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LOW TEMPERATURE POLYMORPHIC TRANSFORMATIONS
OF CALCINED ALUMINA

AlO₂

R. F. Murray and D. W. Rhodes

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

The factors which affect the transformation of amorphous alumina to crystalline alumina in the temperature range 350° to 650°C were studied. Amorphous alumina, with small amounts of added "impurities", was heated in an atmosphere containing the oxides of nitrogen, air and water vapor, and the amount of crystalline alumina was determined. Alpha alumina was the predominant crystalline form after heating amorphous alumina that had been prepared in a fluid bed calciner. The influence of temperature, composition of the atmosphere, time of heating, impurities, and method of preparation of the amorphous alumina on the transformation to crystalline phases were investigated. An atmosphere containing water vapor and the oxides of nitrogen and a small amount of sodium nitrate in the alumina product were necessary to produce the alpha alumina phase from amorphous alumina at the relatively low temperature of 400°C. Boric acid added to the fluid-bed calciner feed successfully inhibited the formation of the alpha crystalline form.

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I. SUMMARY

Polymorphic transformations of amorphous calcined alumina were investigated in the laboratory to determine the effect of specific calciner variables on the formation of crystalline alumina in a fluid bed calciner. This laboratory investigation was coordinated with a program of pilot plant waste calcination development and demonstration at the Idaho Chemical Processing Plant whose objective is to develop a method for the calcination of the aluminum nitrate-nitric acid waste resulting from the processing of nuclear fuel. The operation of pilot plant fluid bed calciners^(17,18) demonstrated that alpha alumina was the predominant crystalline form in the calcined product under certain operating conditions, and that it greatly affected the operability of the pilot unit. For this reason it was important to isolate and study as many of the calciner variables as possible to evaluate their effect on the transition of amorphous alumina to the alpha form. By subjecting calciner product to different treatments in a static laboratory unit, the effects of the variables, composition of the atmosphere, temperature, time of heating, and impurities were isolated. A two-inch-diameter fluid bed laboratory calciner demonstrated that it was necessary to form the amorphous alumina (> 95% material noncrystalline to X-ray diffraction) under fluid bed conditions to produce "sensitive" material that could be converted to alpha alumina at the relatively low temperature of 400°C. The experimental results from a static test unit showed that an atmosphere containing the oxides of nitrogen and water vapor plus the presence of sodium in the alumina product were necessary to produce alpha alumina from "sensitive" amorphous alumina at temperatures between 300° and 600°C.

II. INTRODUCTION

One method of radioactive waste treatment under intensive development at the Idaho Chemical Processing Plant (ICPP) is the conversion of aqueous, acidic, aluminum nitrate wastes to solid particles by fluid bed calcination. The operation of pilot plant fluid bed calciners with synthetic wastes demonstrated that certain product or process characteristics were associated with the presence of crystalline (alpha) alumina. For example, density, particle size, and the amount of fines elutriated from the bed were apparently related to the quantity of amorphous (> 95% material noncrystalline to X-ray diffraction) or alpha alumina being produced. For this reason, a laboratory experimental program was conducted to isolate some of the chemical factors involved in the transformations of amorphous to alpha or other crystalline forms of alumina. The main factors investigated were composition of the ambient vapor, impurities in the alumina, temperature, and time of heating. By treating calciner product in a static test unit, it was possible to separate these variables to a certain extent.

This report describes the laboratory investigation of the variables which affect the conversion of amorphous calcined alumina to crystalline alumina under simulated calciner conditions. Although it was impossible to simulate actual calciner conditions, the laboratory results were in general confirmed by results from the pilot plant fluid bed calciner.

III. LITERATURE REVIEW

Phase transformations in alumina have been studied extensively over wide ranges of temperature but usually in an air atmosphere, and from an alkaline system. Normally, a temperature of about 1050°C is necessary to transform gamma alumina or aluminum salts to alpha alumina in air. Diaspore⁽¹⁾ ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) will change to alpha alumina at 450°C in air at atmospheric pressure; however, the diaspore can be formed only under high-pressure hydrothermal conditions. Brindley and Choe⁽²⁾ and Tertian⁽³⁾ reported that the transition from gibbsite ($\alpha \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) to alpha alumina can take two courses, depending on particle size and

origin of the gibbsite as well as rate, pressure, and type of additives. J. W. Newsome⁽¹⁶⁾ described a method for making alpha alumina by heating $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in steam at 450° to 500°C and at 350-1000 psig for 0.5 to 2.5 hours. J. A. Hedvall⁽⁴⁾ discussed atmosphere effects on the reactivity and surface properties of alumina. He found that the gases oxygen, nitrogen, and sulfur dioxide activated either alpha or gamma alumina in its behavior toward calcium oxide, while sulfur trioxide had an opposite effect. It was postulated that the activation was caused by a loosening of the surface structure and by a deep-seated change in the lattice. Huttig⁽⁸⁾ and Markus also reported the effects of foreign gases on the transition of $\gamma \text{Al}_2\text{O}_3$ to $\alpha \text{Al}_2\text{O}_3$. At 850°C, hydrogen chloride produced gamma and alpha phases while sulfur trioxide + air, hydrogen bromide, chlorine, nitrogen dioxide + air and sulfur dioxide produced only gamma alumina. Noda⁽⁹⁾, et al, reported that various chlorides, fluorides, and borax produced crystallites of different size and shape. It was suggested that salts which accelerated crystal growth did so by accelerating the mobility of the oxide lattice ions. Nakai,⁽¹¹⁾ et al, found that borax, lithium oxide, cupric oxide, and ferric oxide promoted crystal growth and increased the mechanical strength of alumina in the order given.

Investigations by Stirland⁽¹²⁾, et al, on thermal transformations in alumina brought out the importance of impurities on transformations. Impurities such as silica, potassium oxide, sodium oxide, and lithium oxide can combine with alumina at temperatures above 600°C to give lines in X-ray spectra foreign to those of the alkali oxide phases.

The surface sensitivity of alumina is discussed in reports by Atlas and Firestone⁽¹³⁾ as well as Rieke and Daniels⁽¹⁴⁾. Samples exposed to gamma rays and light rays showed variations of thermoluminescence when various impurities were present. Annealing in oxygen and introduction of calcium ions lowered luminescence. Interestingly, with complete dehydration the thermoluminescent area increased linearly with the addition of sodium ions. A peak at 236°C was found only with sodium and not with other impurities. These observations are especially important, because they demonstrate changes in the electronic trapping levels

at the surface that can greatly affect the surface reactivity.

The bulletin⁽¹⁵⁾, "Alumina Properties", by Newsome, et al, is an excellent reference on the subject of alumina and its crystalline modifications and characteristics. Figure 1 shows the decomposition sequence of alumina hydrates to form alpha alumina as reported by these authors.

PATH a: 1 ATM. PRESS.; DRY AIR; HEATING RATE, $> 1^{\circ}\text{C}/\text{min.}$; ALKALI PRESENT; $> 100\ \mu$ PARTICLES.

PATH b: 1 ATM. PRESS.; DRY AIR; HEATING RATE, $< 1^{\circ}\text{C}/\text{min.}$; ALKALI ABSENT; $< 10\ \mu$ PARTICLES

Figure 1. Decomposition Sequence of Alumina Hydrates⁽¹⁵⁾

IV. EXPERIMENTAL PROGRAM

A. Purpose

The investigation of the polymorphic transformations of alumina under fluid-bed calcination conditions was initiated to find the effect of some of the chemical variables on the transformation of amorphous alumina to a crystalline form, usually alpha alumina. Because of the difficulties associated with the isolation of some of these variables in

fluid bed calciners, laboratory experiments were conducted to isolate the effect of time and temperature of heating, chemical impurities, composition of the atmosphere, and method of preparation of the alumina on the transformation from amorphous to alpha or other crystalline alumina.

B. Techniques and Equipment

Much of the experimental work was performed in a static test unit that was designed to hold alumina samples in a gas stream at a fixed temperature. In this device, nitric acid was dropped onto a porous ceramic plate through which air passed at a superficial velocity of about 1.0 foot per second countercurrent to the flow of liquid. The gas stream containing air and the decomposition products of nitric acid was passed through a vertical pipe which contained the alumina samples in screen bottomed cylinders. Approximately 510 liters of air per hour and 0.2 liter of 6.8M nitric acid per hour were used to simulate calciner vapor conditions. Experiments were also conducted in this unit with nitric oxide or nitrogen dioxide gas instead of air, and with water instead of nitric acid. The entire unit was maintained at the desired "calcination" temperature by means of a combustion tube furnace with an automatic pyrometer controller. A schematic diagram of the static test unit is shown in Figure 2; a photograph of the actual unit is shown in Figure 3.

In addition to the static test unit, a 2-inch-diameter fluidized bed calciner (Figure 4) made of Vycor glass was fabricated to produce alumina in the laboratory by a technique which simulated the rapid drying process obtained in a pilot plant fluid bed calciner. Alumina was also produced by batch drying and calcination of aluminum nitrate and synthetic feed mixtures in a muffle furnace. The identification of crystalline material formed during calcination was made by X-ray diffraction. Reference to amorphous alumina throughout this document refers to alumina which contained less than 5% crystalline material when the gross sample was subjected to X-ray diffraction. Most of the identifications were made on the X-ray diffractometer, but powder camera techniques were used when a more accurate measure of low levels

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Figure 2. Static Test Unit for Conversion of Amorphous Alumina to Crystalline Alumina

Figure 3. Sample Holder Cup and Sample Holder Tube Extending from Static Test Unit

of alpha alumina in the presence of amorphous alumina was required. In addition, the amorphous alumina was removed from some samples by leaching with hot nitric acid. The amount of crystalline alumina was then determined by measuring the amount of amorphous alumina and other chemical components that had been dissolved and determining the amount and crystal composition of the residue. Electron microscopy and electron diffraction techniques were also used for detailed studies of alumina particles. This work was done both at the University of Utah, Salt Lake City, Utah, and at Stanford Research Institute, Menlo Park, California⁽¹⁹⁾.

The concentrations of cations other than aluminum in the calcined product were determined by emission spectroscopy. Nitrate concentrations were measured by the Kjeldahl method.

Figure 4. The Two-Inch-Diameter Fluid Bed Calciner

V. EXPERIMENTAL RESULTS

A. Batch Calcination

Alumina was prepared in the laboratory by the thermal decomposition of aluminum nitrate in air and by precipitating hydrous aluminum oxide with ammonium hydroxide or sodium hydroxide followed by ignition of the precipitate in air. Samples of alumina prepared in the above manner were heated up to 165 hours in the static test unit at 500°C in an atmosphere of air and nitric acid vapors. The X-ray diffraction results of the heated samples are shown in Table I together with a standard sample, which consisted of amorphous alumina from the 24-inch pilot plant calciner.

Table I

Formation of Alpha Alumina by Heating
Calcined Alumina in the Laboratory Test Unit

Conditions: Heating Temperature, 500°C. Liquid feed 6.8M HNO_3
Standard: Pilot plant calciner material IV-A prepared at 400°C;
contained ~2% by wt. of Na.

Method of Preparation	Weight per cent alpha alumina (by X-ray diffraction) after heating (Hours of Heating)				
	0	5-10	18-22	90-95	140-165
Standard	< 5	9	15	46	62
Decomposed $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	< 5	< 5	< 5	< 5	< 5
NH_4OH Precipitation of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in Solution	< 5	< 5	< 5	< 5	< 5

Although alpha alumina was consistently absent in the samples that were prepared batchwise, even after heating in the static test unit, gamma alumina was formed. In addition, dissolution of the amorphous alumina with hot nitric acid left a small amount of crystalline residue which was identified as chi alumina, a low-temperature transition compound in the transition series alpha alumina trihydrate to alpha alumina. Addition of sodium nitrate to the aluminum nitrate solutions to produce a solid with the same chemical composition as the control did not affect the crystal-forming characteristics.

B. Laboratory Fluid Bed Calcination

The 2-inch-diameter Vycor fluid bed calciner was operated with aluminum nitrate-nitric acid feed containing various concentrations of sodium nitrate. Although this calciner did not duplicate the spray and fluidizing conditions of the pilot plant calciners, it did permit rapid conversion of the liquid to a solid in an atmosphere containing nitric acid vapors and air. The material produced in this calciner consistently had different physical properties than the product produced in the pilot plant calciners. The bulk density was only about one-third of the pilot plant product bulk density, and the particles were fluffy and of irregular shape instead of spherical as the pilot plant product. The residence time of the laboratory-prepared product in the calciner bed was only 1-2 hours; consequently, the material was amorphous to X-ray diffraction, but when heated in the static test unit some of the material was converted to alpha alumina. The highest amount of alpha alumina produced by this method was 30% after heating for seven days at 500°C. Gamma alumina was observed in most of the samples after heating in the static test unit. These results indicate that the calcined product produced in the laboratory fluid bed calciner was intermediate with respect to "alpha forming ability" between the pilot plant product and alumina that had been prepared batchwise. The results of this experiment did, however, demonstrate the important part played by the method of particle formation in determining the particle "crystal-forming potential."

On at least two samples of the overhead fines from the laboratory calciner, X-ray diffraction analysis revealed the presence of crystalline material. X-ray diffraction patterns indicated that this crystalline material was similar to material which had crystallized from an 8M dibasic aluminum nitrate solution during several years' standing. These results suggest that the calcined material may represent a compound intermediate between aluminum nitrate and alumina. The X-ray diffraction patterns are shown in Figure 5.

C. Effect of Sodium on Phase Transformation

As a result of chemicals introduced into the process stream during the chemical processing of enriched uranium fuels, the resulting waste

Figure 5. Comparison of X-Ray Powder Diffraction Patterns of Overhead Fines from the Laboratory Fluid Bed Calciner with a Diffraction Pattern for Dibasic Aluminum Nitrate

contains approximately 0.1M sodium as sodium nitrate. To test the effect of sodium nitrate on the formation of crystalline alumina, samples of amorphous alumina from the pilot plant calciner with 0.1 gram of sodium nitrate added per gram of alumina were heated in the static test unit in an atmosphere of air-nitric acid vapors. The results of this heating test are shown in Table II.

Table II

Effect of Added Sodium Nitrate on the Formation of Crystalline Alumina from Amorphous Alumina 1/

Sample No.	NaNO ₃ ^{2/} Added	Temp. °C	HNO ₃ Feed to Test Unit, M	Heating Time, Hrs.	Product by X-ray Diffraction		
					% α	% γ	Other
78A	No	400	6	21	< 5	low	-----
76A	Yes	400	6	21	29	low	NaNO ₃
53A	Yes	500	6	21	24	20	NaNO ₃
53B	Yes	500	6	69	35	20	NaNO ₃
65C	Yes	500	6	69	41	low	NaNO ₃
65D	Yes	500	6	161	51	low	NaNO ₃
58	No	500	H ₂ O	69	6	~90	-----

1/ Amorphous alumina from the same calciner run was used for all of the samples.

2/ 0.1 gram sodium nitrate added per gram of alumina.

From the data in Table II, it is evident that much more alpha alumina formed in the samples containing sodium nitrate than in samples without sodium nitrate receiving similar treatment. A definite increase in crystalline alumina with time was also evident; however, later results indicated that the rate of formation of alpha alumina from amorphous alumina from different pilot plant runs was not consistent. Gamma alumina also was observed in the samples after heating. One sample (58) heated only with air and water vapor transformed almost completely to gamma alumina. Additional heating of samples high in gamma alumina did not, however, convert the gamma to alpha alumina, indicating that, at least in the system under study, the gamma alumina was not a precursor to the alpha alumina.

D. Effect of Temperature

The effect of temperature on the conversion of amorphous alumina to crystalline alumina was studied in the static test unit. A series of identical samples was placed in the test unit with the bottom of the unit maintained at 350°C and the top at 500°C while air and nitric acid vapors were passed through the samples for 48 hours.

The experiment was then repeated with the bottom of the unit maintained at 500°C and the top at 650°C. The only temperature measurements

made were at the ends (near the top and bottom samples). X-ray diffraction patterns for samples heated within the range 350° to 650°C are shown in Figure 6, with the peak heights indicating the extent of the conversion to alpha alumina. These results suggest that the highest conversion to alpha alumina occurred in the vicinity of 500°C. In later experiments with different calcined alumina, no consistent difference in the amount of alpha alumina formed at temperatures of 400°C or 500°C was observed. Apparently the extreme temperatures (350° and 650°C) produce less alpha alumina than the range in between; however, there did not appear to be a "best" temperature within the range 400° to 500°C for the conversion as determined by the experimental techniques and measurements available. For this reason most of the laboratory experiments were run at either 400° or 500°C.

E. Effect of Starting Material and Time of Heating on Phase Transformations

Samples of calcined alumina from different runs in the 24-inch pilot plant calciner were heated in the static test unit in an air-nitric acid vapor atmosphere and samples were removed periodically for X-ray diffraction analysis. The calcined alumina contained less than 5% crystalline alumina prior to heating. The results of the X-ray diffraction analysis of materials from two different runs in the pilot plant calciner are shown in Figure 7. From this figure it is evident that while the amount of alpha alumina formed increased with time for both samples, the rate of increase varied with the "sensitivity" or "alpha-forming ability" of the particular material being studied. The rate of conversion to alpha alumina of these two samples is shown again in Figure 8 as a rate in exponential form. Determining the rate of conversion from amorphous to alpha alumina of samples from many different calciner runs produced values varying from $\% \alpha = kt^{0.1}$ to $\% \alpha = kt^{1.0}$. Conversion of amorphous alumina to alpha alumina in successive tests with calcined material from a particular calciner run was, however, reproducible (the material used to produce curve I was used as a standard in other runs). The reasons for the variation in "alpha-forming ability" with material from different runs has not been established. Changes in physical variables such as

Figure 6. X-Ray Powder Diffraction Patterns of Amorphous Alumina from a Fluid Bed Calciner After Heating in the Static Test Unit

Figure 7. Conversion of Amorphous Alumina to Alpha Alumina as a Function of Time of Heating

feed rate, nozzle air-to-liquid feed ratio, type of nozzle, fluidizing characteristics, etc., are assumed to be instrumental in producing solids having different "alpha-forming ability."

Other crystalline forms in addition to alpha alumina were produced in small amounts in many of the samples. These were identified as iota, kappa, and gamma. Crystalline sodium nitrate was also present whenever appreciable quantities of alpha alumina were formed. X-ray diffraction patterns for one run in the static test unit in which a variety of crystalline materials was produced from amorphous alumina are shown in

Figure 9.

F. Effect of Calciner Atmosphere on Phase Transformations

Calcination of aluminum nitrate-nitric acid wastes in a continuously fed fluid bed calciner creates a gaseous atmosphere in which nitric acid vapor (oxides of nitrogen), air and water vapor are intimately mixed and in constant contact with the alumina solids. The very fact that the alumina literature indicates that a temperature of about 1000°C is required to convert amorphous alumina to alpha alumina in air suggests that the atmosphere within the fluid bed calciner is an important factor in the transition of amorphous to alpha alumina at the relatively low temperature of 400°C.

To determine the lowest temperature required to convert fluid bed-produced amorphous alumina to alpha alumina in air, samples of calcined alumina containing sodium but < 5% alpha alumina were heated in a muffle furnace at various temperatures. The results are shown in Table III.

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Figure 8. Rate of Conversion of Amorphous Alumina (from two Different Calciner Runs) to Alpha Alumina as a Function of Time of Heating

Figure 9. X-Ray Powder Diffraction Patterns of Amorphous Alumina After Heating in the Static Test Unit for 17 Hours at 500°C
 (1 and 11, aluminum from fluid bed calciner)
 (2 thru 10, alumina from decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ on hot plate)

Table III

Conversion of Amorphous Alumina to Alpha Alumina by Heating in Air

Heating Temperature, °C	Heating Time, Hrs.	Crystalline Alumina (by X-ray diffraction)	
		% Alpha	% Gamma
500	954	< 5	25
826	978	15	60
927	978	80	0

As indicated by Table III, the formation of appreciable quantities of alpha alumina from fluid bed-produced amorphous alumina in air apparently requires a temperature of about 900°C; however, some alpha alumina formed at about 800°C, and gamma alumina was produced at a temperature as low as 500°C.

To test the effect of the oxides of nitrogen and water vapor on the formation of alpha alumina from amorphous alumina, samples of amorphous alumina were heated in the static test unit with various combinations of oxides of nitrogen, air and water vapor. The results of this experiment are shown in Table IV.

Table IV

Conversion of Amorphous Alumina to Alpha Alumina in Various Gaseous Atmospheres

Temperature: 400°C

Time of Heating: 24 Hours

Calcined Material	Before Heating	Alpha Alumina Content (wt. %)				
		After Heating in:				
		HNO ₃ +air	NO ₂	NO ₂ +H ₂ O	NO	NO+H ₂ O
A	< 5	76	9	76	7	56
B	< 5	76	< 5	84	< 5	60
C	< 5	81	< 5	79	< 5	52

From the data in Table IV, it is evident that both water vapor and the oxides of nitrogen are essential for the formation of appreciable amounts of alpha alumina at the relatively low temperature of 400°C.

The nitrogen dioxide with water vapor was somewhat more effective than the nitric oxide with water vapor in promoting the phase change; however, either gas with water vapor was clearly superior to the dry gas alone.

G. Effect of Additives on Phase Transformations

One possible method for inhibiting the transformation of amorphous alumina to alpha alumina is to add a chemical which prevents the transition from occurring. The inhibiting effect might be due to interference with the formation of the crystalline alumina lattice or removal of the "catalytic" effect of the sodium. Boron is known to have an anti-crystallizing effect in the production of glasses⁽¹⁹⁾ and was, therefore, a likely additive for inhibiting the formation of alpha alumina.

Solid boric acid was intimately mixed with calcined alumina from the pilot plant, and the resulting mixture was heated in the static test unit to test the inhibiting effect of boric acid on the amorphous-alpha alumina transformation. In addition, 0.2M boric acid was added to the aluminum nitrate-nitric acid feed of a fluid bed calciner under conditions which previously had produced predominantly alpha alumina at steady-state operation without boric acid. The results of these tests are shown in Table V.

Table V
Effect of Boric Acid on Alumina Phase Transformations

		Temperature: 400°C	
		Time of Heating: 24 Hours	
		Atmosphere: HNO ₃ vapors + air	
Sample No.	Boric Acid ⁽¹⁾ Added	Alpha Alumina, weight per cent	
		Before Heating	After Heating
23-B1	None	< 5	47
23-B12	Lab	< 5	< 5
23-B2	None	28	71
23-B22	Lab	28	38
23-B3	Feed	15	22
23-B3	Feed	26	31
DWCF-5	None	5	47
DWCF-52	Lab	5	5

- (1) "Lab" indicates 3 weight per cent boron added as solid boric acid prior to heating in the static test unit. "Feed" indicates boron added as 0.2M boric acid in the calciner feed solution.

These results (Table V) indicate clearly that boric acid added to an aluminum nitrate-nitric acid calciner feed solution or to calcined alumina represses the growth of alpha alumina from amorphous alumina even though the calcined alumina is already "seeded" with alpha crystals. In addition to repression of alpha alumina formation, crystalline sodium nitrate formation was apparently repressed when boric acid was added. For example, the X-ray diffraction patterns of the samples listed in Table V showed definite sodium nitrate peaks after heating when boric acid was absent. With boric acid present, sodium nitrate was not detectable in the X-ray diffraction patterns. In addition, X-ray diffraction data were obtained from a run (run 5) producing alpha alumina in the Demonstrational Waste Calciner Facility at the ICPP. These data demonstrated that within a few hours after 0,2M boric acid was added to the feed, the sodium nitrate peaks, which had been clearly evident in X-ray diffraction patterns of the calcined product up to that time, completely disappeared suggesting a possible chemical combination between the sodium and the boric acid. However, later results indicated that boric acid inhibited the formation of alpha alumina in a fluid bed calciner when the boron-to-sodium molar ratio was as low as 1 to 8, suggesting that other mechanisms were also active in repressing the formation of alpha alumina.

H. Leachability of Calcined Alumina

The rate of leaching of calcined alumina (crystalline and amorphous) is an important consideration in the handling of overhead solids (fines) and the removal of possible "plugs" in a fluid bed calciner system. A sample of amorphous alumina from the pilot plant fluid bed calciner (overhead fines) was heated in a muffle furnace at 1100°C for 48 hours to produce pure alpha alumina for leaching experiments. An X-ray diffraction pattern of the ignited solid indicated that the sample was essentially 100% alpha alumina. Ten grams of this ignited sample were contacted with three successive 500-ml portions of 4M nitric acid at 96°C. Each contact was for 24 hours. The results of a chemical analysis of the supernatant liquid indicated that there was less than 0.125 gram per

liter (detection limit) of aluminum in solution. The alpha crystalline form is apparently highly insoluble in hot 4M nitric acid.

To determine the leachability of amorphous (to X-ray diffraction) calcined alumina and the nature of any acid resistance residue, ten-gram samples of the type of amorphous material that had been used as a standard in the static test unit, pilot plant alumina IV-A, were digested in 500 ml of 4M nitric acid at 96°C for 24 hours. Approximately 92% of the total solid dissolved in the nitric acid. The residual solid from this digestion was determined by X-ray diffraction to be 82% alpha alumina. Apparently a small amount of acid resistant alpha alumina, which was not measurable by routine X-ray diffraction of the gross sample, was present in the "amorphous" alumina. In addition, an even smaller amount of acid resistant amorphous material (18% of the residue) appeared to persist in the residue. This insoluble amorphous fraction may result from lack of physical disintegration of some of the alumina particles thus preventing adequate contact between the nitric acid and the solid. On the other hand, the resistant, apparently amorphous fraction, may consist of alpha crystallites that are too small to be detected by X-ray diffraction. Acid digestion of alumina from various calciner runs and X-ray diffraction of acid resistant residues indicated that alumina which appeared to be amorphous by X-ray diffraction of the gross sample always contained a small amount of alpha alumina; usually 2% or more.

The important point demonstrated by the leaching experiments, however, is that alpha alumina will be essentially totally insoluble in a nitric acid scrub solution while amorphous alumina, especially fines, will essentially all dissolve.

VI. CONCLUSIONS AND DISCUSSION

The fluid bed calcination of aluminum nitrate-nitric acid solutions at a bed temperature of 400°C produces gross quantities of alpha alumina under favorable conditions. Based on laboratory experiments, the following considerations appear to be important in the formation of alpha alumina at the relatively low temperature of 400°C.

1. Sodium aids in the formation of the alpha phase. The laboratory data to this effect are supported by the observation that in the pilot plant sodium has always been present in the feed when alpha alumina was formed. The role of sodium in this transformation has not been clearly established. It may act as a mineralizer, whereby the relatively low melting compound, sodium nitrate (m.p. = 306.8°C), provides a medium for the aluminum and oxygen atoms to rearrange into an orderly crystalline form, or it may be a constituent part of a transition compound which can transform to the alpha form under favorable conditions. Sodium may also function in some as-yet-unknown manner in forming the alpha phase.

2. The oxides of nitrogen and water vapor are necessary to form the alpha phase at a calcination temperature of $\sim 400^{\circ}\text{C}$. The nitrate may be a part of one or more basic aluminum nitrates that exist only as transition compounds between the amorphous and alpha alumina phases. Another possibility is the formation of localized high-pressure regions within the particle due to decomposition of nitrates. With water vapor also present, hydrothermal conditions on a micro-scale may exist which accelerate the formation of crystal phases.

3. Although the amount of crystalline material always increases with time of heating, widely different rates of formation of alpha alumina were obtained in the laboratory experiments with material from different runs in the pilot plant calciner. These results, together with the lack of phase transitions in beaker-prepared material, emphasize the important part that the method of particle formation plays in producing a material that is susceptible to phase transitions.

4. A temperature of 400°C is adequate to form high alpha content material ($> 50\% \alpha$) from amorphous material under favorable conditions. Alpha alumina was produced in the temperature range 350° to 550°C in the pilot plant calciner. No consistent trend with temperature was observed in the laboratory experiments. Some materials formed more alpha alumina at 400°C , while others formed more at 500°C .

5. The addition of boric acid to calciner feed solution or to amorphous alumina inhibits the formation of crystalline alumina. The mechanism of this inhibiting effect is not known; however, a reaction

between the sodium and boric acid may occur which effectively reduces the "catalytic" effect of the sodium. On the other hand, it is possible that the boron simply interferes with the formation of the alumina crystal structure. Although repression of crystalline alumina by the use of boric acid has been adequately demonstrated, the effect of the additives on other properties of the product, such as particle size, hardness, etc., must be demonstrated in an operating fluid bed calciner before the additive can be considered for long-term use in an actual waste treatment process.

The effect of sodium, time of heating, and composition of the calciner atmosphere were all shown to affect the transformation of amorphous alumina to crystalline alumina; however, control of any of these variables to inhibit the formation of crystalline alumina in the ICPP fluid bed calciners using existing aluminum nitrate-nitric acid wastes is not practicable. For this reason, the most feasible method of controlling the phase transformation from amorphous to alpha alumina appears to be by the addition of "phase transformation inhibitors", such as boric acid, to the calciner feed solution. On the other hand, if alpha alumina is the desired product, this material can be produced by deliberately setting the calciner operating conditions and adjusting the composition of the feed solution to form a product high in alpha alumina.

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