent, hard, well-formed crust. Upper surface wetted rapidly. Slowly eroded or dissolved by flux and sinks, or is fragile, after 5 to 10 min. Small plates and slurry formed in bath, dissolving slowly.

5) Very hard crust, cohering strongly, and firmly attached to graphite container. Upper surface wetted rapidly. No appreciable breaking or weakening after 10 min. When forcibly immersed, the crust sinks as a continuous disc before breaking into hard plates which persist for up to 1 h if not agitated.

## Test Conditions

The categories given above are necessarily somewhat subjective, but proved useful in differentiating—semiquantitatively—the very different crusting behavior observed. To make comparisons valid, however, standard conditions were chosen for most of the tests; variations in conditions caused all aluminas to give either poorer or harder crusts.

a) Flux Composition. A standard melt (of composition given earlier) was used in most of the tests, although mixtures containing either 1 pct $MgF_2$ and 1 pct LiF, or no $MgF_2$ or LiF were used in some runs (see Table II). These fluxes gave relatively weaker crusts than those with 2 pct $MgF_2$ and 2 pct LiF.

b) Temperature Above Liquidus. Additions made at temperatures close to the liquidus gave better-formed crusts than additions at higher temperatures if other parameters were constant. A standard of 20°C above the liquidus was chosen. For the flux defined above, the first and second alumina additions were normally made at about 968°C (948 + 20°C) and 957°C (937 + 20°C).

c) Alumina Temperature. Additions were made with alumina at room temperature or preheated at temperatures up to 900°C. As expected, crust-forming ability was much poorer at higher temperatures and, conversely, most aluminas gave fairly hard crusts when added cold. An alumina temperature of 500 to 550°C was taken as standard. (This temperature was not chosen to parallel cell conditions, although it is probably similar to that of alumina resting on the

Table I. Physical Properties of Aluminas Used in the Tests

| | Commercial Aluminas | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *A** | *B* | *C* | *D* | *E* | *F* | *G* | *H* | Laboratory Calcined† |
| Particle size distribution, pct | | | | | | | | | |
| <45 μm | 6(9) | 9 | 8 | 44 | 35 | 22 | 23 | 30 | 19 |
| 45 to 53 μm | 13(15) | 5 | 14 | 33 | 9 | 9 | 26 | 7 | 14 |
| 53 to 75 μm | 31(32) | 44 | 29 | 12 | 33 | 50 | 26 | 31 | 21 |
| 75 to 105 μm | 40(36) | 36 | 39 | 9 | 17 | 16 | 21 | 16 | 37 |
| >105 μm | 10(9) | 6 | 10 | 2 | 6 | 3 | 4 | 16 | 9 |
| Angle of repose | 33 | 32 | 33 | 39.5 | 36 | 33 | 38 | 37 | 31.5(1000°C)<br>33.5(1250°C) |
| α-Alumina content | 37(100) | 27 | 57 | 33 | 46 | ND | 100 | 95 | ‡ |
| Specific surface, $m^2/g$ | 32(5) | 77 | 36 | 27 | 43 | 39 | 4 | 4 | ND |
| Bulk density: | | | | | | | | | |
| Tamped | ND | 1.18 | 1.20 | 1.29 | 1.26 | 1.23 | 1.05 | 1.22 | ND |
| Untamped | ND | 0.97 | 0.97 | 1.00 | 1.00 | 1.00 | 0.77 | 0.92 | ND |

*Bracketed values: Alumina *A* after recalcining to 1350°C.

†Unless stated otherwise values were unchanged at different calcination temperatures.

‡1000°C 1 pct 1200°C 23 pct
1100°C 2 pct 1250°C 55 pct
1150°C 6 pct 1300°C 62 pct
1175°C 23 pct

crust. Alumina fed directly from a hopper or bin would, however, be close to room temperature).

d) Alumina Content of Melt. The crusting behavior did not vary greatly with the alumina content of the melt although the second addition (with 2 pct more alumina present) tended to give a slightly harder crust. No standard of alumina content was thus needed.

## Aluminas Used in the Tests

The aluminas used in the experiments were obtained from eight industrial plants, and varied greatly in their physical properties and in their method of production. In addition, alumina hydrate (gibbsite) was calcined at temperatures of 1000 to 1300°C in the laboratory, using a muffle furnace. A 'soak' time of about 4 h at the required temperature was allowed. The properties of the aluminas are summarized in Table I.

Aluminas *A*, *B* and *C* were typical sandy reduction aluminas as commonly used in North America. They were calcined at relatively low temperatures and had a high surface area and low α-alumina content. *D* and *E* were European aluminas made by flash-calcination at moderate temperatures in a fluidized bed. They were characterized by a high proportion of fines, a high surface area and by a low α-alumina content. They were floury in nature. (*D*1 was similar to *D* but less highly calcined). Alumina *F* was prepared similarly to *D* and *E* but the decomposition process was modified to reduce considerably the fines content. *F* was sandy in nature.

Alumina *G* was calcined at a high temperature and in consequence was floury, of low surface area and with a high α content. *H* was also highly calcined but had a wider particle size distribution with a fairly high fines content. The surface area was low and the α-alumina content high. The alumina was floury.

All samples of laboratory-calcined aluminas were sandy and of low fines contents (a similar particle size distribution to the original gibbsite). The α-alumina content increased from 1 pct to 62 pct as the calcination temperature was increased from 1000 to 1300°C.

## RESULTS

Table II summarizes the experimental conditions of sixty separate alumina additions, and gives the crusting behavior observed. Normally two separate additions of 160 g (2 pct by weight) were made to each melt. In Tests 1 to 47 the standard melt was used and the alumina was preheated to 500 to 550°C; there was, however, some deviation in melt temperature from the standard 20°C above liquidus. Tests 48 to 53 show the results with two different melt compositions, and in Tests 54 to 60 the effect of adding cold aluminas is given.

The results show that crust-forming behavior appears to be largely determined by two characteristics of alumina—the sandiness or flouriness, and the degree of calcination as reflected by the surface area and the α-alumina content. More specifically, a well-formed crust is not produced unless the alumina is both sandy and has a moderate or high surface area. Test 44 (Category 2) is the only exception to this observation, although Test 40 shows a similar sandy, high surface sample rated only in Category 3. Both aluminas are, however, "borderline" samples, *i.e.* calcined at temperatures intermediate between those which gave aluminas forming clearly weak, and clearly strong crusts, and this may account for the anomalous behavior. The effects of calcination temperature, and of flouriness and sandiness on crusting behavior can be illustrated with examples from Table II:

a) A typical sandy alumina (*A*) was changed from good to poor crust-forming ability by calcining to ~1300°C, although its physical properties of angle of repose and particle size distribution were almost unchanged. Although 1300°C is not high enough (in the

### Table II. Crust Formation Following Alumina Additions: Summary of Tests.
### a) Commercial Aluminas

| | | Characteristics of the Aluminas | | | | |
|---|---|---|---|---|---|---|
| Test Number | Temperature of Melt Above Liquidus, °C | Alumina | Sandy(*s*) or Floury(*f*) | Surface Area, m$^2$/g *h*(High) > 20 *l*(Low) < 20 | α-Alumina Content, Pct | Type of Crust* |
| 1 | 10 | *A* | *s* | *h* | 36 | 5 |
| 2 | 16 | | | | | 4 |
| 3 | 15 | | | | | 5 |
| 4 | 15 | | | | | 5 |
| 5 | 25 | | | | | 5 |
| 6 | 40 | | | | | 4 |
| 7 | 10 | *A*, calcined to ~ 1300°C | *s* | *l* | 100 | 2 |
| 8 | 11 | | | | | 2 |
| 9 | 11 | *H* | *f* | *l* | 95 | 1 |
| 10 | 10 | | | | | 1 |
| 11 | 20 | *H*, + 45 μm | *f* | *l* | – | 2 |
| 12 | 20 | | | | | 2 |
| 13 | 20 | *G* | *f* | *l* | 100 | 1 |
| 14 | 21 | | | | | 2 |
| 15 | 20 | *G*, + 45 μm | *s* | *l* | – | 2 |
| 16 | 20 | | | | | 2 |
| 17 | 11 | *D* | *f* | *h* | 49 | 3 |
| 18 | 10 | | | | | 2 to 3 |
| 19 | 21 | | | | | 1 to 2 |
| 20 | 15 | | | | | 1 to 2 |
| 21 | 20 | *D*1 | *f*-*s* | *h* | – | 5 |
| 22 | 40 | | | | | 4 |
| 23 | 20 | *D* | *f* | *h* | 33 | 2 |
| 24 | 20 | | | | | 2 |
| 25 | 20 | *D*, + 53 μm | *s* | *h* | – | 5 |
| 26 | 19 | *D*, + 45 μm | *s* | *h* | 29 | 5 |
| 27 | 20 | | | | | 5 |
| 28 | 20 | *E* | *f* | *h* | 46 | 2 to 3 |
| 29 | 20 | | | | | 2 to 3 |
| 30 | 21 | *F* | *s* | *h* | – | 5 |
| 31 | 25 | *B* | *s* | *h* | 27 | 5 |
| 32 | 40 | | | | | 5 |
| 33 | 20 | *C* | *s* | *h* | 57 | 5 |

### (b) Laboratory-Calcined Aluminas

| | | Characteristics of the Aluminas | | | | |
|---|---|---|---|---|---|---|
| Test Number | Temperature of Melt Above Liquidus, °C | Approximate Calcination Temperature, °C | Sandy(*s*) or Floury(*f*) | Surface Area, m$^2$/g *h*(High) > 20 *l*(Low) < 20 | α-Alumina Content, Pct | Type of Crust* |
| 34 | 20 | 1000 | *s* | *h* | 1 | 5 |
| 35 | 19 | 1100 | *s* | *h* | 2 | 5 |
| 36 | 20 | 1150 | *s* | *h* | – | 4 |
| 37 | 21 | | | | | 5 |
| 38 | 20 | 1175 | *s* | *h* | 23 | 5 |
| 39 | 20 | | | | | 5 |
| 40 | 20 | 1175 (+53 μm) | *s* | *h* | – | 3 |
| 41 | 20 | | | | | 3 to 4 |
| 42 | 20 | 1175 (−53 μm) | *f* | *h* | – | 1 |
| 43 | 20 | | | | | 1 |
| 44 | 20 | 1200 | *s* | *h* | 23 | 2 |
| 45 | 20 | 1250 | *s* | *l* | 55 | 2 |
| 46 | 20 | 1300 | *s* | *l* | 62 | 2 |
| 47 | 20 | | | | | 2 |

### (c) Alumina Additions Under Nonstandard Conditions

| | | | | | | |
|---|---|---|---|---|---|---|
| | | Alumina *A* at 500 to 550°C | | | | |
| 48 | 20 | 0 pct LiF | *s* | *h* | 36 | 4 |
| 49 | 19 | 0 pct MgF$_2$ | | | | 3 |
| 50 | 20 | | | | | 2 to 3 |
| 51 | 20 | | | | | 3 |
| 52 | 21 | 1 pct LiF | | | | 5 |
| 53 | 40 | 1 pct MgF$_2$ | | | | 1 |
| | | Alumina additions at room temperature: | | | | |
| 54 | 19 | *E* | *f* | *h* | 46 | 4 |
| 55 | 19 | | | | | 4 to 5 |
| 56 | 19 | *H* | *f* | *l* | 95 | 3 |
| 57 | 20 | | | | | 4 |
| 58 | 19 | *G* | *f* | *l* | 100 | 4 |
| 59 | 20 | | | | | 3 |
| 60 | 20 | Lab-calcined at 1300°C | *s* | *l* | 62 | 4 |

*1 = poorest, 5 = hardest. See text for full definitions.

absence of a mineralizer) to produce platelets of $\alpha$-alumina, the surface area decreased from 32 to 5 m$^2$/g, and the $\alpha$-alumina content increased from 37 to 100 pct. (Tests 7 and 8).

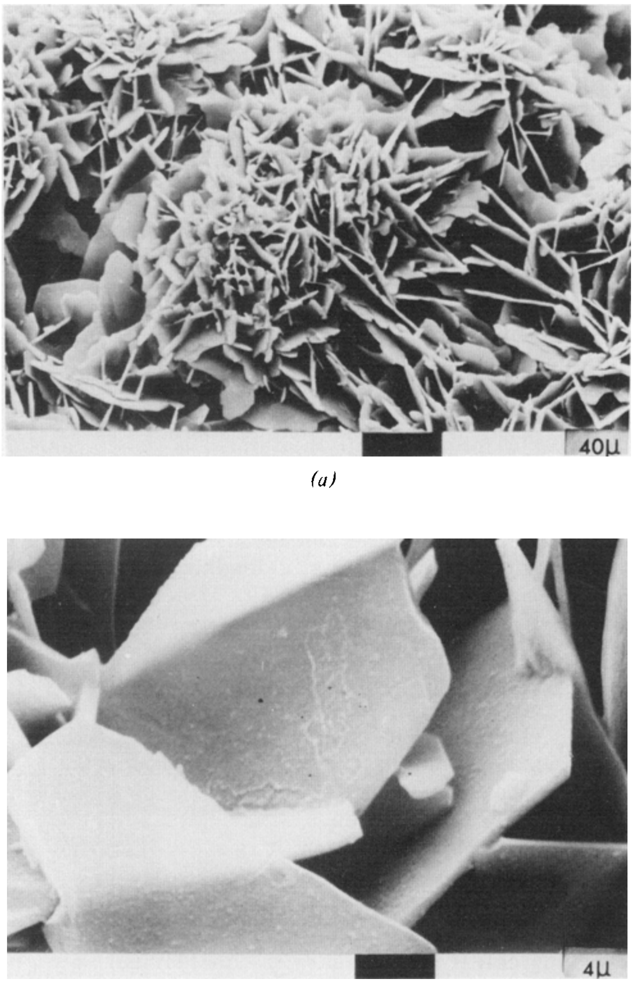
b) Alumina *D* was floury because of its high fines fraction. The relatively low calcination temperature, however, gave a high surface area. Removal of the $-45$ $\mu$m fraction changed the material to a sandy alumina of good crusting ability. (Tests 25 to 27).

c) Similar removal of the fines from the floury, highly calcined Alumina *G* did not improve crust-forming characteristics, although a sandy alumina resulted (Tests 15 and 16).

d) Alumina *F* was from the same source as Aluminas *D* and *E* but the decomposition process had been modified to reduce considerably the fines content. It was sandy and of good crust-forming ability (Test 30).

## DISCUSSION

From tests with commercially available and laboratory-calcined aluminas it has been shown that both sandiness and a relatively low calcination temperature are necessary for the formation of strong crusts. As confirmation, modifications were made, by sieving and by calcining at high temperatures, which gave changes in crust-forming abilities in conformity with these observations. An attempt can be made to relate the findings to the mechanism of crust formation.



(a)

(b)

Fig. 2—(*a*) and (*b*) Typical network formation of thin $\alpha$-alumina platelets formed on addition of a sandy, low $\alpha$ content alumina (*A*) to a cryolite melt.

## Mechanism of Crust Formation

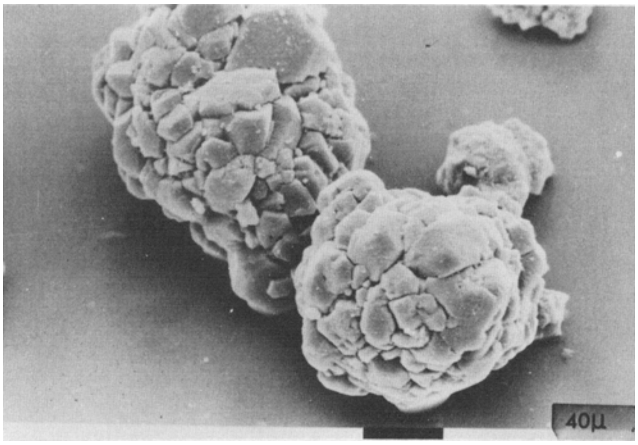
The addition of alumina that is at a temperature well below that of the molten cryolite will have a substantial cooling effect particularly at the melt surface. Partly this is due to the heat capacity of the alumina and partly to its heat of dissolution in the melt. To raise the temperature of a 2 pct addition of alumina from 500 to 1000°C would, if distributed evenly, cool the melt by $\sim$7°C; dissolution of the alumina would lower the temperature by a further 32°C (at 0 pct $Al_2O_3$). Substantial freezing of cryolite will thus occur following penetration into the alumina, which will lead to the rapid formation of a (probably weak) crust of cryolite/alumina.

Although smelter aluminas, particularly if calcined at relatively low temperatures, have many fine pores and fissures and a large internal surface, it is likely that flux penetration initially will be into the intergranular, *i.e.* larger, voids. The volume is approximately 75 pct voids. The alumina contents of three recovered crusts were 35, 34 and 36 pct, only slightly less than the 39 pct expected from penetration of cryolite ($d = 2.1$) into alumina powder of bulk density 1.0 and real density 3.96 g/cm$^3$.

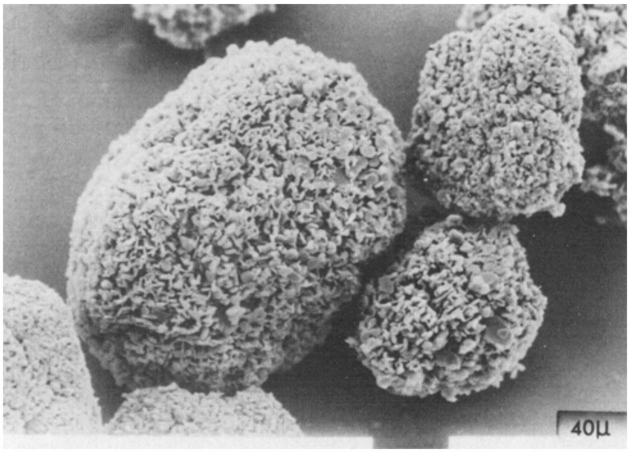
If no further process occurs following the flux penetration, the cryolite will remelt and the alumina being no longer bonded, will deposit as a slurry. It was observed, however, in many of the tests, that not only was the crust initially strong but that its strength and cohesion persisted for long periods, even when partially or fully immersed in melt at a temperature considerably above the liquidus. In such conditions melting of the initially-frozen cryolite must be assumed, and a further mechanism to account for the strength of the crust must be considered.

It is well known that fluorides act as "mineralizers" during calcination and greatly aid the conversion of alumina to the stable $\alpha$ phase; large plate-like crystallites, 1 to 3 $\mu$m in thickness, are formed. If an alumina of low $\alpha$ content is added to molten cryolite, it seems likely that a similar conversion will occur even though the temperature is lower than that normally reached during calcination. Such a change, from $\gamma$- to $\alpha$-alumina, has been reported[2] to be completed within 1 min.

Figs. 2(*a*) and (*b*) are Stereoscan micrographs of a strong crust formed from a sandy alumina (*A*) from which the cryolite has been dissolved with aluminum chloride. The formation of a network of interlinked $\alpha$-alumina platelets can be seen clearly and may be compared (Fig. 3(*a*)) with the typically rounded structure of the alumina before addition to the melt. Highly calcined aluminas, initially fully or almost fully in the $\alpha$ form, cannot undergo a large fluoride-induced modification. Fig. 3(*b*) shows such an alumina (*G*) before addition, and Fig. 4 is of the (poorly-formed) crust after aluminum chloride extraction. The $\alpha$-



(a)



(b)

Fig. 3—Aluminas before addition to melt. (*a*) sandy (*A*); (*b*) highly calcined, floury (*G*).

alumina platelets, which were present before addition to the flux, are observed, but cross-links are not formed.

That a low $\alpha$ content, or a high surface area, is not sufficient to give a persistent crust is attested by the poor crust-forming abilities of aluminas such as *D* and *E*. A second property–ease of wetting by cryolite–is needed. If flux penetrates slowly into the alumina there will be a) a reduced localized cooling effect on the flux (the alumina will have time to heat up by radiation), and b) less opportunity for the fluoride-induced formation of $\alpha$-alumina linkages; both effects will tend to weaken the final crust.

The wettability of an alumina is observed to be poor if it is floury in nature; conversely a sandy alumina is readily wetted. This is analogous to the difference seen on adding flour and sand to water. Air appears to be trapped within a floury alumina (air permeabilities are considerably lower for floury than for sandy aluminas), and the penetration of liquid is resisted. Flouriness is caused either by the presence of a large proportion of fine particulate (defined approximately as <45 $\mu$m in diam), or by particles (not necessarily small) having a plate-like structure. Sandiness is associated with rounded, large particles.

Although a plate-like alumina will have a high $\alpha$ content–both properties being produced by high temperature calcination–flouriness (or sandiness) is not in general directly related to $\alpha$ content. Sandy and floury aluminas each include samples with high and low $\alpha$ contents. Similarly the surface area as measured by the BET isotherm is largely unrelated to the flouriness or sandiness of the alumina. An undercalcined alumina will have a large internal surface area, caused by fine pores, but may consist of large rounded particles and be sandy in nature.

## Crust Formation in Commercial Cells

It must be emphasized that the crusting behavior observed in laboratory tests may not correspond exactly with that observed in a commercial cell, where heat loss from the surface, and agitation by anode gases and bath circulation are important.

In a center-broken cell there is strong agitation in the center channel which is sufficient normally to break a crust formed (as in the current tests) by additions of alumina to the open bath following a break. Such a crust (which may be defined as an ''alumina crust'') will, depending upon its strength, form either a slurry or coherent plates in the bath. A ''cryolite crust'' will now start to form by freezing of the melt. Further additions of alumina to the partially-formed cryolite crust (as is practiced at some smelters) is likely to give a mixed cryolite/alumina crust if the alumina has a good crust-forming ability; if crusting ability is poor a predominantly cryolite crust is likely which will take longer to form. If, moreover, no alumina crust is formed, the alumina will fall to the cathode and accumulate along the center channel. A floury, highly calcined alumina may therefore produce more bottom deposits in a center-broken cell than a sandy, crust-forming alumina.

In a side-broken cell (either Soderberg or prebake) the conditions following a break are slightly different from those occurring in a center broken cell. The melt is likely to be nearer to its liquidus, and the agitation to be less–two conditions which aid ''alumina crust'' formation. If an alumina of good crusting ability is used, a strong crust is likely to form and to remain at the surface. The advantages of this will be a reduction in the amount and duration of open bath, and the possibility of self-feeding of alumina from the crust (with likely benefits to cell operation). If, however, an alumina crust of sufficient stability can be formed from a less sandy alumina, this may be advantageous in giving a soft, easily broken crust, and one which when broken will form a good ''ridge.'' A sandy, low temperature-calcined alumina may form a hard crust (difficult to break manually) and give plates or slabs in the bath that do not readily form ridges.

From this brief discussion, it is clear that alumina solubility, and the formation of crusts and sludges in working cells are complex phenomena. To gain a better understanding of their interaction in a working cell it is necessary to consider not only the physical properties of the alumina used, but the design of cell and the methods of operation.

It is interesting to note that the center-broken cell has been designed to operate with the sandy aluminas of the American continent, whilst a floury,

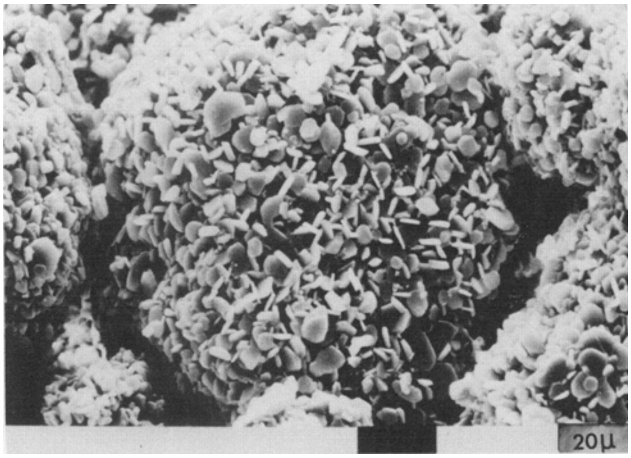


Fig. 4—Addition of a highly calcined, floury alumina (*G*) to a cryolite melt.

relatively highly calcined alumina has been developed to suit the side-broken cells of Europe. Only now with the more open markets in alumina supplies are the problems of running cells with unmatched aluminas being realized.

## CONCLUSIONS

A test has been devised which shows clearly the relative abilities of aluminas to form crusts, and to disperse and dissolve in a cryolite melt. It has been shown that stronger crusts are formed by aluminas that are both sandy and of relatively high surface area (this latter condition may be equated with a low calcination temperature and a low $\alpha$-alumina content). Crust formation is aided by low temperatures of melt and of alumina.

A mechanism of crust formation has been postulated, involving initial penetration of the alumina by cryolite and freezing of the melt, followed by the growth of an interlocking network of $\alpha$-alumina platelets.

Of the samples tested, *H*, the most floury alumina, gave the poorest crust. Aluminas *D* and *E* (floury, but of low $\alpha$ content) also gave weak crusts but by removal of the $-45$ $\mu$m fraction by sieving, or by modifying the production process (Alumina *F*), these became of good crust-forming ability. Under-calcined, sandy aluminas, *A*, *B* and *C* all gave strong crusts. Laboratory samples formed strong crusts when calcined at temperatures below ~1150°C and poor crusts above ~1200°C–a difference attributed to the increase in the $\alpha$-content.

An attempt has been made to apply the laboratory findings to the prediction of crusting and dispersion/dissolution behavior in working cells. The problem is however, complex and further work in the laboratory, and observations of both side-broken and center-broken commercial cells are needed.

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## REFERENCES

1. J. Thonstad, F. Nordmo, and J. B. Paulsen: *Met. Trans.*, 1972, vol. 3, pp. 403-08.
2. I. S. Kachanovskaya, V. I. Osovik, and T. N. Kukhotkina: *Tsvet. Met.*, 1971, vol. 44, no. 10, pp. 40-42.