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DEVELOPMENT OF A FLUIDIZED BED CALCINATION
PROCESS FOR ALUMINUM NITRATE WASTES
IN A TWO-FOOT-SQUARE PILOT PLANT CALCINER

PART II: FACTORS AFFECTING THE INTRA-PARTICLE
POROSITY OF ALUMINA

B. R. Wheeler, E. S. Grimmer and J. A. Buckham

**PHILLIPS
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ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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A B S T R A C T

A seven- to twenty-fold volume reduction can be obtained from fluidized bed calcination of aqueous aluminum nitrate wastes, depending on the operating conditions employed and their effect on the intra-particle porosity and absolute density of the calcined alumina. Among the calcining variables, only the bed temperature and the feed aluminum concentration had a significant effect on the intra-particle porosity of alumina generated during studies conducted primarily in a two-foot-square fluidized bed calciner. A quantitative correlation of the effect of these variables is presented. Alumina with an intra-particle porosity as low as five per cent can be generated by employing a suitable combination of low bed temperature and dilute aluminum feed concentration. Feed sodium concentration and product alpha alumina content were found to have minor effect on intra-particle porosity.

Results obtained incidental to the main purpose of the study show that an inverse relationship exists between the nitrate content of the calcine and the calcination temperature.

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I. SUMMARY

Aluminum nitrate waste solutions are proposed as the initial feed for conversion by the fluidized bed calcination process into a free-flowing solid in the Demonstrational Waste Calcining Facility (DWCF) at the Idaho Chemical Processing Plant. Certain properties of the resulting alumina, such as intra-particle porosity, absolute density, thermal conductivity, and particle size distribution define the size, cooling requirements, and cost of the solids storage facilities.

Intra-particle porosity of the alumina generated by fluidized bed calcination was found to vary from 60 to 5 per cent, equivalent to a seven- to twenty-fold volume reduction from that of the stored waste aluminum nitrate solutions. Factors found to have a major effect on the intra-particle porosity of the alumina were bed temperature and feed aluminum concentration. Low-porosity alumina is generated by employing a suitable combination of low bed temperature and dilute feed.

Some minor effects were observed. Use of unusually high concentrations of sodium in the feed appears to cause a slight decrease in the intra-particle porosity of calcined alumina; the presence of alpha crystalline material in the calcine, if not created by the addition of large amounts of sodium to the feed, generally causes a slight increase in intra-particle porosity. No other factor was found to have a significant effect on calcine intra-particle porosity; among the factors found to have an insignificant effect under the test conditions employed are the nitric acid, boric acid, and mercuric nitrate concentrations in the feed, method of feed introduction, feed nozzle design, atomizing nozzle air-to-liquid volume ratio, superficial fluidizing gas velocity, feed rate, dry fines return, equipment size, and equipment configuration.

Sand starting beds, employed for a portion of the runs in the pilot plant calciner during this study, were advantageous because identifiable trends in alumina properties could be established early in a run, the effect on product attributes of the history of the bed was eliminated, and particle growth characteristics could be observed easily.

Results showing the inverse relationship of nitrate content of the calcine with temperature were obtained incidentally to the main purpose of the study and are also reported.

II. INTRODUCTION

Intensive effort has been expended by all major atomic energy agencies to develop a method of permanent storage of radioactive wastes resulting from the processing of spent nuclear fuel elements. These wastes are currently stored in the form of corrosive liquid in large underground tanks. Obviously, this form of storage is temporary and potentially hazardous. Converting the liquid waste into suitable solids would minimize most of the long-range problems associated with storage of the waste, and at the same time would reduce the storage volume considerably.

Research and development work performed at the Argonne National Laboratory⁽¹⁾ and at the Idaho Chemical Processing Plant⁽²⁾ demonstrated that the fluidized bed calcination process could reduce liquid waste to a solid form and satisfy many of the requirements for permanent storage. The design criteria of a large-scale Demonstrational Waste Calcining Facility were based on this early work and were reported previously by MacQueen and Stevens⁽³⁾. Early pilot plant studies on this process were conducted in a six-inch-diameter calciner and were reported by Evans⁽⁴⁾. Brown, Grimmett, and Buckham⁽⁵⁾ have reported on the equipment development and initial process studies in the two-foot-square pilot plant calciner.

The heart of this calcination process is a fluidized bed calciner in which an aqueous solution of metal salts is converted into free-flowing granular oxides by spraying the solution into a heated (250-550° C) fluidized bed of granular material. The water vapor and volatile decomposition products leave with the fluidizing medium, which can be any suitable gas (e.g., air, steam, a reducing gas, or an oxidizing gas). The granular solids continuously overflow from the calcining vessel and are pneumatically transported to storage vaults.

Aluminum nitrate waste solutions resulting from chemical processing of aluminum alloy nuclear fuels are proposed as the first type of liquid waste to be converted into a free-flowing solid in the DWCF. The alumina product can be amorphous or partly the alpha crystalline form, depending on operating conditions employed. Certain physical characteristics of these alumina materials, such as intra-particle porosity, thermal conductivity, and particle size, affect long-term storage considerations. The stored volume of alumina can vary over two-fold, depending on the intra-particle porosity and the absolute density of the product being generated. Also, the thermal conductivity of the alumina would be expected to increase as the porosity decreases, thereby permitting larger unit storage volumes without exceeding any given storage temperature limitation. The studies reported herein were made primarily in a two-foot-square calciner pilot plant to determine the effect of operating variables on the intra-particle porosity of calcined alumina.

III. EQUIPMENT

The two-foot-square fluidized bed calciner⁽⁵⁾ was used for most of the studies made to determine the factors affecting the intra-particle porosity of the alumina product. A schematic drawing of the process and equipment is shown in Figure 1. An aluminum nitrate solution is sprayed through an atomizing nozzle into a heated fluidized bed of suitable granular particles. (During these studies, alumina, sand, or a combination of both were used as bed material.) The majority of the spray droplets are deposited and calcined on the granular particles in the bed; however, some of the spray droplets may be dried and calcined as such and be carried out of the calciner by the off-gas. The decomposition gases leave the calciner with the fluidizing gas, while the alumina product in the form of free-flowing granular particles continuously overflows from the bed to a product collection vessel.

Heat is supplied to the fluidized bed in the calciner by circulating NaK through heat exchange tubes located in the bed. An oil-fired furnace is used to heat the NaK to the required temperature (between 800 and 1400° F). Off-gas cleanup is effected by means of a cyclone, a venturi-scrubber, and a condenser, all arranged in series.

Data for correlating the factors affecting intra-particle porosity of calcined alumina were obtained on Runs 11 through 29. Equipment used on these runs was that described previously⁽⁵⁾, with the following two exceptions:

1. A single feed nozzle was employed in lieu of the two pairs of opposed feed nozzles used on earlier runs. On Run 20, a Spraying Systems Company Type 1/4 LN No. 12 single-fluid pressure nozzle was used in conjunction with a jet grinder consisting of five 1/8-inch-diameter orifices. During all other runs, four different types of caps were used on a Spraying Systems Company Type 1/2 J pneumatic nozzle; an extended divergent cap⁽⁹⁾ was used on Run 13, two types of extended convergent caps^(9,10) were used on Runs 14 and 19, and flat-faced caps⁽⁹⁾ were used on the other runs. These nozzle variations were imposed for the purpose of evaluating the performance of the various nozzles, but they also permitted a determination of the effect of atomizing characteristics on intra-particle porosity.

2. The dry fines return system was modified after Run 14 to permit the return of dry fines to the bed on Runs 15-20 through a three-inch inlet port on the calciner vessel between the support plate and the lower NaK tube and in a position directly beneath the atomizing nozzle. At the same time, the atomizing nozzle was relocated 180° from its original position to increase the probability of the returned dry fines being captured by spray droplets. The inlet port to the bed was made the maximum practical size to keep the velocity of the inlet gas below about ten feet per second to minimize bed attrition and disturbance. When the dry fines return system was operated prior to Run 15, the fines were introduced below the support plate where they were mixed with the fluidizing air and forced through the distributor plate nozzles. Dry fines were not returned to the bed on Runs 21 through 29.

Fig. 1 Schematic Diagram of Two-Foot-Square Pilot Plant Fluidized Bed Calciner System

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Factors affecting the intra-particle porosity, which is a measure of the relative volume of interstices or pores in the alumina particles, were studied to determine how a greater volume reduction of liquid waste to solids could be effected during calcination. The data in this report were obtained from and are representative of a large number of calcination runs using a wide variety of equipment and operating conditions; much of the data for this study, however, originated from a single series of short runs using common equipment and sand starting beds to calcine feed solution of different aluminum concentrations at various bed temperatures. Data from earlier and later runs substantiated the data from this series of short runs.

Intra-particle porosity of alumina was determined from analytical values of the absolute density and apparent particle density of alumina product, and is reported as per cent voids. Sample calculations are shown in the Appendix. For most runs, the absolute and bulk densities of the product being generated were determined every four hours of the run, making it possible to calculate the intra-particle porosity of the alumina periodically. On several runs, including the special series mentioned above, the intra-particle porosity of the alumina shell around a sand core was determined from measured properties of the sand and the other usual values. A detailed discussion of these calculations is also given in the Appendix.

Detailed operating conditions for runs from which intra-particle porosity values were obtained and correlated are given in Table 3 in the Appendix.

A. Effect of Calcination Factors on the Intra-Particle Porosity of Alumina

1. Aluminum Feed Concentration and Bed Temperature

The intra-particle porosity of calcined alumina is significantly affected by both bed temperature and aluminum concentration in the feed. An amorphous alumina with an intra-particle porosity of about five per cent was generated by employing either the combination 1.80M aluminum nitrate solution and a bed temperature of 250° C, or the combination 0.80M aluminum nitrate solution and a bed temperature of 300° C. When more concentrated aluminum nitrate feed solutions or higher bed temperatures were employed, the intra-particle porosity of the resultant alumina was higher, as shown in Figure 2. The highest intra-particle porosity (60 per cent) for amorphous alumina was observed when 1.90M aluminum nitrate solution was calcined at a bed temperature of 500° C.

Alumina with any desired porosity between 5 and 60 per cent can be generated by an appropriate selection of feed concentration and bed temperature. The relationship shown in Figure 2 is of considerable importance to calcination economics, because a reduction in the porosity of the alumina will result in a reduction in the solids storage volume required per unit volume of liquid aluminum nitrate waste calcined.

KEY

Δ - 550° C	◊ - 425° C	X - 350° C
◇ - 500° C	○ - 400° C	□ - 300° C
◊ - 450° C	▽ - 375° C	◑ - 250° C

(FEED SODIUM CONTENT-0.08-0.09M)

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Fig. 2 Effect of Aluminum Feed Concentration and Bed Temperature on the Intra-Particle Porosity of Amorphous Alumina Calcine Produced Under a Wide Variety of Other Operating Conditions

The calculated effect of intra-particle porosity on the volume reduction obtained with 1.72M aluminum nitrate feed solution is shown in Figure 3. As this figure shows, it is possible to achieve a volume reduction between seven- and twenty-fold during calcination of the waste by generating alumina with a suitable porosity; the volume reduction achieved is also dependent upon the absolute density of the alumina, a property primarily dependent upon the alpha alumina content.

The 1.72M aluminum nitrate waste solution stored in WM-185 tank probably will be the first radioactive waste fed to the DWCF. To generate alumina with a low intra-particle porosity, this solution would have to be diluted; however, this is not a serious problem, since the concentration of aluminum in the feed to the DWCF is dependent on the quantity of venturi scrubber slurry returned to the feed stream as well as upon the quantity of aluminum in the fresh feed. The intra-particle porosity of the alumina generated in the DWCF, therefore, can be controlled by appropriate selection of an operating bed temperature and by adjusting the quantity of scrub slurry returned to the feed stream.

Increasing the quantity of scrub slurry to the feed stream will, of course, reduce the net throughput of waste to the calciner per unit time. An economic comparison between the calciner operating costs and the cost of unit storage volume would indicate the optimum intra-particle porosity for alumina generated in a fluidized bed calciner.

Fig. 3 Effect of Intra-Particle Porosity of Alumina on Liquid Waste Volume Reduction

2. Feed Composition

In addition to aluminum nitrate, feed solutions from waste tanks will contain nitric acid, mercuric nitrate, sodium nitrate, and fission products. Also, control of the crystalline nature of the alumina product may be effected by addition to the feed of additional sodium nitrate (to promote alpha alumina formation) or boric acid (to inhibit alpha alumina formation). Consequently, the effect of these other feed constituents is of interest.

An increase in sodium content of the feed appears to reduce the intra-particle porosity of alumina calcine, although a thorough study of this effect has not been made. Sodium concentration in the feed was held essentially constant at about 0.08-0.09M except on Runs 22, 26, 27, and 29. On those runs, much higher sodium concentrations of 0.2 to 0.25M were employed. The intra-particle porosity of the alumina calcine was 32 to 38 per cent on three of those runs, compared to 45 per cent on

similar runs at the lower feed sodium concentration. The porosity values observed on part of Run 26 were even lower, about 28 per cent, but these lower values may have been due to the presence of an undetermined amount of sand in the material used as the starting bed on that run.

The effect on intra-particle porosity of variations in mercuric nitrate and nitric acid concentrations in the feed appears to be very small. This is most vividly shown by a comparison of conditions for the second part of Run 15 and for Run 17, two runs of prolonged operation during which alumina of similar porosity (46 to 49 per cent) was generated. On these runs, made at 400° C, the aluminum concentration was similar, 1.40M and 1.50M, as was the sodium concentration, but the concentrations of mercury and nitric acid were vastly different, as shown in Table 3 in the Appendix. Further evidence of the lack of effect of changes in mercury concentration is given by the fact that mercury was withdrawn from the feed for a portion of Run 21 without significant effect on the porosity of the alumina product.

No significant effect on the intra-particle porosity of alumina calcine was observed when various concentrations of boric acid, a feed additive used to inhibit alpha alumina formation, was added to the feed during Runs 23, 24, and 25.

3. Crystalline Alumina

Intra-particle porosity appears to be only slightly dependent upon the crystalline content of the alumina. In general, an increase in alpha alumina content, not created by the addition of large amounts of sodium to the feed, results in a small increase in intra-particle porosity. Changes in the alpha content between 0 and 25 per cent have been accompanied by changes in intra-particle porosity of up to eight per cent on Runs 17, 23, and 24. Intra-particle porosity is compared to the alpha content of alumina as a function of time during Run 17 in Figure 4. Although it is significant that the intra-particle porosity rose and declined twice along with corresponding changes in the alpha

Fig. 4 Effect of Alpha Alumina on the Intra-Particle Porosity of Alumina

alumina concentration on that run, this effect was a smaller one than those generally caused by changes in the feed aluminum concentration and calcining bed temperature.

On rare occasions, the gamma and iota crystalline forms have been observed in the calcine; data have been insufficient to distinguish an effect, if any, of these crystalline forms on the intra-particle porosity.

4. Other Variables

No significant effect on the intra-particle porosity of the alumina product was observed when changes were made in the feed rate, the nozzle air-to-liquid volume ratio, the superficial fluidizing gas velocity, or when nozzle caps of different design were employed on the pneumatic nozzle. Among the calcination variables, only the bed temperature and aluminum feed concentration employed during Runs 12, 13, and 14 were similar; values of the other variables differed widely. Yet the intra-particle porosity on these runs varied only over the narrow range between 42 and 49 per cent; this small variation of intra-particle porosity is attributed largely to small variations in the aluminum feed concentration.

Operating the calciner at a reduced superficial fluidizing gas velocity of 0.5 ft/sec (compared to the usual value of about 1.0 ft/sec) had no significant effect on the intra-particle porosity of alumina product generated during Run 24.

No significant effect due to use of a pressure-atomizing, single-fluid nozzle was observed on the intra-particle porosity of alumina generated on Run 20. The intra-particle porosity of the alumina generated on that run varied between 39 and 47 per cent, as compared to an observed average value of 44 per cent for alumina generated during use of pneumatic-atomizing feed nozzles at the same bed temperature and aluminum feed concentration.

The intra-particle porosity of alumina generated in a calciner used for special feed introduction studies at Battelle Memorial Institute⁽⁶⁾ was consistent with the correlation of the effect of feed concentration and bed temperature shown in Figure 2. The aluminum nitrate was introduced in the Battelle calciner through the top of the vessel and sprayed on top of the fluidized bed of alumina, as contrasted to the use of submerged atomizing nozzles to obtain the data presented in Figure 2.

Equipment size and configuration appear to have no effect on the intra-particle porosity of alumina calcine; alumina generated in both the DWCF and the new twelve-inch-diameter pilot plant calciner had the same intra-particle porosity as material generated in the two-foot-square pilot plant calciner at the same bed temperature and feed aluminum concentration. During DWCF Run WCN-005 when calcining 1.3-1.5M aluminum nitrate solutions at 400° C bed temperature, alumina was generated with an average intra-particle porosity of 40 per cent; this is consistent with values shown in Figure 2. The intra-particle porosity of product from earlier DWCF runs could not be compared to pilot plant data because of the difficulty of measuring apparent particle density for the extremely fine

material produced on those runs. In two runs in the twelve-inch-diameter pilot plant calciner using recycled off-gas for fluidizing, the product intra-particle porosity averaged 52 per cent for a bed temperature of 400° C and a feed aluminum concentration of 1.74M; this also agrees with the correlation shown in Figure 2.

Dry fines return to the bed appears to have no effect on the intra-particle porosity of alumina calcine. Alumina generated during Runs 21 through 29 in which no dry fines return was employed had intra-particle porosities consistent with those shown in Figure 2.

B. Reliability of the Porosity Data Obtained

The intra-particle porosity data for all alumina generated in the two-foot-square pilot plant calciner have been consistent with those shown in Figure 2, as are the data obtained to date in the DWCF. In each of the prolonged pilot plant calciner runs in which sand was used as a starting bed (Runs 17, 18-J, 19, 20, and 21), the intra-particle porosity value calculated after only 24 hours of operation was consistent with the value observed for the alumina product at the end of the run six to ten days later. The agreement of these data indicates that Figure 2 represents a reliable basis for prediction of the effect of calcination factors on intra-particle porosity.

C. Calcine Storage Considerations

1. Results of Heat Treating Low-Porosity Alumina

Samples of low-alpha-content, low-intra-particle-porosity alumina were converted to 55 per cent alpha alumina by maintaining the temperature of the alumina at about 1020° C for 200 hours in a laboratory furnace. The objective of this test was to determine the effect that high-temperature storage might have on the porosity and bulk density of the stored alumina. Temperatures near 1000° C will effect a change in the physical structure of much of the amorphous alumina to the more dense alpha form. Such a change must obviously be accompanied either by an increase in bulk density or by an increase in the void spaces within or between the particles. Data obtained from this test, shown in Table 1, indicate that the intra-particle porosity increases as a result of the conversion. The difference between the initial and final bulk density values shown in the table is not considered significant.

2. Thermal Conductivity of Low-Porosity Alumina

From a storage viewpoint, it is desirable that the thermal conductivity of the alumina be as high as possible, since the fission product heat must be removed by thermal conduction. Material with a high thermal conductivity will permit use of large-sized, lower-cost storage containers for a given maximum allowable centerline temperature. Although quantitative studies of the effect of porosity on the thermal conductivity of calcined alumina have not yet been made, theoretical and experimental studies⁽⁷⁾ indicate that the thermal conductivity for porous materials varies inversely with the porosity of the material.

Table 1

COMPARISON OF PHYSICAL CHARACTERISTICS OF LOW-POROSITY ALUMINA
BEFORE AND AFTER PROLONGED HEAT TREATMENT

	Average Property Values for Two Samples	
	Before Heating	After Heating at 1020° C for 200 Hours
Absolute density, g/cc	3.10	3.34
Particle density, g/cc	2.38	2.28
Bulk density (calculated), g/cc	1.41	1.35
Alpha alumina content, weight per cent	5.0	55.0
Nitrate content, millimole/gram	1.32	0.06
Intra-particle porosity, per cent	23.0	32.0

D. Effect of Bed Temperature on the Nitrate Content of Alumina

A corollary result of these studies was a quantitative determination of the effect of bed temperature on the residual nitrate content of calcined alumina. The nitrate content of amorphous* alumina is shown as a function of the calcining bed temperature in Figure 5. As expected, the nitrate content of the alumina is inversely related to the bed temperature. Some data scatter is evident, possibly due to a minor effect of feed concentration.

Fig. 5 Effect of Bed Temperature on the Nitrate Content of Amorphous Alumina

Although the nitrate content is several-fold higher for alumina created at a low bed temperature than it is for alumina created at a high bed temperature, no significant storage problems due to nitrate evolution are visualized for alumina created in the DWCF at low bed temperatures. Certainly some nitrogen oxides will be slowly evolved during storage if the calcining temperature used in generation of the alumina is less than the eventual storage temperature. Possibly radiolytic decay will result in additional gas evolution. However, the rate of gas evolution during storage is not an important factor, if the calcine is not stored in pressure-tight containers.

* The nitrate content of calcine has also been observed to decrease with increasing alpha alumina content⁽⁸⁾.

V. CONCLUSIONS

1. The intra-particle porosity of alumina is significantly affected by the bed temperature and aluminum concentration of the feed employed during calcination. Alumina with porosities as low as five per cent may be generated by employing a suitable combination of low bed temperature and dilute feed concentration. Calcine intra-particle porosities as high as 60 per cent can be generated by employing high bed temperatures and concentrated feed solutions.

2. An increase in the sodium content of the feed from 0.08 to 0.25M slightly decreases the intra-particle porosity of alumina calcine. The presence of the alpha crystalline phase in alumina, if not generated by the addition of large amounts of sodium to the feed, slightly increases the intra-particle porosity. However, these effects are minor compared to the effect of bed temperature and aluminum concentration.

3. Other factors such as concentrations of mercury, boric acid, and nitric acid in the feed, feed nozzle design, nozzle air-to-liquid volume ratio in the case of pneumatic nozzles, feed rate, dry fines return, superficial fluidizing air velocity, the location of feed introduction to the calciner, equipment size, and equipment configuration were found to have no significant effect on the intra-particle porosity of the alumina being generated.

4. A seven- to twenty-fold volume reduction can be obtained by calcining aluminum nitrate wastes, depending on the intra-particle porosity and absolute density of the alumina being generated.

5. The nitrate content of calcined amorphous alumina varies inversely with the bed temperature at which the alumina is generated. Calcination of aluminum nitrate solution at bed temperatures of 250° C will result in product containing as much as 16 per cent nitrate; at 550° C, the product contains only about four per cent nitrate.

6. The use of sand as a starting bed in the calciner during those runs from which most of the intra-particle porosity data were obtained reduced the necessary operating time of the study 60 to 80 per cent. The reliability of the data resulting from this procedure was shown to be satisfactory by several extended periods of operation.

VI. ACKNOWLEDGMENTS ..

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VIII. APPENDIX

A. Definitions

Absolute density is applied only to the material portion of the product particles; the volume associated with this density excludes all voids within and between individual particles. The absolute density of the alumina was determined from the displaced volume of CCl_4 , which is believed to penetrate all voids between and within particles.

Apparent particle density is applied to individual particles of the product. The volume in this density determination includes the volume of the material and intra-particle pores, but excludes the void space between and around individual particles; it is determined from the displaced volume of mercury which at low pressure penetrates voids around particles but forms a protective envelope around particles because of the high interfacial tension and does not penetrate internal pores in particles.

Bulk density is applied to the poured bulk product. The volume in this density determination includes the material volume, the intra-particle pore volume, and the inter-particle void volume.

Intra-particle porosity is applied to the void space within individual particles and is determined by calculation. A typical calculation is shown in paragraph C3 of the Appendix.

Inter-particle void fraction is applied to the space between particles. The inter-particle void fraction for typical calcined alumina produced in pilot plant calciners has a constant value of 0.41; pertinent data are given in the following section.

B. Inter-Particle Void Fraction

The bulk density of alumina generated with a pneumatic nozzle is consistently about 59 per cent of the particle density over the particle size ranges encountered in these studies, as shown by the correlation in Figure 6. Thus, the inter-particle void fraction of this material is 0.41. This correlation did not appear applicable when a jet grinder was utilized to control the particle size of the alumina during Run 20. Apparently the jet grinder changes the size distribution and shape of the product so that the resultant inter-particle void space is also changed.

C. Sand as a Starting Bed

1. Advantages

Sand was used in lieu of alumina as a starting bed on Runs 17 through 21, and this resulted in several advantages: Identifiable trends in alumina properties could be established early in a run; consideration of history of the bed, an undesirable variable which may affect product attributes, was made unnecessary; and particle growth characteristics could be easily observed.

Fig. 6 Relationship Between Bulk and Particle Densities of Alumina Calcine

Prior to Run 17, alumina generated from previous calciner runs was used as an initial starting bed. This was undesirable because the old material may influence the attributes of the newly formed product; furthermore, it was not possible to determine porosity, alpha alumina content, attrition index, and other similar product characteristics of newly generated alumina until a high fraction of the starting bed was replaced. Use of a different material, such as sand, for a starting bed made it possible to determine the characteristics of newly generated alumina early in a run by eliminating the influence of the starting material on measurements and analysis through suitable calculations.

During Run 17, for the first time, the intra-particle porosity, alpha alumina content, and other properties of the new alumina were known just a few hours after the run began. The success achieved on Runs 17 and 18 with the use of sand as a starting bed reduced the experimental operating time of this study by 60 to 80 per cent.

2. Properties of the Sand

Some of the properties of the sand used as a starting bed for Runs 17 through 21 are compared in Table 2 with those of alumina calcine.

Table 2

COMPARISON OF VARIOUS PROPERTIES OF SAND AND ALUMINA

	Sand		Alumina	
	Value	Temp.	Value	Temp.
Thermal conductivity Btu/(hr)(ft ²)(°F/ft)	0.19	20° C	0.08 0.17 0.198	100° C 400° C 500° C
Specific heat, Btu/lb	0.19	20° C	0.20 0.274	100° C 1500° C
Absolute density, g/cc	2.62		2.62 - 3.95	
Bulk density, g/cc	1.46 - 1.53		0.7 - 1.6	
Particle density, g/cc	2.56		1.18 - 2.0	
Intra-particle porosity, per cent	2		5 - 60	
Mass median particle diameter, d ₅₀ , mm	0.26		0.26 - 1.20	

3. Bed Replacement Rate

Although it was possible to calculate the rate of bed replacement prior to Run 17, the calculated values could not be verified. For Run 17 and subsequent runs in which sand was used as the starting bed, the replacement of the sand by alumina was easily followed by chemical analysis of the bulk product; a derived bed replacement or "washout" equation then could be checked. The washout equation is based on the assumption that the fluidized bed is perfectly mixed.

Bed replacement occurs basically in terms of volume instead of weight; therefore the washout equation must be expressed in terms of a volume fraction. When more than one component exists in a bed and the weight fraction of one of the components is desired, the particle densities of the components involved must be used in the calculations. For a two-component system, the following equations therefore can be used to calculate, for any given time, the weight fraction of the material which has replaced the original bed:

$$X_v = 1 - e^{-\frac{Pt}{W}} \quad \text{Eq. 1}$$

$$X_w = \frac{X_v \rho_f}{\rho_o + X_v (\rho_f - \rho_o)} \quad \text{Eq. 2}$$

where the meaning of the symbols and the usual units employed is

X_v = volume fraction of final bed material
 X_w = weight fraction of final bed material
 P = product rate, kg/hr
 W = bed weight, kg

t = time, hours
 ρ_f = particle density of final bed material, g/cc
 ρ_o = particle density of original bed material, g/cc

The calculated values from the above equations are in excellent agreement with analytical values for various alumina concentrations.

4. Calculations of Intra-Particle Porosity of Alumina Shell

The porosity of the alumina fraction of the alumina-sand product particles was calculated by using the relationship between the absolute and apparent particle densities derived in the following discussion and shown in Equation 3. Analytical values were available for the bulk density and absolute density of the sand-alumina product; however, the apparent particle density and absolute density of the alumina portion of the product had to be calculated. (Coincidentally and conveniently, the absolute density of the sand used in this study and of amorphous alumina is the same, 2.62 g/cc.) The relationship of porosity to the absolute and apparent particle densities and the method used to calculate the absolute and particle densities of the alumina fraction of the product are as follows:

Let V_a = particle material volume (excluding voids), cc
 V_v = particle void volume, cc
 V_p = total particle volume, cc
 ρ_p = apparent particle density, g/cc
 ρ_a = absolute density, g/cc

The intra-particle porosity percentage is defined as $\frac{V_v}{V_p} (100)$

or $\frac{(V_p - V_a)}{V_p} (100)$; for one gram of product, $V_p = \frac{1}{\rho_p}$ and $V_a = \frac{1}{\rho_a}$.

Therefore,

$$\text{intra-particle porosity} = \frac{\frac{1}{\rho_p} - \frac{1}{\rho_a}}{\frac{1}{\rho_p}} (100) = \frac{(\rho_a - \rho_p)(100)}{\rho_a} \% \quad \text{Eq. 3}$$

The bulk density of alumina averages 59 per cent of the particle density. The bulk density of sand was found to vary between 57 and 59 per cent of the particle density in the same units of measure; an average value of 58 per cent was, therefore, used for alumina-coated sand product. For example, when the product bulk density was 1.06 g/cc, its particle density was found to be 1.83 g/cc, as shown by the following calculation:

$$\rho_p \text{ of product}^* = \frac{1.06}{0.58} = 1.83 \text{ g/cc}$$

* The particle density of the alumina sand product may also be determined analytically, and when jet grinders were used it was necessary to do so. However, the particle density of the alumina fraction of the alumina-sand product still must be calculated.

The particle density of alumina may be calculated from the following equation:

$$\rho_p \text{ of alumina} = \frac{(\text{the particle weight of alumina})}{(\text{the particle volume of alumina})} \quad \text{Eq. 4}$$

but, based on one cc of actual product, the particle volume of alumina =

$$1 - \frac{(\rho_p \text{ of product})(\text{weight fraction sand})}{(\rho_p \text{ of sand})} \quad \text{Eq. 5}$$

The particle density of sand, determined analytically, is 2.56 g/cc. Therefore, the volume of the alumina shell in this example for a material containing 50 weight per cent sand is calculated from Equation 5 to be:

$$1 - \frac{(1.83)(0.50)}{2.56} = 0.642 \text{ cc.}$$

On the same basis, the weight of the alumina shell =

$$(\rho_p \text{ of product})(\text{weight fraction alumina}) \quad \text{Eq. 6}$$

or $= (1.83)(0.50) = 0.915 \text{ gram}$ for the same example.

Therefore, from Equation 4 the particle density of the alumina shell

$$= \frac{0.915 \text{ g}}{0.642 \text{ cc}} = 1.43 \text{ g/cc.}$$

The absolute density of the alumina shell of alumina-sand product was calculated in a manner similar to that used to obtain particle densities.

Equation 3 was used to calculate the porosity of the alumina, as follows:

$$\text{Porosity} = \frac{(2.62 - 1.43)(100)}{2.62} = 46 \text{ per cent}$$

D. Summarized Pilot Plant Calcining Conditions

Summarized operating conditions and average intra-particle porosity values are shown in Table 3 for those runs from which data were obtained for the correlations given in this report. Each of the pilot plant runs lasted 200 to 300 hours, and measurements of all known independent and dependent variables were taken at intervals ranging from one to four hours throughout each run. Detailed data not pertinent to this report are not given herein, but will be incorporated into subsequent reports in this series.

Table 3

PERTINENT CALCINING CONDITIONS FOR RUNS IN TWO-FOOT-SQUARE CALCINER

Run No.	Bed Temp. °C	Average Feed Composition					Fluidizing ⁽¹⁾ Velocity ft/sec	Dry Fines Return	Feed Rate 1/hr	NAR ⁽²⁾	Starting Bed	Type of Nozzle Cap on Pneumatic Nozzle	Intra- Particle Porosity (Per Cent)
		Al, M	HNO ₃ , M	Na, M	Hg, M	H ₂ BO ₃ , M							
11	500	1.85	1.84	0.103	0.0065	None	0.78	None	80	120-590	Alumina	Flat	60
12	400	1.22	2.84	0.078	0.014	None	0.90	None	112,120	300	Alumina	Flat	43
13	400	1.30	2.95	0.079	0.015	None	1.0	Yes	45-100	400-1100	Alumina	Divergent	45
14	400	1.31	2.97	0.081	0.015	None	1.0	Yes	100-115	250-400	Alumina	Convergent, long	44
15	500, 400, 500	1.40	2.89	0.086	0.016	None	1.0	Yes	90	400	Alumina	Flat	47-57
16	400	1.89	1.24	0.103	0.0061	None	1.0	Yes	90	400	Alumina	Flat	59
17	425	1.50	1.26	0.088	0.0060	None	1.0	Yes	90	300-450	Sand	Flat	42-47
18 A	500	1.90	1.25	0.092	0.0060	None	1.0	Yes	90	400	Sand	Flat	58
B	400	1.96	1.27	0.087	0.0058	None	1.0	Yes	90	400	Sand	Flat	55
C	450	1.54	1.25	0.090	0.0062	None	1.0	Yes	90	400	Sand	Flat	49
E	550	1.00	1.28	0.092	0.0060	None	1.0	Yes	90	400	Sand	Flat	52
F	350	1.00	1.22	0.090	0.0059	None	1.0	Yes	90	400	Sand	Flat	16
J	350	0.98	1.24	0.090	0.0058	None	1.0	Yes	90	400	Sand	Flat	24
K	300	1.25	1.36	0.089	0.0058	None	1.0	Yes	90	400	Sand	Flat	21
L	300	0.99	1.23	0.092	0.0062	None	1.0	Yes	90	400	Sand	Flat	10
M	375	1.01	1.26	0.091	0.0060	None	1.0	Yes	90	400	Sand	Flat	30
N	350	1.81	1.24	0.089	0.0060	None	1.0	Yes	90	400	Sand	Flat	40
P	250	1.80	1.24	0.088	0.0060	None	1.0	Yes	90	400	Sand	Flat	5
Q	350	1.28	1.21	0.091	0.0060	None	1.0	Yes	90	400	Sand	Flat	31
R	300	0.80	1.22	0.091	0.0058	None	1.0	Yes	90	400	Sand	Flat	5
S	300	1.51	1.27	0.094	0.0062	None	1.0	Yes	90	400	Sand	Flat	22
19	400	1.29	2.84	0.078	0.015	None	1.0	Yes	80, 90	250, 500	Sand	Convergent, short	40
20	400	1.29	2.84	0.078	0.015	None	1.0	Yes	40	No Nozzle Air	Sand	(3)	44
21	400	1.29	2.34	0.078	0, 0.015	None	1.0	None	80	400, 500, 600	Sand	Flat	40
22	400	1.29	2.34	0.078	0.015	None	1.0	None	80	600	Alumina	Flat	35-47
				0.25, 0.03									
23	400, 500, 550	1.29	2.34	0.078	0.015	0.20	1.0	None	80	600, 450	Alumina	Flat	45-50
24	400	1.29	2.34	0.078	0.015	0.05	1.0	None	80	450	Alumina	Flat	45
25	400	1.29	2.34	0.078	0.015	0.10	0.5-0.8	None	80, 40	450, 900, 150	Alumina	Flat	43
26	400	1.29	2.34	0.2	None	None	0.5	None	80, 40	250-900	Alumina	Flat	25(4)
27	400, 550	1.29	2.34	0.078, 0.2	None	0, 0.01, 0.1	0.5, 1.0	None	80-150	300, 450, 800	Alumina	Flat	35-46
28	400	1.29	2.34	0.078	None	0.01	0.5, 1.0	None	80	225, 450	Alumina	Flat	43
29	400	1.29	2.34	0.20	None	None	0.5	None	120, 150	150, 200	Alumina	Flat	35
										250, 300			

(1) The superficial fluidizing velocity is determined on the basis of the empty cross section of the calciner at the calciner bed temperature and vessel pressure, and includes the fresh air and dry fines return gas; it does not include the nozzle air, the water vapor, or decomposition products of the feed.

(2) The air volume in the nozzle air-to-liquid volume ratio is determined at the metered temperature and vessel pressure.

(3) A Spraying Systems Company Type 1/4 LN No. 12 single-fluid atomizing nozzle was used.

(4) Low values may be due to an undetermined quantity of sand in the starting bed.

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