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ALUMINA CALCINATION IN THE FLUID-FLASH CALCINER

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In the mid 40's, Alcoa turned to fluidized solids techniques as a means of improving the efficiency of the alumina calcining process. This paper traces calciner development from the first pilot operation in 1946 through the first plant fluid-bed unit in 1952, the early "fluid-flash" calciner designs in 1960, the first 300 ton/day fluid-flash calciner at Alcoa's Bauxite, Arkansas plant in 1963, the 600 ton/day calciners installed in Suriname and Australia in 1965 and 1966, up to the 1500 ton/day Mark III calciners now operating in Jamaica, Australia and the United States. These Mark III fluid-flash calciners have provided a 30 to 40 percent fuel saving in addition to major savings in capital investment and maintenance costs.

In the electrolytic production of aluminum, it is first necessary to produce an essentially pure aluminum oxide (alumina) as feed for the electrolytic cells, or smelting pots as they are called in the industry. The alumina is generally recovered from its ores by treatment with caustic solution, which dissolves the alumina while leaving the impurities as a residue. The clarified alumina-containing solution is cooled and seeded to precipitate a hydrated alumina. Since the water of crystallization would react unfavorably in the smelting pots, it is necessary to remove the combined water by heating at elevated temperatures.

The normal product of the Bayer process for alumina refining is gibbsite $(Al(OH)_3)$. When this material is heated above 350°F, water is driven off as a function of time and temperature. As the temperature is increased. water can be removed down to lower and lower levels as rapidly as heat can be transferred to the particle. At each temperature there is a corresponding residual water content (loss on ignition) that is attained on rapid heating. Further retention time at constant temperature results in loss of water at a much reduced rate. For example, aluminum hydroxide instantaneously heated to 600°F will reach an L.O.I. of about 15% corresponding to about 65% removal of the initial combined water. Continued heating at 600°F will remove about 80% of the combined water in one hour and about 82% in six hours. Rapid heating at 1800°F will produce about 0.7% L.O.I. (over 99% water removal) while continued heating for three hours at 1800°F gives about 0.20% L.O.I.

During decomposition, the aluminum hydroxide passes through a series of intermediate crystalline forms or phases prior to reaching the final alpha alumina or corundum form. The alpha form is essentially anhydrous and inert. The lower crystalline forms will contain some combined water and will adsorb water on exposure to humid atmospheres.

Aluminum hydroxide calcination requires about 1600 Btu/lb of combined water removed (77°F datum), which corresponds to 850 Btu/lb of alumina. If the calcination is continued to the alpha form, an exothermic reaction occurs which releases about 120 Btu/lb of alumina.

Historically, this calcination has been carried on in rotary kilns. By the mid 40's kiln and codler improvements had reduced heat requirements from early figures of 4000 Btu/lb of alumina to about 2100 gross Btu/lb. This figure was still 2-1/2 times the theoretical heat requirement for calcining alumina, but was approaching the practical limit imposed by rotating kiln design.

648

At about this time fluidization was being successfully applied in petroleum refining, and Alcoa Research recognized that the technique could have wide application in the aluminum industry. Based on bench and pilot studies begun in 1946, a fluid bed calciner design was completed in 1951 and operation started at the end of 1952.

Light Metals

The static calciner of fluidized bed design avoided many of the problems of the rotary kiln. Adequate thermal insulation was provided; temperatures were measured accurately; combustion temperatures were uniform and constant; countercurrent heat exchange between feed solids and stack gases and product alumina and combustion air was obtained by the use of multiple beds. The ideal control capability of the fluidized system resulted in note-worthy improvement in product quality.

This unit shown in Fig. 1 incorporated two stages of heat exchange at the feed end, two combustion zones and five stages of alumina cooling by direct contact with combustion air.

Free moisture was reduced in a drying filter followed by a fluid bed preheating stage where 50 - 60% of the combined water was removed. The high rate of heat transfer in the fluidized bed provided practically instantaneous water removal. The partially calcined alumina entered the first combustion fluid bed where again instantaneous water release was achieved.

In order to minimize velocity, this combustion zone was operated at the lowest practical combustion temperature (1400°F), which was also sufficient to remove essentially all of the combined water. The second combustion zone was supplied with only that fuel and combustion air required to supply the sensible heat to raise the essentially anhydrous alumina to the temperature required for the desired properties. Cyclones were supplied in the zones handling the highest vapor volumes to permit fluidization velocities in the range of high entrainment. To achieve increased capacity in economically sized units, the calciners were operated under pressure. The capacity of the fluid caleiner was set by the quantity of fuel that could be burned within the fluid beds in the two combustion zones. Higher fuel input resulted in after-burning with excessive temperature in the disengaging zone and cyclones above the bed. For the 12 ft dia. unit capacity was limited to about 12,000 lb/hr at atmospheric pressure and 25,000 lb/hr (300 ton/day) with pressure operation.

Our studies on alumina calcination next turned to dispersed phase contacting systems, which showed promise of avoiding the capacity limitations of the fluidized bed process. A 1960 study produced the revised calciner shown in Fig. 2. The upper hearth of the prior unit has been removed, the internal cyclone has been replaced with an external refractory lined cyclone returning to the combustion vessel. It was proposed to operate a single combustion zone well above conveying velocities and control density of the dispersed phase by setting the rate of alumina withdrawal. In this manner, the entire vessel volume is available for combustion. At the higher velocities, it was estimated that the 300 ton/day rate could be attained without pressure operation.

Continuing studies resulted in the design shown in Fig. 3. The combustion zone has been further simplified by eliminating hearths entirely. The furnace takes the shape of a vertical cylinder with conical top and bottom. Heated combustion air enters at the bottom of the furnace. Fuel--gas or oil-- is introduced at several points around the periphery of the lower portion of the cylindrical section. Partially calcined alumina from a cyclone heat exchanger is fed to the combustion zone through an inclined conduit aimed to spout the alumina into the central portion of the furnace. The calcined alumina and combustion products leave the top of the furnace and enter a cyclone where the solids separate from the gas stream and fall into a fluidized bed in the lower portion of the cyclone vessel. Complete combustion and maximum calcining temperature are achieved in the dispersed phase (flash) calcination stage. The holding period in the fluid bed, at calcining temperature or slightly below due to losses to radiation and fluidizing air, provides control of L.O.I. and surface area.

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This system is now used in the Alcoa "fluid-flash" calciners, which combine the advantages of dense phase fluidization and dilute phase techniques. All of the high volume combustion products and released water vapor are handled in high velocity, low density suspension systems to keep vessel diameters and pressure drops at a minimum. Dense phase fluidized beds provide high heat transfer rates for indirect heat exchange and thermal and mass capacity to make close process control feasible.

Light Metals

In the fluid-flash calciner moist filter cake is fed into a flash drying section where surface moisture is removed by contact with combustion products and water vapor. The dried hydroxide is held in a fluidized bed dryer, which provides a "thermal fly wheel" to allow for feed variations and insure dryness of the hydroxide. Dry hydroxide is conveyed from the dryer to the calcining section at a controlled rate to maintain constant calcining temperature. Calcined alumina leaving the combustion zone is retained in a fluidized bed for the desired period of time by control of bed level. The combination of calcination temperature and retention time determines the physical characteristics of the product alumina. The calcined alumina is first cooled by direct contact with combustion air in a series of cyclone heat exchangers and finally in a twodeck fluid bed cooler. A tubular heat exchanger in the upper deck heats air for the fluid dryer, and water-cooled tube bundles provide the final cooling in the lower deck.

The original fluid bed-calciner at the Bauxite, Arkansas alumina plant was modified to the "Fluid-Flash" design and began operation in 1963. This was followed by 600 ton/day Mark II units at Alcoa installations in Suriname in 1965 and at Kwinana in Western Australia in 1966. Design modifications to the Mark II units gradually raised the design rating to 900 ton/day. In 1971 an improved and enlarged Mark III calciner began operation at Alcoa's Point Comfort, Texas works to be followed by additional units at the new Clarendon Works in Jamaica and the Pinjarra Works in Western Australia. The Mark III carried a nominal design rating of 1200 ton/day but now exceeds 1500 ton per day. Including the original Bauxite Works unit, and another 300 ton/day unit in Brazil, Alcoa has 24 fluidflash calciners in operation, with 4 additional units presently approved.

Fuel requirement for the Alcoa Calciner is approximately 1400 gross Btu/lb of alumina and, due to the high heat exchange efficiency, is practically independent of calcining temperature. About 100 Btu/lb of alumina is available for heating process water. Power consumption is about 20 KWH/ton.

The Mark III Claciner is 90 ft in height and occupies a building area 50 ft X 106 ft.

In addition to a 30% fuel saving over Alcoa's best rotary kiln practice with a soft burned aluminas -- upwards of 40% for hard burned, the Alcoa fluidflash calciner has provided major savings in capital investment and maintenance costs.

Spiraling fuel costs and environmental problems with rotary kilns have now reached the point that fuel and maintenance savings of the Alcoa calciner make replacement of older existing rotary kiln facilities attractive.



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FIGURE 4 Kwinana Fluid-Flash Calciners, 900 tons/day



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FIGURE 5 Aerial View of Clarendon Plant



FIGURE 7 Clarendon Fluid-Flash Calciners, 1500 tons/day



FIGURE 6 Aerial View of Clarendon Plant



FIGURE 8 Brazil Fluid-Flash Calciners, 300 tons/day
