

ALCOA PRESSURE CALCINATION PROCESS FOR ALUMINA

S. W. Sucech and C. Misra

Alumina and Chemicals Division
Alcoa Laboratories
Alcoa Center, PA 15069Abstract

A new alumina calcination process developed at Alcoa Laboratories is described. Alumina is calcined in two stages. In the first stage, alumina hydrate is heated indirectly to 500°C in a decomposer vessel. Released water is recovered as process steam at 110 psig pressure. Partial transformation of gibbsite to boehmite occurs under hydrothermal conditions of the decomposer. The product from the decomposer containing about 5% LOI is then calcined by direct heating to 850°C to obtain smelting grade alumina. The final product is highly attrition resistant, has a surface area of 50-80 m²/g and a LOI of less than 1%. Accounting for the recovered steam, the effective fuel consumption for the new calcination process is only 1.6 GJ/t Al₂O₃.

Introduction

Energy requirements for alumina calcination have decreased from 4.5 GJ/t Al₂O₃ to about 3.2 GJ/t Al₂O₃ following the replacement of rotary kilns by stationary calciners. Several stationary calciner designs are now available. The Alcoa fluid-flash calciner (1,2) and the Lurgi circulating bed system (3) have been in commercial operation for several years. Developments of other systems have also been reported (4,5,6).

In general, higher gas velocities used in the stationary calciners result in higher dust generation due to attrition. This has forced producers to take a closer look at the properties of the precipitated hydrate and relate these to attrition and breakdown behavior - both during calcination and of the final calcined alumina (4). There is some evidence that large "blocky" crystals (called radial growth), when present in the hydrate agglomerate, tend to produce a weak, dusty alumina. A similar effect has also been reported when sodium oxalate crystals are included within the hydrate.

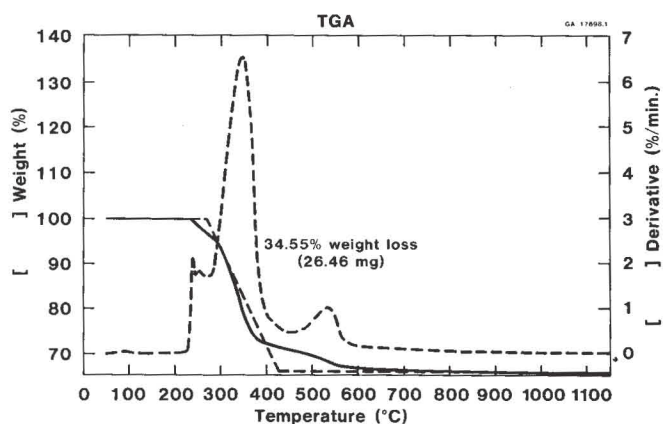
Alcoa Pressure Calcination Process

The pressure calcination process developed at Alcoa Laboratories addresses both the questions of energy use and fines generation. It enables a substantial recovery of calcination energy together with the production of a stronger alumina.

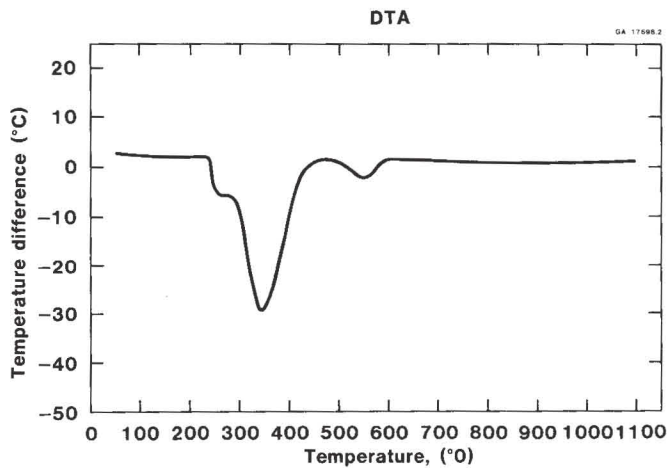
In this process, alumina hydrate is calcined in two stages. In the first stage alumina hydrate is heated indirectly to 500°C in a decomposer vessel under a steam pressure of about 8 atm. About 85% of the combined water is released and is recovered as process steam. There is also a partial transformation of gibbsite to boehmite during decomposition involving alteration of the crystal morphology. The product from the decomposer has about 5% LOI and is calcined by direct heating to 750-850°C to obtain smelting grade alumina. The alumina product has high attrition resistance.

Heat Effects in Hydrate Decomposition

The process of thermal decomposition of alumina hydrate can be studied from DTA and TGA data. The TGA plot for a typical American Bayer hydrate is shown in Figure 1 for atmospheric pressure calcination. As can be seen, more than 85% of the water is released below about 520°C. Some boehmite is formed due to hydrothermal conversion within the crystals. This is shown by the exothermicity at 270°C and endothermicity at 520°C in the DTA plot (Figure 2).



TGA Analysis of Hydrate
Figure 1



DTA Analysis of Hydrate
Figure 2

Heat requirements have been estimated from DSC measurements and are:

For water removed between 200-350°C = 3660 J/g H₂O
 For water removed between 350-1000°C = 1686 J/g H₂O
 Overall = 1128 J/g hydrate

Similar tests carried out under eight atmospheres (120 psig) steam pressure show, as expected, larger amounts of boehmite formation and, unexpectedly, an 11% decrease in heat requirements to reach the final LOI value of about 1%.

Characteristics of Pressure Decomposer Product

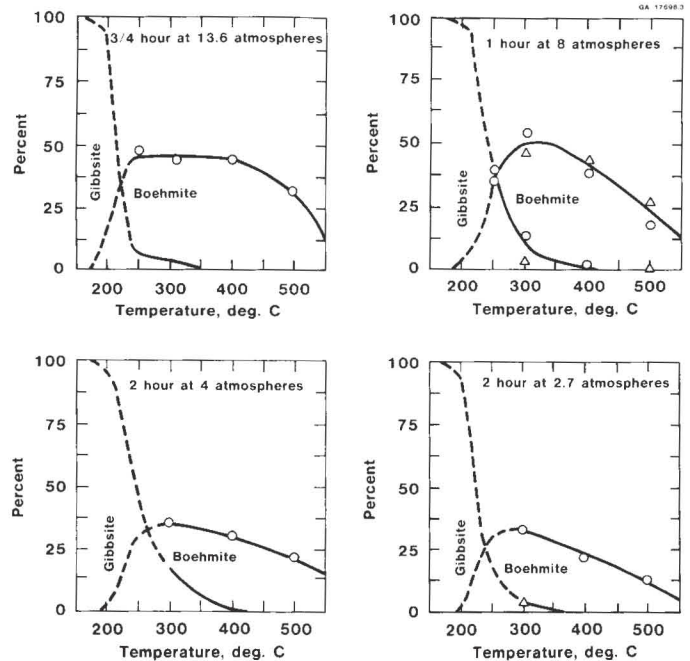
Bench scale decomposition experiments were carried out in a modified autoclave system with provision to inject dry alumina hydrate. In a typical run the autoclave was brought to pressure and temperature by starting with a small amount of water. Hydrate was then charged from the injection vessel by pressurized gas. A venting arrangement maintained constant steam pressure in the autoclave during the test. Range of conditions studied were:

Pressure: 4-30 atmospheres
 Temperature: 250-650°C
 Residence Time: 30-120 minutes

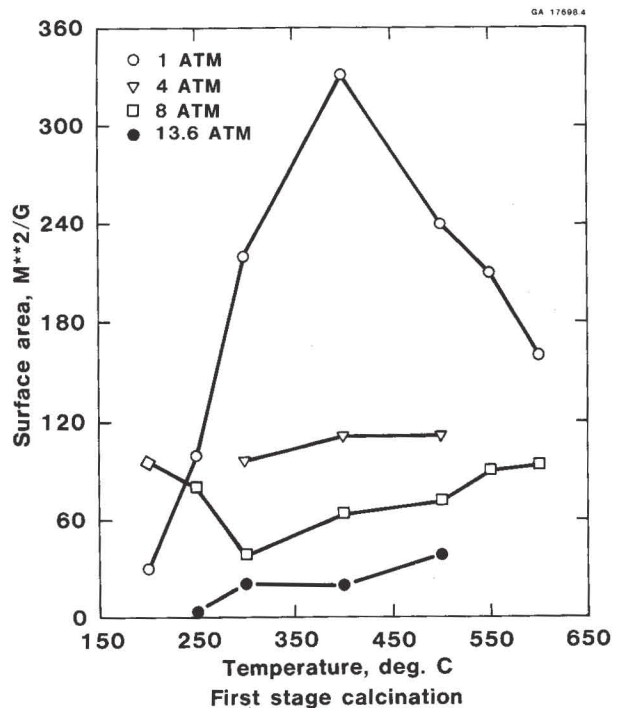
At the end of the test the autoclave was vented fully and cooled. The product was removed and examined for properties.

Figures 3, 4, and 5 show boehmite content, surface area, and LOI values of decomposition products for various test conditions. Table 1 shows particle size analyses (by sieving) of the feed hydrate and product after decomposition.

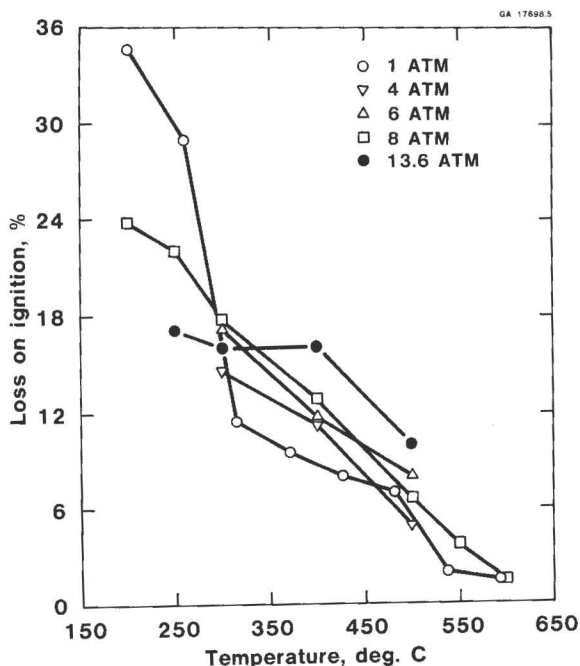
The decomposed products were then subjected to the second stage atmospheric calcination in an electric furnace for one hour at the desired temperature. The products were again analyzed for LOI, surface area, attrition resistance and crystalline phase. Morphological features were examined by SEM and also by sectioning the alumina particles.



Phase Composition vs. Temperature at Various Calcination Pressures Showing Percentage of Boehmite and Gibbsite.
Figure 3



Surface Areas of Pressure Calcined Aluminas
Figure 4



Loss on Ignition of Pressure Calcined Aluminas
Figure 5

Results of these tests, which have a direct bearing on the development of a practical pressure calcination process, are summarized as follows:

- More than 50% transformation of gibbsite to boehmite occurs at 120 psig pressure and 500°C for a residence time of 60 minutes. A part of the boehmite subsequently converts to $\gamma\text{-Al}_2\text{O}_3$.
- This transformation affects the development of surface area. There is no rapid rise in surface area; the surface area increases to about 70 m²/g under above conditions. This surface area value remains practically unchanged after second stage calcination at 750-850°C.

- The above decomposer conditions result in a product having a LOI of about 5%. A final LOI of <1% (corresponding to smelting grade alumina) can be attained by carrying out the second stage calcination at the relatively low temperature of 750-850°C. The final product consists largely of $\gamma\text{-Al}_2\text{O}_3$ with the complete absence of $\alpha\text{-Al}_2\text{O}_3$.
- The formation of boehmite has considerable impact on the internal structure of the alumina and consequently on the attrition behavior.

Figures 6 and 7 show SEM pictures of internal structures of atmospheric and pressure calcined (after second stage) aluminas. The absence of cracks and fractures in the pressure calcined material is remarkable.

Attrition test results confirm the above observations. First, there is little particle breakdown during the pressure decomposition stage. Results actually show a slight coarsening effect. Second, the product from the second stage has very high attrition resistance as measured by the usual modified Forsythe-Hertwig test. Some results are given in Table 2.

Results also suggest that the residence time of the hydrate in the decomposer, and hence the extent of transformation to boehmite, strongly influences later attrition behavior. Higher attrition resistance corresponded with longer residence time.

Pilot Scale Continuous Decomposer

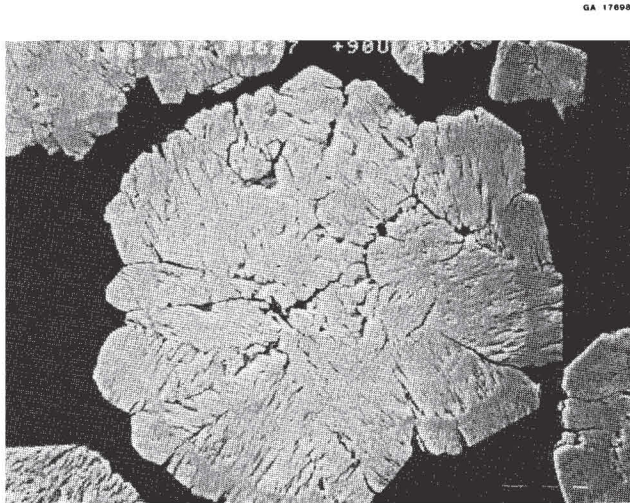
A pilot continuous decomposer was designed and operated to test some concepts of indirect heating of the hydrate and compare product quality results from batch operated bench tests with continuous decomposition tests. The aim was to obtain information useful for the final design and construction of a full scale pressure calcination system. This must include geometry to incorporate a large amount of surface area for indirect heat transfer from hot combustion gases, practical feed and discharge schemes for the decomposer, and recovery of clean steam.

Table I. Sieve Analysis⁽¹⁾ Comparing Hydrate Particle Size Distribution To Pressure Calcined Alumina⁽²⁾ Particle Size Distribution

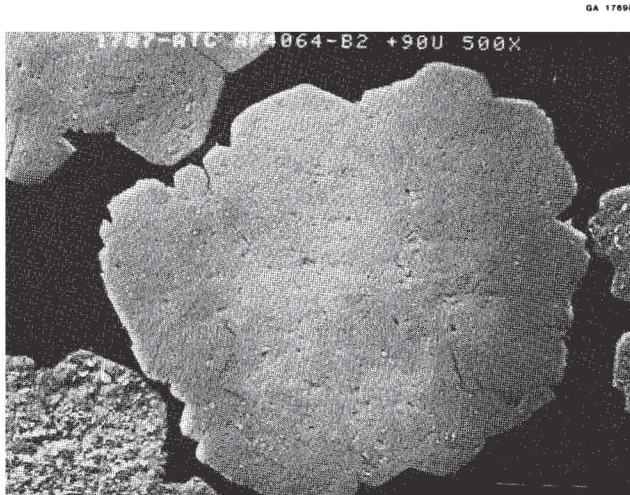
Sieve Size	Hydrate 1		Hydrate 2		Hydrate 3	
	Hydrate	Alumina	Hydrate	Alumina	Hydrate	Alumina
+100	9	9	17	18	5	6
+150	32	35	54	59	31	34
+170	44	50	76	77	53	59
+200	61	67	89	90	74	80
+270	85	89	98	99	95	98
+325	93	96	99	100	98	100

NOTES:

- Values represent cumulative weight percent retained on indicated sieve size.
- Average of all aluminas pressure calcined at 8 atmosphere 1st stage and 2nd stage at 1 atm and 850°C.



Section of Atmospherically Calcined Alumina
Figure 6



Section of Pressure Calcined Alumina
Figure 7

Several practical decomposer designs were considered. Observations in an externally heated, transparent quartz tube showed that the decomposition of the hydrate bed is self-fluidizing due to release of steam. This fluidizing effect can be utilized to improve heat transfer to the hydrate bed. On this basis, the most economical design concept for the decomposer resembles a vertical

shell and tube heat exchanger with a self-fluidized bed of hydrate flowing down the tubes and hot combustion gases flowing counter currently upwards in the shell.

A picture of our pilot pressure decomposer is shown in Figure 8. The design is based around a single tube identical to what would be used in the plant calciner. It resembles a double pipe heat exchanger, with solid hydrate flowing down the tube and hot combustion gases flowing upwards in the annulus. Continuous feed to and discharge from the system were through pressurized lock-hopper arrangements. System steam pressure was maintained through a back pressure regulator. A gas-fired combustion system supplied hot combustion gases. A computerized data acquisition system connected to sensors provided flow, temperature and pressure data and computed mass and energy balances, heat transfer coefficients and pressure drop measurements along the column.

In general, pilot plant findings fully confirmed bench scale results with respect to product properties. Some results are displayed in Table 3. Heat transfer results showed the gas side coefficient to be limiting with overall heat transfer coefficients in the range of 8-10 BTU/ft²/hr/°F.



Pilot Pressure Calciner
Figure 8

Modeling of the fluidizing behavior inside the tube showed that the bed behaves as a bubbling fluidized bed in the top 80% of the tube and as a packed bed in the bottom section.

Heat Balance for Pressure Calcination Process

A simplified heat and mass balance for the pressure calcination process is displayed in Figure 9.

Calculations show that 1020 lbs of steam at 120 psig and 400°F are produced when calcining 1 t of alumina (0.5% LOI). The gas burning rate is 115 lbs which works out to 2.8 GJ/t Al₂O₃. Subtracting the

heat available in recovered steam (1.25 GJ) the effective fuel consumption for the process is only 1.55 GJ/t Al₂O₃.

Design of Industrial Pressure Calciner

Preliminary design of a large, 76 t/hr Al₂O₃ capacity pressure calciner has been worked out based on bench and pilot plant experience. The design allows retrofitting of an existing Alcoa fluid-flash calcination system to operate in the pressure calcination mode. The design utilizes a pressurized lock-hopper system for feeding dry hydrate to the decomposer vessel. Development work is continuing on a product discharge system which promises to be much simpler in design and operation.

Table II. Sieve Analysis⁽¹⁾ and Attrition Indices of Bench Pressure Calcined Aluminas⁽²⁾

Sieve Mesh	Hydrate	1 Atmosphere ⁽³⁾	8 Atmospheres		
			300°C	400°C	500°C
+100	17	12	17	19	17
+150	54	48	56	60	55
+170	76	64	74	78	74
+200	89	78	87	91	90
+270	98	90	96	99	99
+325	99	93	98	100	100
Attrition Index (325 Mesh)	2	6	6	2	2

NOTES:

- (1) Numbers represent cumulative weight percent retained on indicated sieve size.
- (2) Second stage calcination at 850°C for 1 hour.
- (3) Atmospheric calcination performed in laboratory flash calciner for 30 minutes at 850°C.

Table III. Sieve Analysis⁽¹⁾ and Attrition Indices of Pilot Pressure Calcined Aluminas

Sieve Size	Test 1		Test 2		Test 3	
	Feed	Product	Feed	Product	Feed	Product
+100	3	3	2	3	8	9
+150	27	28	22	26	36	39
+170	42	44	38	42	50	52
+200	73	75	71	74	73	76
+270	94	96	94	95	93	97
+325	97	98	97	98	96	99
Attrition Index (325 mesh)	3	2	4	3	3	4

NOTES:

- (1) Numbers represent cumulative weight percent retained on indicated sieve size.

Conclusions

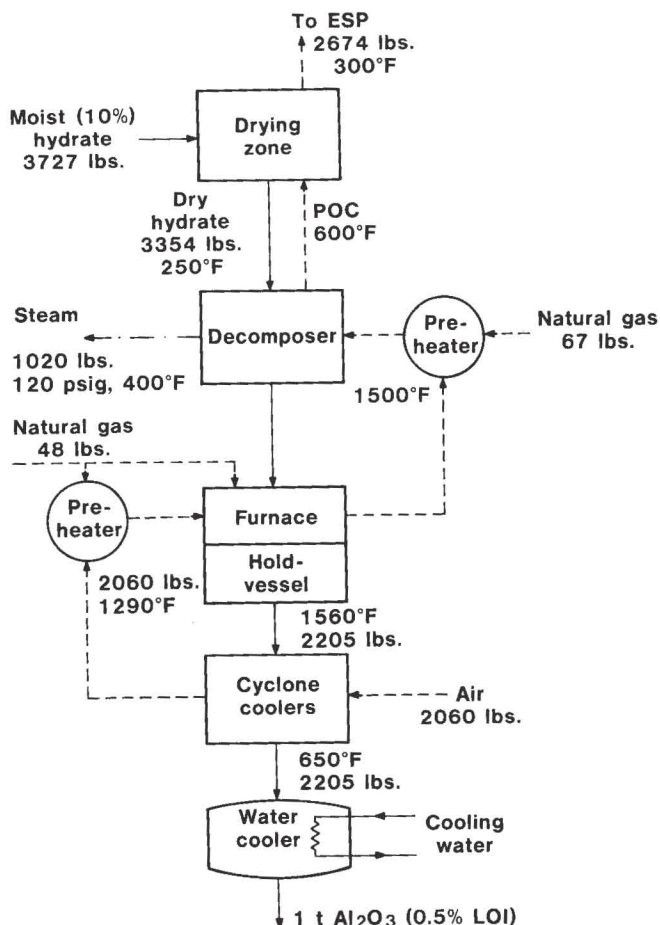
By recovering the water released during alumina calcination as process steam, the new Alcoa pressure calcination system decreases effective heat requirement for alumina calcination to less than 1.6 GJ/t Al_2O_3 .

The large gibbsite - boehmite transformation occurring during pressure calcination results in a strong attrition resistant product and enables the production of <1% LOI smelting grade alumina at the low calcining temperature of 750-850°C. The surface area of the product is around 70 m²/g suitable for effective F recovery.

The process was studied in bench and continuous pilot units and design for a large 76 t/hr alumina pressure calciner has been developed.

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Pressure Calcination Process Flowsheet
Figure 9

Future Developments

Further developments of the pressure calcination process are likely to be in the following directions:

- a. The decomposer temperature of 500°C is related to economical material of construction of the tubes. A higher temperature design (650°C) will give 1% LOI at the decomposer discharge, thus making the second step calcination unnecessary.
- b. Indirect calcination eliminates the problem of contaminants originating from the fuel. This opens up the possibility of using low grade fuel oils and even solid fossil fuels for alumina calcination.
- c. Efficient solids pumping devices are being investigated based on experience from coal gasification and pressurized fluidized bed combustion systems. This type of system will replace the lock-hopper design for feeding hydrate to the decomposer vessel.

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