

PRESSURE CALCINATION REVISITED

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Bayer Process, Calcination, Pressure

Abstract

Twenty-five years ago at the TMS 100th anniversary meeting of the Hall-Heroult Process, two Alcoa scientists, S. W. Sucech and the co-author of this paper, C. Misra presented a paper on an improvement to the alumina calcination process – pressure calcination.

The improved process offered an opportunity for a net energy reduction in fluid flash calciners of 1.6 GJ/ton alumina (and the subsequent green house gas reductions). This could be retrofitted into existing fluid flash calciners and produce an alumina meeting smelting requirements with the added advantage of high attrition resistance and thus low dust generation.

The question is: Why hasn't this improvement been incorporated into today's alumina plants?

Technical data in the previous paper will be reviewed and updated in the present paper.

Introduction

Energy requirements for alumina calcination have decreased from 4.5 GJ/t Al_2O_3 to less than 3.0 GJ/t Al_2O_3 following the replacement of rotary kilns by stationary calciners. Since the commercial introduction fluid flash calciners in the 1960s, there have been numerous papers on the development and improvement in design as well as increases in installed throughput capacities of this class of calcination equipment [3, 5, 6, 7, 8, 9, 12, 15, 18, 19, 20, 28, 30]. One major drawback of the new calciners was that the type of alumina trihydrate particles being produced in alumina refineries using the new calcination technology tended to break down and create a significant amount of fine dust during calcination and that dust, in addition to being an environmental problem, led to a range of feeding problems for alumina smelters using the flash calcined aluminas [1].

This problem of dust creation has been mitigated over the years by the alumina refineries changing precipitation practices to create "sandy" "mosaic" crystal habit alumina trihydrate particles [22, 23, 24, 26, 31], reduction in internal velocities and sharpness of bends in calciner design [8, 28], and methods of measuring or characterizing the potential attrition resistance of alumina trihydrate particles [2, 4, 10, 13, 14, 16, 17, 21, 22, 23, 28].

Today, the majority of the calcined alumina produced has been calcined in some form of fluid flash calciners as opposed to rotary kilns. The problem of alumina fines, while reduced, remains a continuing problem for handling and smelter cell feeding systems.

In 1986, an Alcoa paper at the TMS meeting introduced the concept of pressure calcination [25]. The present paper will re-introduce the data presented in that paper.

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 X-ray diffraction, DTA and TGA data [27]. The TGA plot for a typical American Bayer hydrate is shown in Figure 1 for atmospheric pressure calcination.

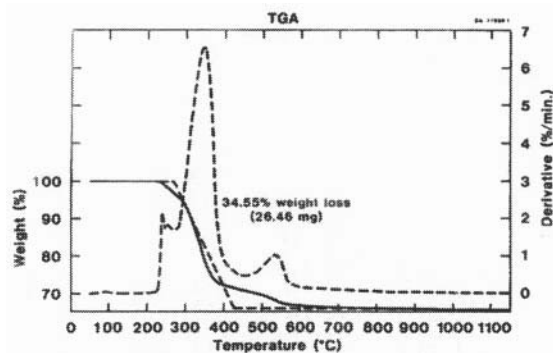


Figure 1, TGA Analysis of Hydrate

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).

Heat requirements have been estimated from DSC measurements and are:

For water removed between 200-350°C = 3660 J/g H_2O

For water removed between 350-1000°C = 1686 J/g H_2O

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%.

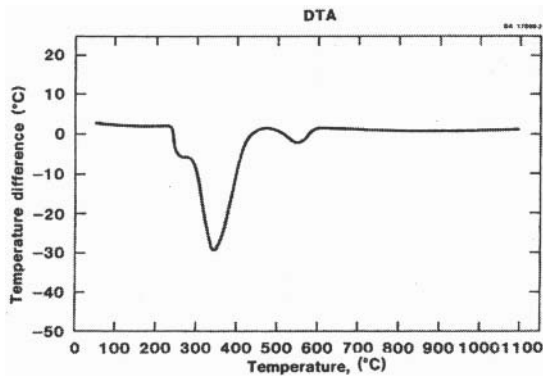


Figure 2. DTA Analysis of Hydrate

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.

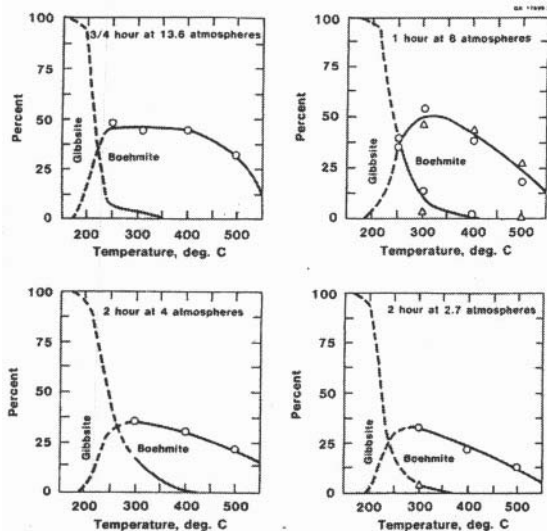


Figure 3 Phase Composition vs. Temperatures at Various Calcination Pressures Showing Percentage of Boehmite and Gibbsite.

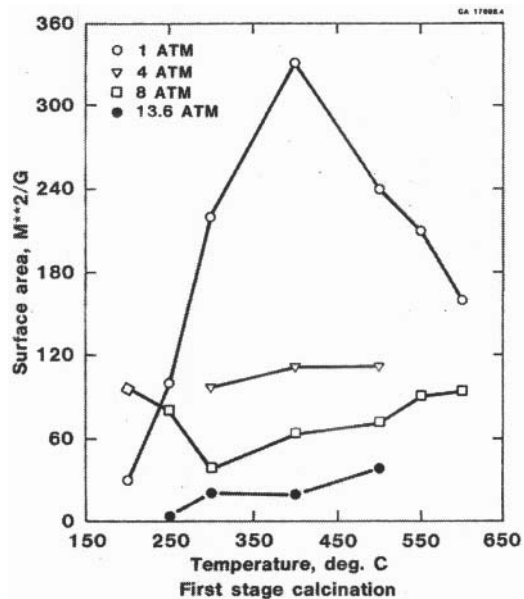


Figure 4. Surface Area of Pressure calcined Aluminas

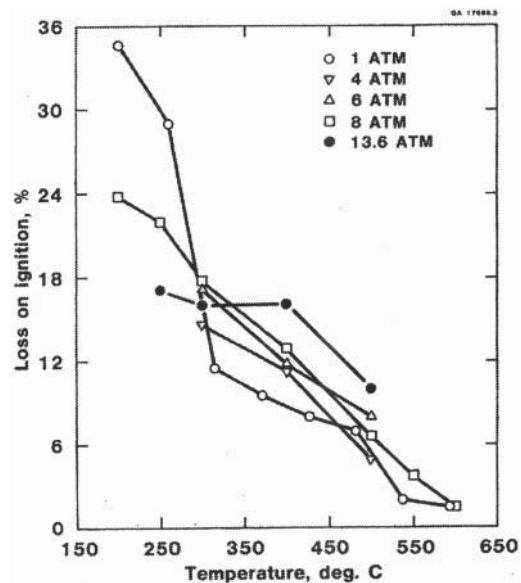


Figure 5. Loss on Ignition of Pressure Calcined Aluminas

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.

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:

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

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

- a. 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 γ -Al₂O₃.
- b. 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 the above conditions. This surface area value remains practically unchanged after second stage calcination at 750-850°C.
- 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 γ -Al₂O₃ with the complete absence of α -Al₂O₃.
- d. 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.

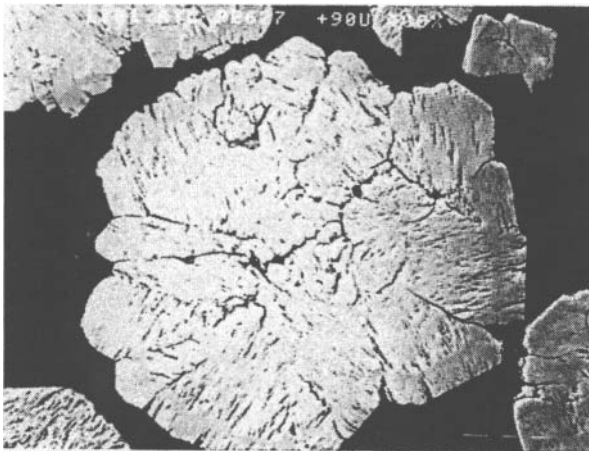


Figure 6. Section of Atmospherically Calcined Alumina

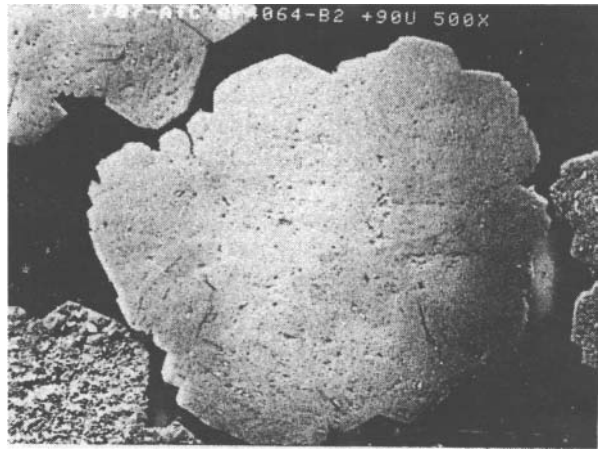


Figure 7. Section of Pressure Calcined Alumina

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 II.

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

Sieve Mesh	Hydrate	1 Atmos.	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

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.

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.

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 the 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 backpressure 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.

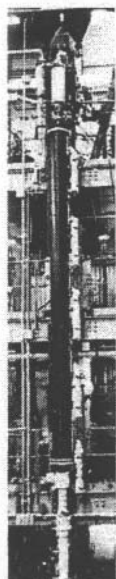


Figure 8. Pilot Pressure Calciner

In general, pilot plant findings fully confirmed bench scale results with respect to product properties. Some results are displayed in Table III. 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.

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

Sieve Mesh	Test 1		Test 2		Test 3	
	Feed	Prod.	Feed	Prod.	Feed	Prod.
+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
A. I.	3	2	4	3	3	4

Notes:

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

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.

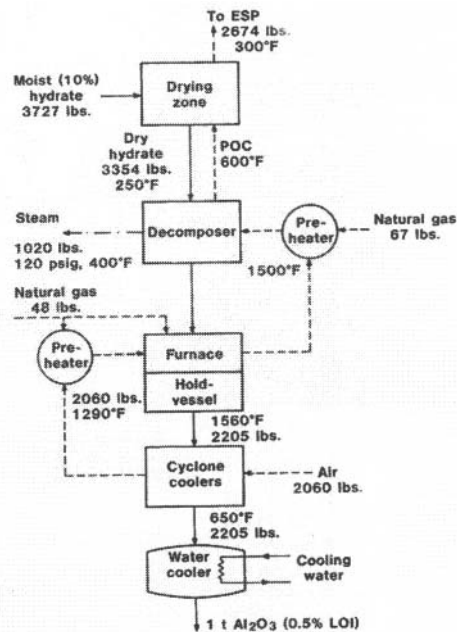


Figure 9. Pressure Calcination Process Flowsheet

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 be 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

At the time of the original paper the preliminary design of a 76 t/hr Al₂O₃ capacity pressure calciner was 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 utilized a pressurized lock-hopper system for feeding dry hydrate to the decomposer vessel. Further development work and implementation of this technology, however, was stopped at this point.

Discussion

An even more energy efficient unit, not discussed in the previous paper, would be to build a stand-alone pressure calciner. Wet filter cake would be fed into a pressurized dryer/decomposer unit where the alumina would exit at 850°C. A tubular design with self-fluidized hydrate/alumina on the inside of the tubes and POC on the outside, similar to the retrofit unit discussed above, is visualized. The hot alumina product could then go to a two-stage atmospheric indirect cooling section using air and water to cool the alumina to handling temperature and preheat air for fuel combustion. In this case all of the steam latent heat from hydrate moisture and water of hydration would be recovered as usable steam. Dust collector flow volume and particle load sizing would be significantly less than in current flash calciners.

Conclusions

By recovering the water released during alumina calcination as process steam, the Alcoa pressure calcination system decreases effective heat requirement for alumina calcination to less than 1.6 GJ/t Al₂O₃.

The large gibbsite - boehmite transformation occurring during pressure decomposition 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 an initial design for a 76 t/hr alumina pressure calciner was developed but not implemented.

With the energy saving, ability to retrofit into existing fluid flash calciners and the ability to produce a better SGA for smelters, it is very surprising that this technology has languished without being implemented!

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