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Study of effect of alumina quality on solubility in electrolytic bath

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Under the present alumina electrolysis method for smelting aluminum, the alumina dissolves in the electrolytic bath mostly as is in a powder state and the rest in a crusted state. A number of reports have been published on the dissolution of alumina powder, but they are not necessarily in agreement with one another. Furthermore, there are hardly any reports on the dissolution of crusted alumina. Alumina has recently been attracting wide attention for its adsorption of HF gas released from the electrolytic bath which results in holding down loss of the gas thereby controlling environmental pollution.

We, accordingly, tried on a laboratory scale, taking actual operational conditions into consideration, to clarify the relationship of alumina quality to both powder and crusted alumina dissolution, crusting trend and HF gas adsorptiveness, etc., by varying the quality, especially grain size, the calcining conditions (calcining temperature and amount of mineralizer) and the alpha degree.

We found from the tests that alumina which is 43 maximum in grain size and has been calcined at 1000 °C maximum with no addition of mineralizer is the most suitable for electrolysis.

We followed this with tests at a commercial facility and found that alumina of the above specifications dissolves rapidly and does not precipitate markedly, that its handling, including transportation, is easy and that the surface of the electrolytic bath is not exposed when breaking the crust, etc.

1. INTRODUCTION

One of the important qualities required of alumina as a material in aluminum reduction is ease of dissolution into the electrolytic bath. Generally, alumina charged into a reducing pot enters the bath partly in a powder state and partly in a crusted state. Many reports have been published on the dissolution rate of powder alumina into the bath [1] [5]. All of them, however, do not agree in values because of variations in the methods of tests, etc., that it is not clear what type of alumina is the easiest to dissolve into the bath. There are very few reports that discussed the dissolution rate of crusted alumina. Most of the reports mentioned above dealt with alumina that was comparatively well calcined. Use of active alumina has recently been attracting attention to recover HF gas that generates during electrolytic operations [6]. It is necessary, therefore, to study what type of such alumina is the easiest to dissolve into the bath.

From such standpoint, we prepared various types of alumina that varied in grain size, calcining conditions (calcining temperature and amount of a mineralizer and the α degree) and measured on a laboratory scale the dissolution rate of powder alumina, crusting trend, dissolution rate of crusted alumina and activity to obtain optimum active alumina, taking into consideration the actual charging condition of alumina into commercial pots.

On the basis of the results thus obtained, the most suitable alumina was tested at a commercial plant and the results mentioned above were industrially confirmed.

2. EXPERIMENTAL

2.1. Alumina

2.1.1. *Grain size*

Alumina hydrates obtained by the Bayer process are dried at a temperature of 400 °C and then sieved. Three types of alumina samples were used in the tests: 43 microns maximum, 61-74 microns and 88-104 microns in grain size.

2.1.2. *Calcining conditions*

The samples were calcined in an electric furnace for 30 minutes at temperatures of 800 °C, 900 °C, 1,000 °C, 1,100 °C, 1,200 °C, 1,300 °C and (1,400 °C) respectively.

As a mineralizer 1% or 0% aluminum fluoride was added to said alumina hydrates.

2.2. Electrolitic bath

The composition of the bath was 4% AlF_3 + 5% Al_2O_3 + bal. Na_3AlF_6 and its temperature was 980 °C.

2.3. Crust formation

Figure 1 shows the crust forming apparatus.

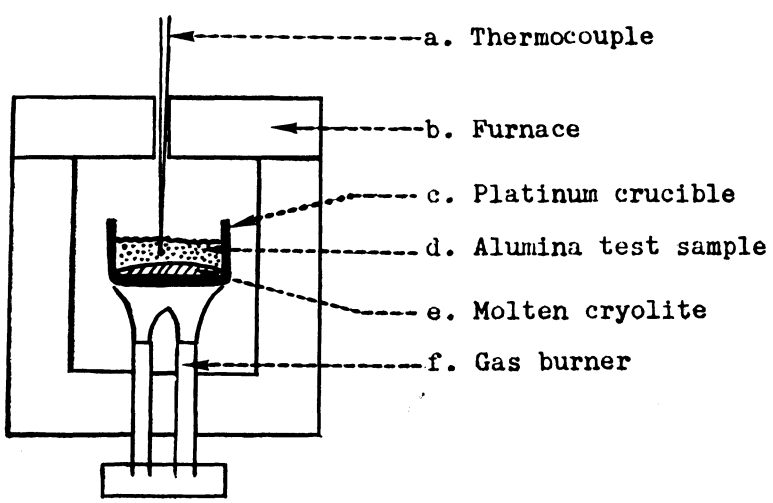


Fig. 1. — Crust forming apparatus

On the bottom of a platinum crucible (capacity 100 cc), 10 grams of cryolite was laid, and 20 grams of an alumina test sample placed thereon and heated with a gas burner from the bottom in a brick insulated furnace, maintaining the temperature of the alumina layer in the interior at 850 °C for 35 minutes to turn the alumina into crust form. By this method a crust was obtained almost similar to that which is observed in a commercial pot.

2.4. Measurement of dissolution time

The apparatus is shown in Figure 2. A platinum crucible containing 100 grams of bath was put in an electric furnace maintaining the bath temperature at 980 °C ± 2 °C.

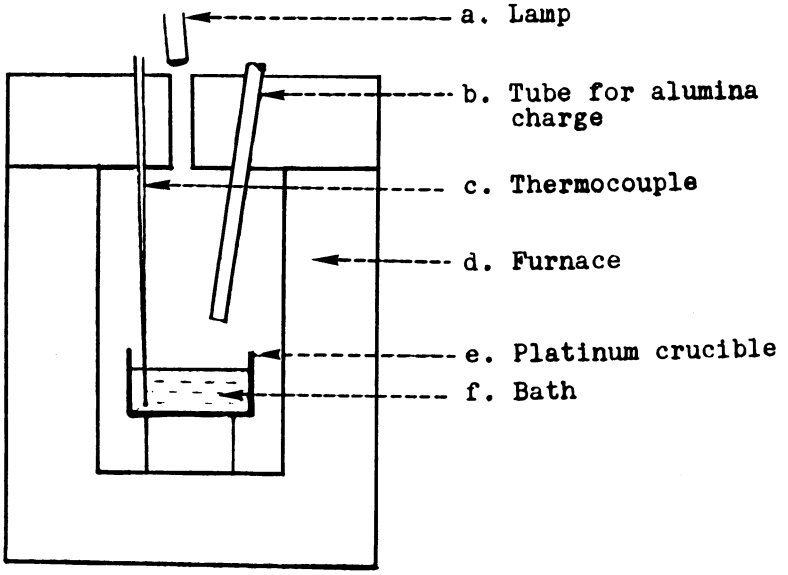


Fig. 2. — Dissolution rate measuring apparatus

1 gram of the alumina sample was heated at 500 °C and added to the bath through a stainless steel tube. The time that elapsed from the addition of the solid alumina until its disappearance was taken as the apparent dissolution time. During the time the bath was not stirred. (With the recent highly mechanized pot, a device is offered to feed alumina about 1% of the molten bath to the bath at a short interval to the place where the bath does not comparatively move.)

3. RESULTS

3.1. Change of alumina caused by calcination

After calcining the alumina hydrates, the α degree was determined by the X-rays diffraction method. The result is shown in Figure 3. In the case of no mineralizer, the alumina hydrates slightly converted to α-Al_2O_3 at a calcining temperature of 1000 °C and largely at 1200 °C, almost completing at 1300 °C.

In the case of calcining alumina with 1% of aluminum fluoride as mineralizer, approximately 30% converts to α-Al_2O_3 at 800 °C and the α degree increases as temperature rises. The shape of alumina grains changes by calcination and some of its examples are shown in Figures 4-1 to 4-5. The fact that the shape of alumina grains varies as calcination proceeds, has already been published [7] [8] and as shown in the above-mentioned Figures, the mineralizer has a marked effect. As compared with the alumina with no mineralizer, the alumina with a mineralizer presents complicated surface and finer grains begin to appear. This trend further proceeds with increasing amount of the mineralizer.

3.2. Apparent dissolution rate of powder alumina

The dissolution rates were calculated by measuring the apparent dissolution time of the various types of alumina. The results are shown in Figure 5. The dissolution time of alumina is greatly subjected to grain size and the finer the grain size, the easier the alumina dissolves.

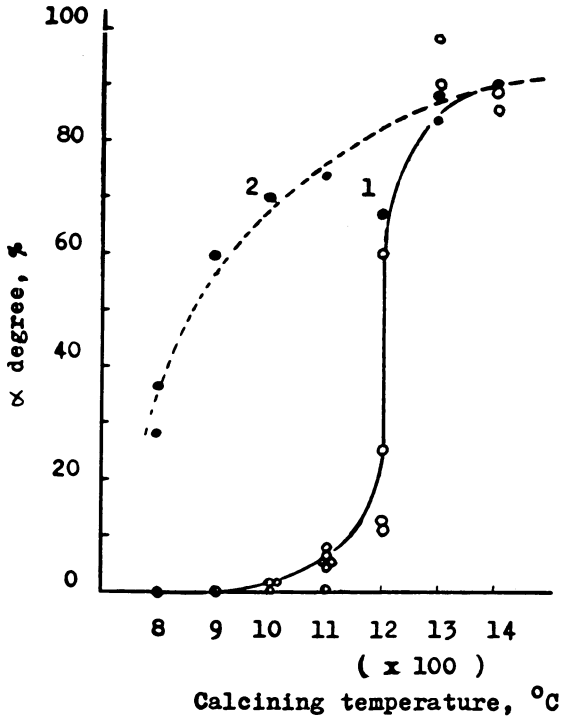


Fig. 3. — Heat transition of alumina

With regard to calcining temperature, dissolution of alumina generally becomes difficult as its calcining temperature is high, especially at temperatures higher than 1100 °C as compared with that under 1000 °C.

When calcined with aluminum fluoride, alumina dissolves easily.

The relationship between the α degree of powder alumina and its dissolution rate is shown in Figure 6.

Any alumina with high α degree does not easily dissolve. In the case of no mineralizer, increase of α-Al_2O_3 up to about 20% makes the dissolution rate abruptly lower, while increase over the level scarcely lower the dissolution rate.

In the case a mineralizer is added, the dissolution rate moderately lowers as α-Al_2O_3 increases. Also in said case, even though the grain size and α degree are the same, the dissolution rate of alumina is high.

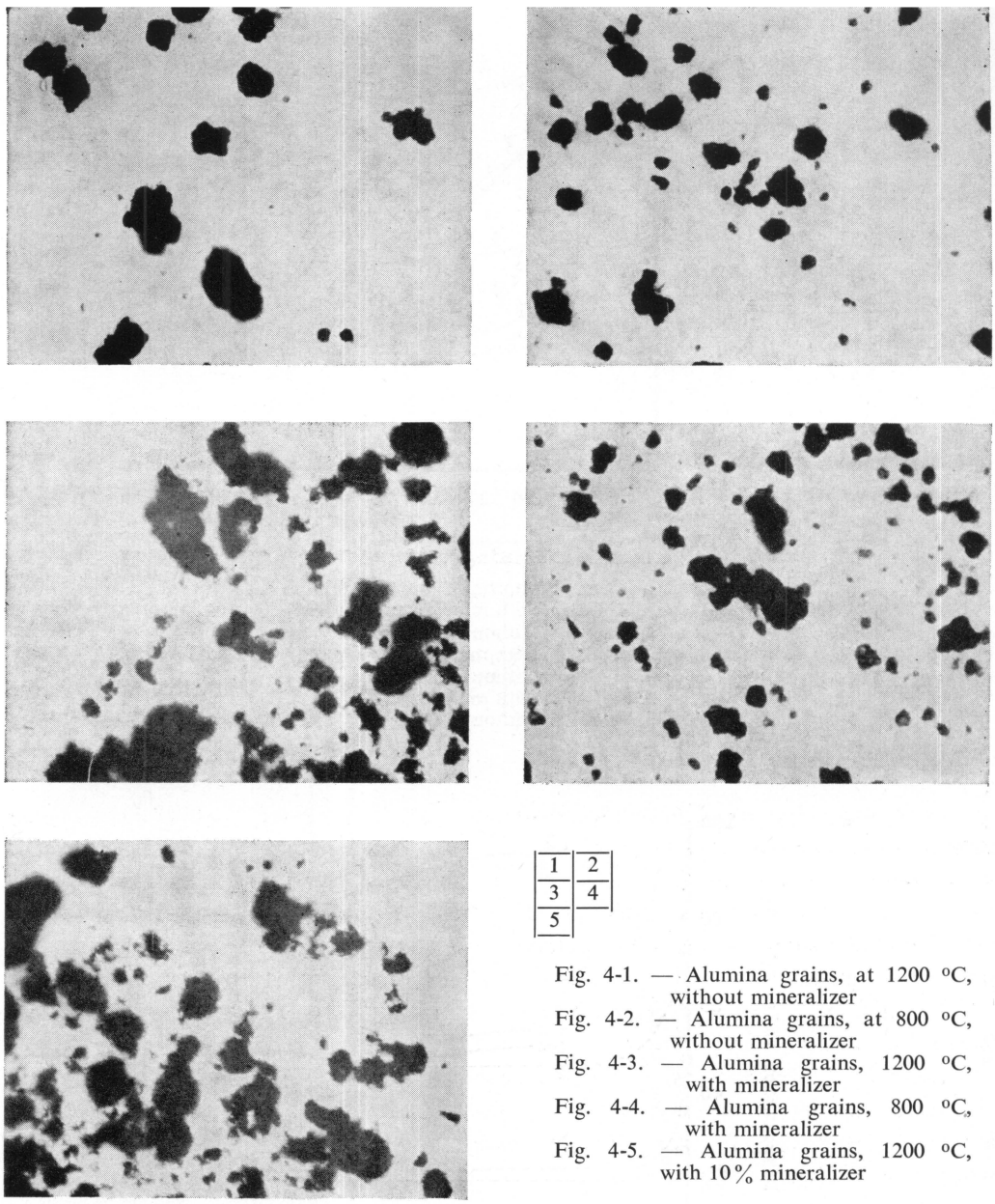
3.3. **Crusting trend of alumina**

By treating alumina to form crust, part of an alumina sample forms crust. This crust differs in hardness and quantity depending on types of alumina. The trend is shown in Figure 7. In this paper the hardness of the crust is classified into three classes; hard, medium and soft. The hardness varies depending on the grain size of alumina, $< 43\ \mu$ forms the softest crust and 88-104 μ the hardest. Although the effect of a mineralizer on the hardness of crust has not been clarified, it seems to soften the crust somewhat and the trend is conspicuous with alumina 88-104 μ in grain size.

Also the calcining temperature ranging from 800 to 1200, °C was observed to have scarcely any effect on the hardness of crust.

The quantity of crust is subjected to the grain size of alumina samples and alumina $< 43\ \mu$ tends to form crust easily on the whole and alumina of 88-104 μ formed crust only a little.

By this crust formation, α degree of alumina markedly increases. The result of measuring the α degree by the X-ray diffraction method is shown in Figure 8.



1	2
3	4
5	

Fig. 4-1. — Alumina grains, at 1200 °C, without mineralizer
Fig. 4-2. — Alumina grains, at 800 °C, without mineralizer
Fig. 4-3. — Alumina grains, 1200 °C, with mineralizer
Fig. 4-4. — Alumina grains, 800 °C, with mineralizer
Fig. 4-5. — Alumina grains, 1200 °C, with 10% mineralizer

3.4. **Dissolution rate of alumina crust**

The dissolution rate of the crusted alumina into the bath was measured (Fig. 9).

The crust usually contains about 30 to 60% Al_2O_3. On the basis of the analytical result of each of the crusts, the addition of crust to the bath was determined that 1 gram of alumina be fed.

As seen from Figure 9, alumina $< 43\ \mu$ with or without mineralizer, and that of 88-104 μ with mineralizer easily dissolve while that of 66-74 μ and 88-104 μ with no mineralizer is difficult to dissolve. Generally, the harder the crust, the dissolution rate is low while the soft crust dissolves easily.

This fact will be due to the reason that since the contact surface is limited for the dispersion of alumina grains being prevented in the bath, the hard crust is difficult to dissolve. However, the effect of alumina calcining temperature on the dissolution rate of the crust could not be clarified.

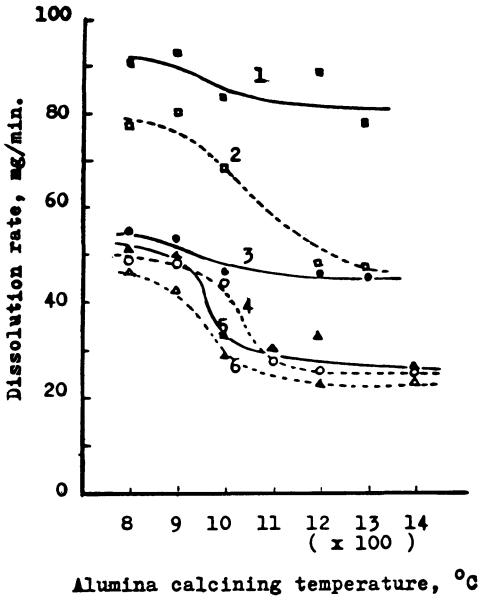


Fig. 5. — Dissolution rate of powder alumina
1. < 43 μ, with mineralizer
2. < 43 μ, without mineralizer
3. 61- 74 μ, with mineralizer
4. 61- 74 μ, without mineralizer
5. 88-104 μ, with mineralizer
6. 88-104 μ, without mineralizer

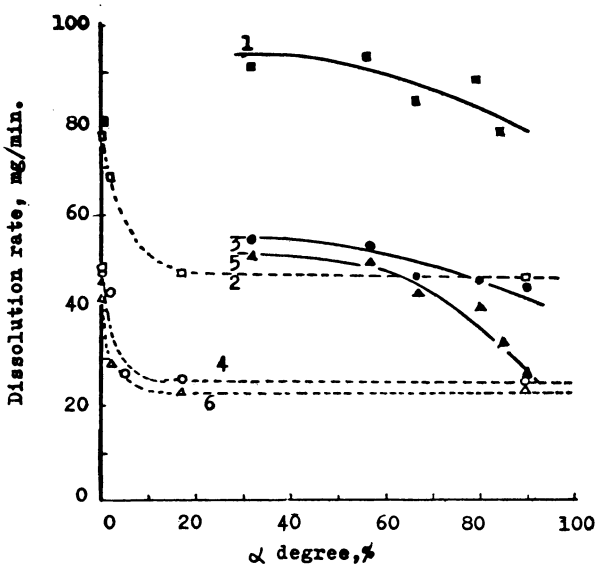


Fig. 6. — Dissolution rate of powder alumina
(The Nos. represent the same as in Fig. 5)

3.5. **Selection of active alumina as a material for aluminum reduction**

As was previously explained, the purpose of this study is to find the active alumina that does not decrease the dissolution rate. Judging from the dissolution rate of alumina in powder and crusted state and the activity represented by the α degree, suitable active alumina could be selected from those < 43 μ in grain size and calcined with no mineralizer.

According to another study by Showa Denko [9] effective adsorption of HF gas can be achieved when the specific surface area of alumina is > 40 m^2/g. The specific surface area

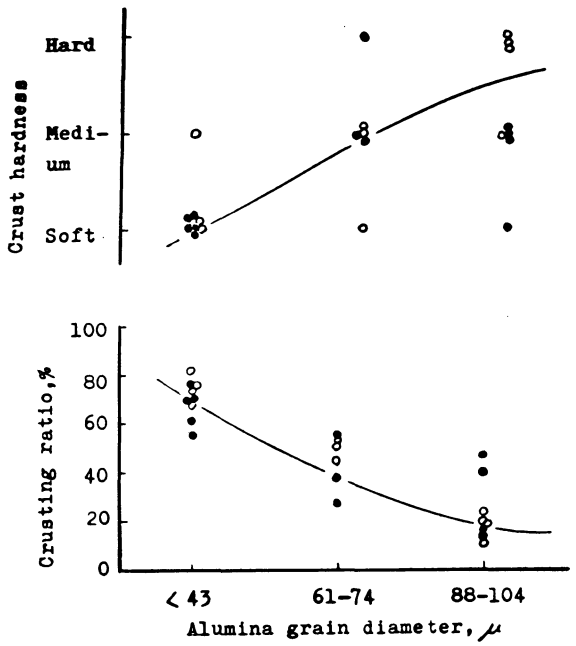


Fig. 7. — Cursting trend
Without mineralizer
With mineralizer

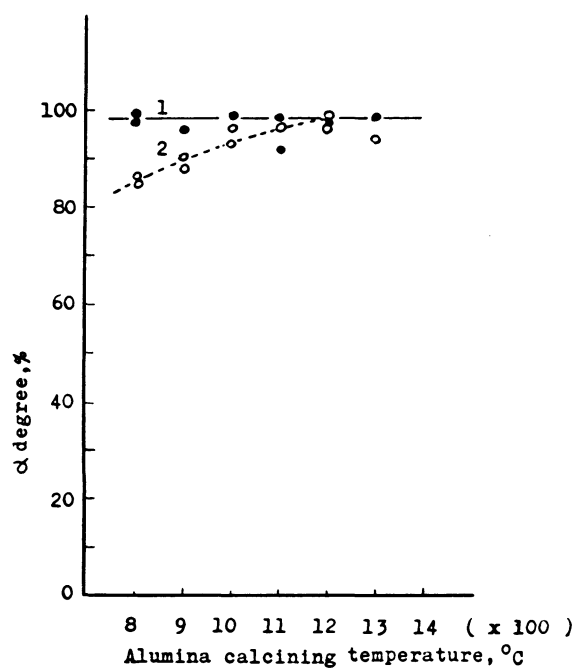


Fig. 8. — α degree of alumina in crust

of alumina calcined with no mineralizer and < 43 μ in grain size which is dealt with in our present study was measured by the BET method, the result of which is given in Figure 10.

It shows that the alumina calcined at a temperature higher than 1100 °C has a specific surface area < 40 m^2/g. It can be said, therefore, that the alumina calcined at a temperature lower than 1000 °C is suitable as active alumina.

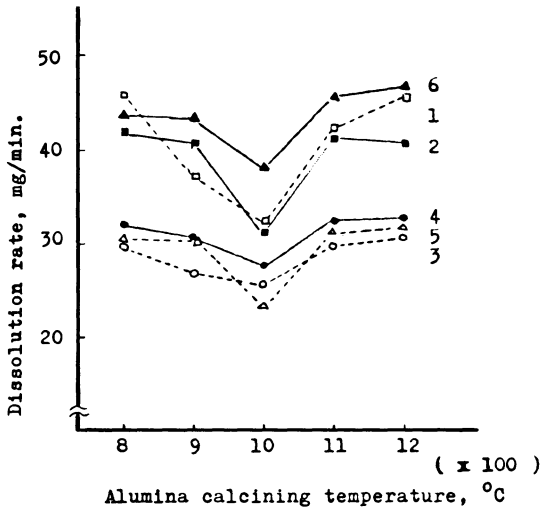


Fig. 9. — Dissolution rate of crusted
1. < 43 μ, without mineralizer
2. < 43 μ, with mineralizer
3. 61- 74 μ, without mineralizer
4. 61- 74 μ, with mineralizer
5. 88-104 μ, without mineralizer
6. 88-104 μ, with mineralizer

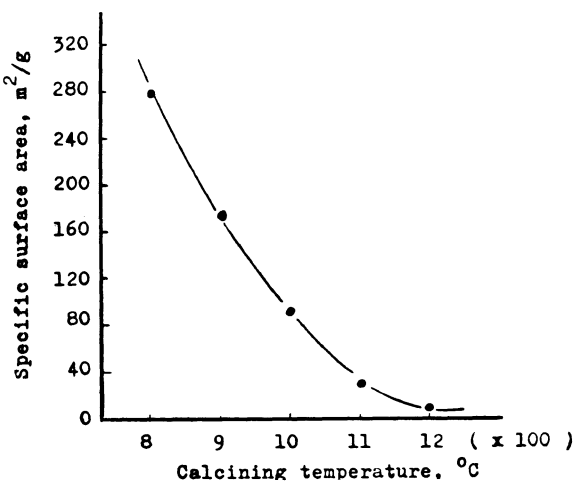


Fig. 10. — Specific surface area of alumina (Alumina < 43 μ calcined without mineralizer)

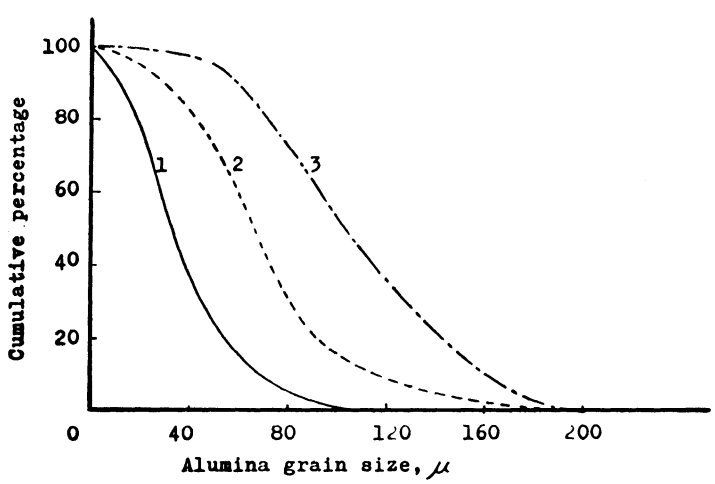


Fig. 11. — Grain size distribution of alumina for testing

4. TESTS IN COMMERCIAL POT

On the basis of the test results obtained in our laboratory mentioned above, tests were conducted using the alumina which was specially manufactured to have quality nearest to the above results.

The average quality of alumina used in the tests is given in Table I and Figure 11.

TABLE I

Alumina for Test Use

Calcining conditions	
Calcining temperature	1000 °C maximum (rotary kiln)
Mineralizer	Not added
Grain size	
Under 43 μ	70% (refer to Fig. 11)
Specific gravity	3.54
Ig. loss	1.15%
Friction angle	32°
Specific surface area	50 m^2/g

Having been calcined at low temperature, this alumina was characterized in being so-called sandy-like despite its consisting of fine grains. Tests were conducted using this alumina in 70 KA prebaked anode pots equipped with an alumina automatic feed apparatus.

In the case of a reduction pot to which alumina is charged from limited positions, generally, alumina tends to precipitate on the bottom without dissolving more than in the case of a pot in which alumina is charged from the entire space around the anode when the bath temperature lowers by the breaking of heat balance.

Accordingly, it is required to have alumina that easily dissolves into the bath. In our pot the alumina concentration in the bath reached the maximum value 30 minutes after charging. In the case of the alumina shown in Table I, the concentration in the bath reached the highest in 20 minutes and the dissolution rate was observed to have advanced. (Fig. 12.) Also in the case of this alumina, precipitation did not occur so much as to form an obstacle to pot operation.

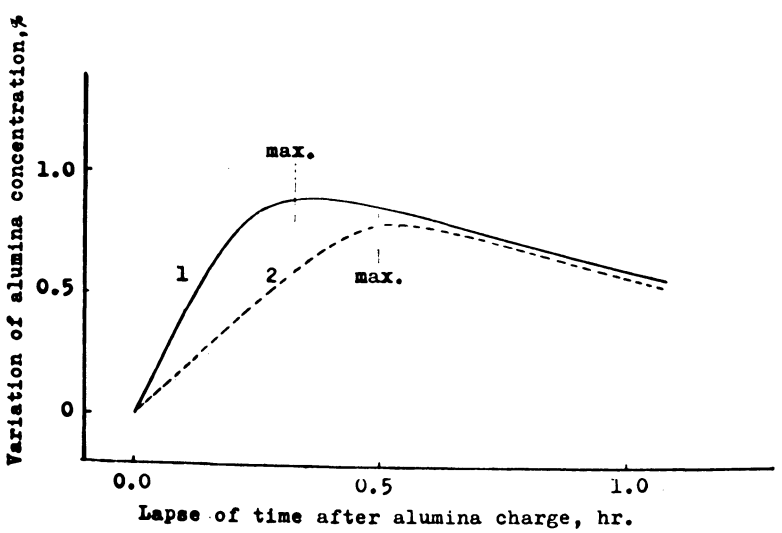


Fig. 12. — Varition of alumina concentration in electrolytic bath (70 KA prebaked anode pot)

The alumina being of a sandy type with a small friction angle, as Table I shows, the transportation from the alumina silo to the pot was so facilitated as to shorten the time required for transportation by 30% than in the case of the conventional floury alumina and the transportation facility could be simplified.

Furthermore, the alumina being so fluid for its small friction angle, the covering of the bath surface with the alumina was easy contributing thus to suppressing the release of HF gas.

This alumina being greatly hygroscopic, as can be presumed from its great ignition loss, dust generation increases when charged to the pot. Our tests showed that loss of alumina by dispersion increased by 5% than in the case of the conventional fluory alumina. Attention should, therefore, be paid to this regard in the case of a pot that is not properly equipped with a dust treating device.

4. DISCUSSION

4.1. Dissolution rate

It is considered that the dissolution rate of alumina into the bath is subjected to such factors as alumina grain size, activity and the coarseness of the grain surface.

4.1.1. *Alumina grain size*

Our experiments showed that fine grains $< 43\ \mu$ easily dissolve. This agrees with the results published by Thonstad [5] and Winkhaus [6] while it does not agree with Becker's and Thaure's opinions. However, there is such as relationship given below,

$$\frac{S_1}{S_2} \simeq \frac{\gamma_2}{\gamma_1}$$

where: S = specific surface area of alumina in ball shape,

γ = radius of alumina in ball shape.

It can be considered from the above that the smaller the alumina grain size, the greater the contact area of the bath with alumina, resulting in more ease of dissolution.

4.1.2. *Effect of alumina calcining method*

Our experiments showed that alumina calcined at lower temperatures dissolved more easily than that at higher temperatures and so was alumina with a mineralizer added than without a mineralizer, and also alumina with lower α degree than that with higher one. This accords with the results published by Belyaev [1] that the alumina calcined at 800-900 °C is easy to dissolve and also by Thonstad [5] that γ alumina is easier to dissolve than α-alumina, but not with those by Winkaus [4] and Becker [3].

The activity of the alumina grain surface could be represented by the active points of pores a few Å in diameter that are produced at the spots where the OH radical is released from alumina hydrates upon calcining. The increase of such active points is almost in proportion to variation of the alumina specific surface area and they decrease as calcining temperature rises. In the case of no addition of a mineralizer as Figures 4-1 and 4-2 show, the roughness of the surface, as viewed from the standpoint of alumina grains, is scarcely subjected to the fluctuation of temperature. Accordingly, in the case of no addition of a mineralizer, the higher the calcining temperature, the smaller the dissolution rate of alumina.

While in the case of being calcined with a mineralizer, the growth of α-alumina crystals is promoted, with the surface of alumina grains assuming complicated state and fine grains appearing. (Figs 4.3-4.5.) V. J. Hill also published this fact at the symposium [8]. Such a change in shape makes the contact area of the bath-alumina interface larger and the uneven grain surface results in better wetting. By these reasons the addition of a mineralizer causes the dissolution rate of alumina to increase.

4.2. Crusting trend

The hardness of the crust varies depending on the permeability of the bath into gaps of the alumina layer and generally, poor permeability produces a soft crust while a crust permeated fully and evenly with the bath is hard. One of the main factors that brings the permeation of the bath into the alumina layer is the gap diameter. The following relationship exists between the alumina grain diameter and the gap diameter in the alumina layer:

$$\left(\frac{\gamma_1}{\gamma_2}\right)^3 \simeq \frac{l_1}{l_2}$$

where: $\gamma_{1,2}$ = alumina grain diameter,
$l_{1,2}$ = gap diameter in the alumina layer.

Separating the permeation of the bath into the alumina layer in the perpendicular and horizontal directions, the permeation in the perpendicular direction can be represented by:

$$H \frac{2\,\sigma \cos\theta}{\rho \cdot g \cdot l}$$

where: H = height of permeation
σ = surface tension
ρ = bath density
l = average gap diameter
θ = contact angle between alumina and bath

or

$$H \simeq \frac{1}{l}$$

The permeation in the horizontal direction can be represented by:

$$\frac{L^2}{t} = \frac{\sigma\, l \cos\theta}{2\,\eta}$$

where: L = permeation distance
η = coefficient of bath viscosity
t = permeation time

or

$$L^2 \simeq l$$

Accordingly, alumina with a small average grain diameter has a good permeability in the perpendicular direction, but not well in the horizontal direction.

Since the bath begins to permeate the alumina layer from the bottom first at points where it comes in contact with the layer or where it can easily permeate, it will permeate upward high in the layer consisting of small alumina grains, but not well in the horizontal direction, the alumina forming thus a crust as a whole with the bath not sufficiently permeated. Consequently, the crust of alumina $< 43\,\mu$ is soft.

On the other hand, an entirely contrary phenomenon will take place in the layer consisting of larger alumina grains. Although the bath does not permeate well in the perpendicular direction, it does well in the horizontal direction, the alumina forming a thin, hard crust in the lower part of the alumina layer and leaving the alumina in great quantity in a powder state on top of the layer. Consequently, an alumina layer consisting of large grains on an average is soft as a whole.

The alumina 88-104 μ in size with a mineralizer added has a very wide range of grain size distribution for the appearance of fine particles due to the effect of the mineralizer. When the grain size deviates considerably, permeation will generally occur preferentially

through the spots where it is easier to permeate. This brings about such a phenomenon as the bath does not permeate the spots consisting of grains under certain size. This phenomenon will constitute one of the reasons that the crust of alumina 88-104 μ in size and calcined with a mineralizer is soft.

Since the alumina 61-74 μ in size calcined with or without a mineralizer is not applicable to any of the reasons mentioned above, it seems that a comparatively hard crust forms in quantity.

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