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Calcination of Aluminum Nitrate Nonahydrate in a Fluidized Bed

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CALCINATION OF ALUMINUM NITRATE NONAHYDRATE IN A FLUIDIZED BED

By Jack C. White,[1] Jack L. Henry,[2] and Davis E. Traut[3]

ABSTRACT

As part of an investigation of the production of alumina by the nitric acid leaching of kaolinitic clay, the Bureau of Mines designed, built, and tested a fluidized-bed system for the calcination of aluminum nitrate nonahydrate to alumina, while recovering nitric acid. The calciner consisted of an 8-in-square by 36-in-tall vessel containing 18 in of fluidized solids. Molten aluminum nitrate, sprayed directly into the fluidized solids, formed sandy, granular alumina by growth of successive layers on fluidized particles. Solids were fluidized in a dense bed at temperatures of 250° to 500° C with steam, air, or mixtures thereof. Decomposition of nitrate ranged from 4 to 10 pct during single-pass steam or air fluidization, respectively. Alumina dust losses and low throughput are significant unsolved problem areas.

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INTRODUCTION

The United States depends on imports of bauxite and alumina for most of its aluminum requirements. To reduce this dependence, the Bureau of Mines conceived a raw materials-process technologies matrix as a means of systematically investigating the technology options available for processing domestic aluminum resources. In 1973, a research program was initiated based on this matrix. Resources considered were clay, anorthosite, alunite, dawsonite contained in oil shale, and coal ash and coal shale.

The most promising raw material-process technology options were scheduled for investigation in a miniplant (25 lb/hr Al_2O_3) at the Bureau of Mines' Boulder City Metallurgy Research Laboratory (now the Boulder City Engineering Laboratory) to determine if the technology options were workable and potentially practical. (Work at Boulder City has involved both the technical and financial support of industrial cooperators.) To solve problems encountered in the miniplant or known to exist in alumina-extraction technology, laboratory-scale research was planned for other Bureau of Mines research facilities.

One of the technology options under study at the Bureau's Albany Research Center uses the nitric acid (HNO_3) leaching of calcined kaolinitic clay to produce impure aluminum nitrate [$Al(NO_3)_3$] solution, from which iron is removed by solvent extraction. Aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] is then recovered from the purified pregnant solution by crystallation. The final stage of the process, the calcination of aluminum nitrate nonahydrate (ANN) to produce cell-grade Al_2O_3 while recovering costly nitric acid, (HNO_3) from the offgas, has not been effectively achieved to date on a process demonstration scale. The purpose of the present investigation was to quantitatively determine the amount of nitrate lost during the calcination of ANN to produce HNO_3 and Al_2O_3.

At the onset of this project, the decision was made to adapt the dense fluidized-bed calcination technology developed by the U.S. Atomic Energy Commission at its Idaho National Engineering Laboratory (INEL), Idaho Falls, Idaho. INEL's objective is to concentrate highly radioactive waste metal nitrate solutions into storable solid form, with little regard for cost, energy conservation, or recovery of HNO_3 (3-5, 9-10, 12-13, (15-16).[4] In contrast, the Bureau of Mines' objective is to achieve the lowest cost of producing cell-grade Al_2O_3 from ANN, wherein minimum energy consumption and high recovery of HNO_3 and Al_2O_3 are essential. Viewed in another context, INEL's overall objective is the recovery of spent nuclear fuel worth several dollars per gram, whereas the Bureau's overall objective is the production of Al_2O_3 worth around $165 per ton ($0.0002 per gram). This dichotomy of objectives dictated considerable modification of the INEL process and design, as well as very different criteria for success.

Fluidized-bed calcination is inherently attractive because of its high rate of heat transfer, relatively low equipment cost, and simplicity of operation. Calcination of metal nitrates, as practiced by INEL, involves spraying of concentrated solutions of metal nitrates into a heated, dense fluidized-bed composed of the granular product metal oxides. The particles grow in size by accretion of onion-skin-like layers. Air is used for fluidizing the solids and for atomizing nitrate solutions. Process heat, supplied by fuel oil-oxygen combustion within the bed, maintains a bed temperature

[4]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

of 500° C. Production of granular solids from the calciner is approximately 1.59 lb of metal oxides per cubic foot of fluidized bed volume per hour, with a dust loss of 10 to 15 pct. No attempt is made to recover HNO_3 from the offgas.

Research conducted by Hazen Research Inc. on thermal decomposition of ANN and recovery of HNO_3 (1-2) was inconclusive with respect to recoverable HNO_3. A patent by Arthur D. Little Co. also presented no quantitative data on HNO_3 recovery (14). Two patents by Reynolds Metals Co. cover a number of aspects of $Al(NO_3)_3$ processing and decomposition (7-8). The energy of decomposition of aluminum nitrate is presented by Kelley (11).

INEL's high cost of thermal energy (due to fuel oil-oxygen-in bed combustion), nonrecovery of HNO_3, and small scale of operation necessitated considerable modification for potential application to an economical, high-tonnage operation. The equipment designs and results presented in this report are the first Bureau of Mines approach to adaptation of this potentially promising fluidized bed calcination technology for the practical production of cell-grade Al_2O_3 from ANN.

SYSTEM DESIGN--SIGNIFICANT FEATURES

The following features were considered desirable in the design of the calcining system:

1. Fluidization of solids either with superheated steam or preheated air or mixtures thereof, to provide a dense fluidized bed.

2. Spraying of molten ANN [containing 57 wt-pct $Al(NO_3)_3$] beneath the surface of fluidized solids.

3. Heat input by means of electrically heated, finned tubes immersed in the fluidized solids.

4. Calcination temperatures up to 500° C.

5. Cyclone removal of fine solids entrained in the fluidizing gas.

6. Condensation of HNO_3-steam vapor.

7. Absorption of NO_2 from tailgas by contact with sulfamic acid solution.

8. Analysis of tailgas for NO_2, NO, N_2, and N_2O.

A system flow diagram is illustrated in figure 1. Fluidizing gas, either steam or air, heated in separate circulation heaters, flows to the fluidized bed reactor. Offgas from the fluidized bed flows through a cyclone to the condenser where HNO_3 is recovered. Noncondensable gases flow through an absorption column and then to the atmosphere.

The calcination system (fig. 1) was sized on the basis of the minimum size spray nozzle readily available (0.016-in liquid orifice) that would deliver a minimum throughput of approximately 1 gal/hr of molten ANN, at 5 psig, equivalent to a production of 1.76 lb/hr of Al_2O_3. Using the INEL calciner output rate of 1.59 lb of coarse solids per cubic foot of calciner volume per hour as a model, the calciner volume required by the available spray nozzle is

$$\frac{1.76 \text{ lb/hr}}{1.59 \text{ lb/hr} \cdot \text{ft}^{-3}} = 1.1 \text{ ft}^3.$$

However, INEL's dust loss of about 15 pct (not included in the above output) and its data suggesting that higher output is possible at lower temperature, indicated that a calciner volume between 0.5 and 0.75 ft^3 would match the projected ANN input rate. The calcining system was constructed of types 316L and 304 stainless steel. Because a square shape provides convenient mounting of heating elements and spray nozzle, the calcining vessel was designed to be 8 in square by 36 in tall (inside dimensions) with a bed depth of 18 in of fluidized solids. This design provides a working

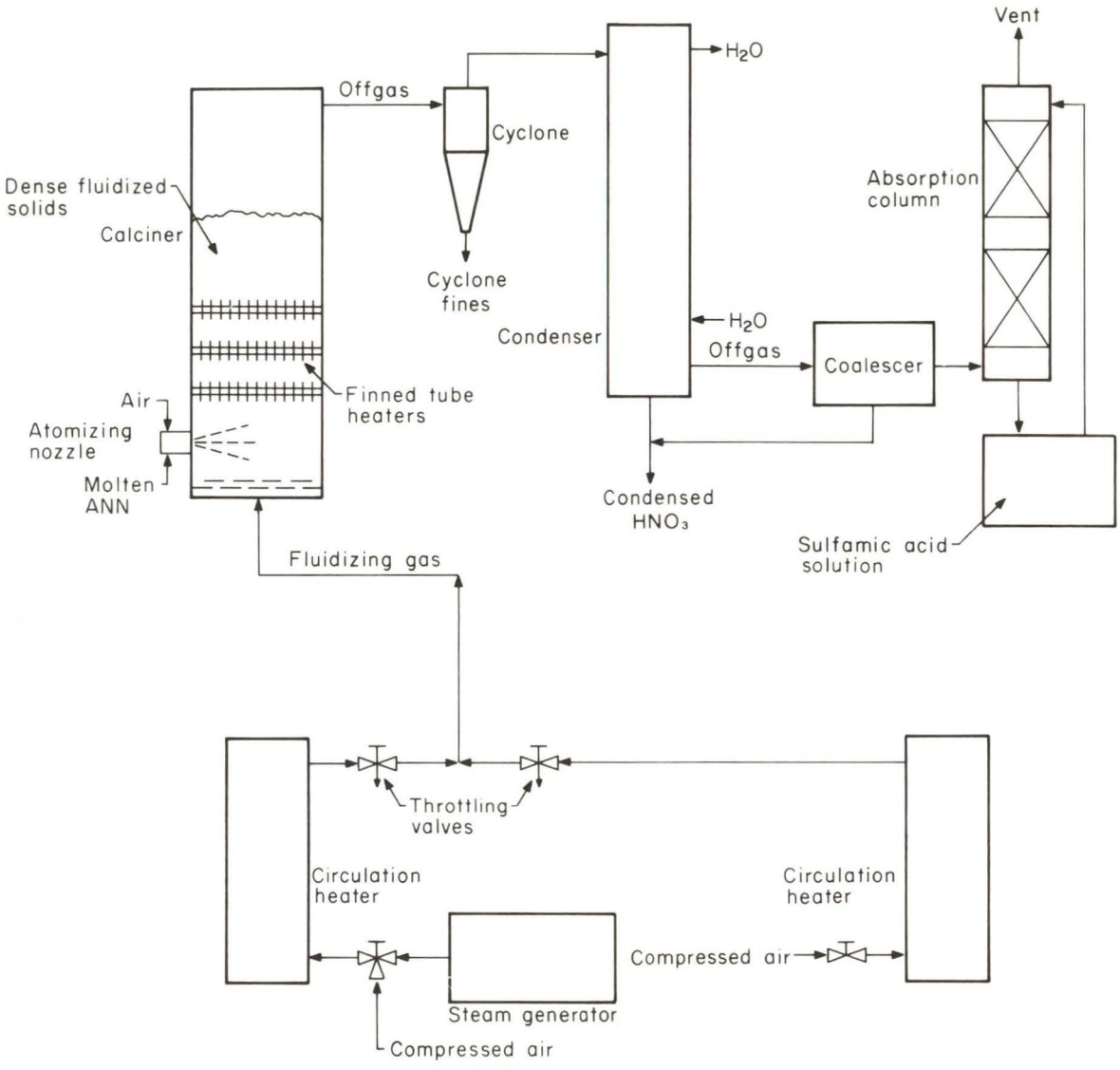

FIGURE 1. - Calcination system.

volume of 0.67 ft^3. Design details are illustrated in figure 2.

A plenum chamber supplied fluidizing gas to the overlying nonsifting bed support plate. Fluidized solids were heated by means of electrically heated finned tubes mounted through the vessel's front wall. The spray nozzle was mounted beneath the finned tubes and flush with the vessel's inner wall. Observation ports were provided. A 10-in-square disengagement section above the calcining vessel provided for retention of coarse solids while fine solids were collected by an adjacent cyclone. Additional details on design, construction, and operation of the calcining system are presented in the appendix.

CHEMISTRY

In nitric acid manufacture, operating conditions of high pressure, low temperature, and the presence of water vapor favor the formation of HNO_3 (6). Presumably the closest feasible approach to these conditions would also minimize decomposition of HNO_3 during calcination. Thermodynamic data, however, demonstrate that, at temperatures of interest, HNO_3 and the nitrogen oxides, N_2O, NO, and

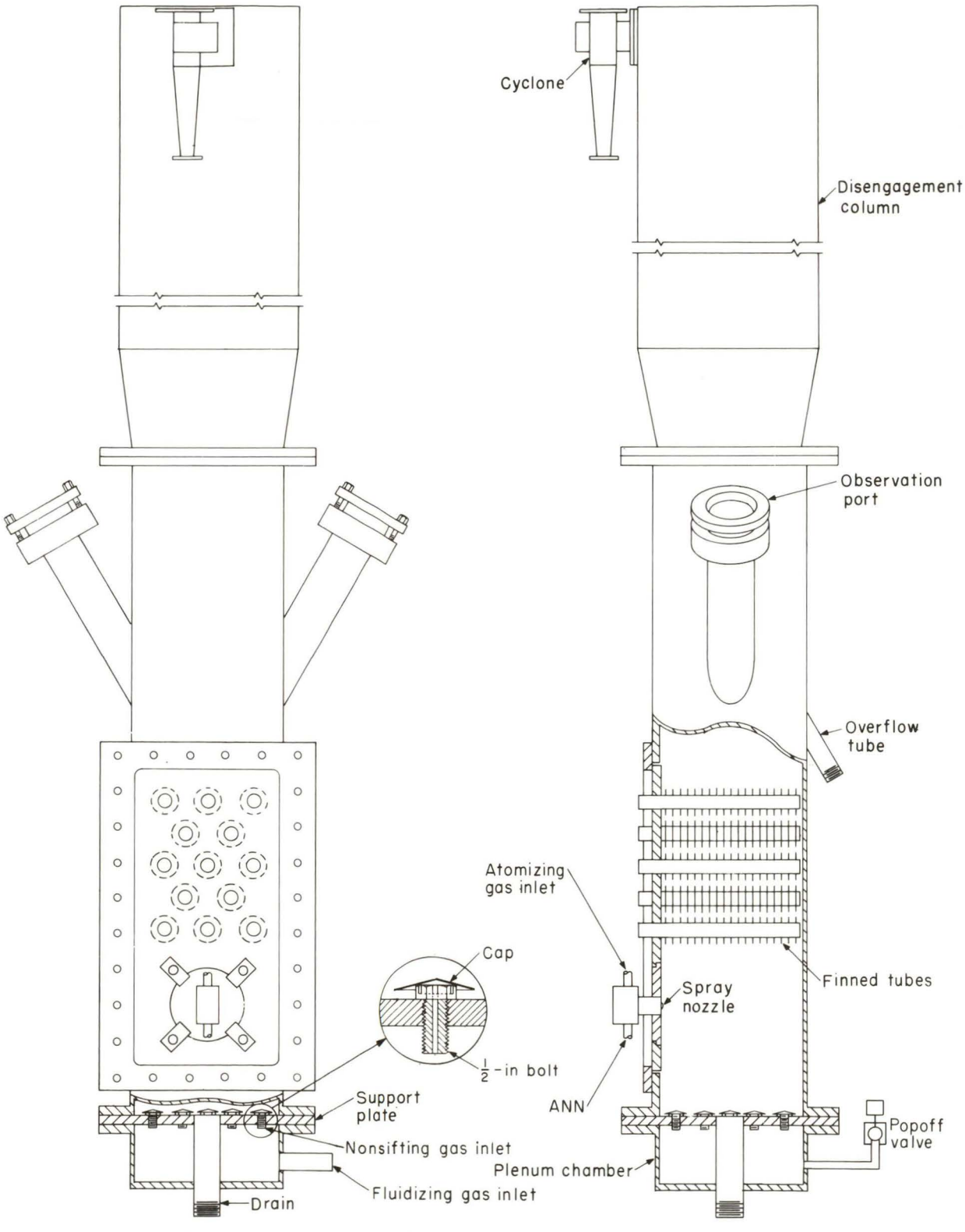

FIGURE 2. - Front and side views of fluidized bed calciner.

NO_2, would exist in insignificant concentrations in equilibrium with their decomposition products; N_2, O_2, and H_2O (table 1, log K values). The large negative changes in free energy associated with these decomposition reactions indicate that HNO_3 and the NO_x gases are vulnerable to catalytic and thermal decomposition during calcination of ANN (table 1).

TABLE 1. - Free energy changes for decomposition per mole of HNO_3 and three NO_x gas species

T, K	Reaction[1]						
	1	2	3	4	5	6	7
FREE ENERGY CHANGE, kcal/mole OF REACTANT							
400....	-14.1	-0.7	6.3	-0.3	-26.7	-20.4	-13.8
600....	-22.8	-7.7	-3.0	-6.0	-30.3	-19.8	-16.8
800....	-31.6	-14.6	-12.4	-11.7	-33.8	-19.2	-19.8
EQUILIBRIUM CONSTANT, LOG K							
400....	15	0.8	-6.9	0.3	29	11	15
600....	17	5.6	2.2	4.4	22	7	12
800....	17	8.0	6.8	6.4	19	5	11

[1]Reactions as follows:

1. $2HNO_3(g) = N_2(g) + 2.5O_2(g) + H_2O(l,g)$
2. $2HNO_3(g) = N_2O(g) + 2O_2(g) + H_2O(l,g)$
3. $2HNO_3(g) = 2NO(g) + 1.5O_2(g) + H_2O(l,g)$
4. $2HNO_3(g) = 2NO_2(g) + 0.5O_2(g) + H_2O(l,g)$
5. $2N_2O(g) = 2N_2(g) + O_2(g)$
6. $NO(g) = 0.5N_2(g) + 0.5O_2(g)$
7. $2NO_2(g) = N_2(g) + 2O_2(g)$

An added complication is that HNO_3 recovery in this calcination system is partially dependent on offgas retention time in the condenser, which operates as an inefficient HNO_3 oxidation-absorption system, similar in action to the oxidation-absorption systems of the old atmospheric pressure HNO_3 plants. Recovery of HNO_3 from NO and NO_2 follows the equations

1. $2NO + O_2 \longrightarrow 2NO_2$.

2. $2NO_2 + H_2O + 1/2\ O_2 \longrightarrow 2HNO_3$.

Although HNO_3 may be formed from NO and NO_2 when these gasses are present in sufficient concentrations, decomposition of the higher nitrogen oxides, nitrate, or nitric acid to the lower oxide N_2O or to N_2 causes an irreversible nitrogen loss from the system. Because of the high cost of HNO_3, excessive formation of N_2O and N_2 would, of course, significantly increase the cost of the process.

The major emphasis of this project was to determine the amount of nitrate decomposed and the nitrogen gas species formed during thermal conversion of ANN to Al_2O_3 in a dynamic system. Because of the short period of time that nitrate was in the system, equilibrium conditions presumably were never achieved. Steady state gas compositions were achieved, however, during most tests, allowing meaningful measurements of gas compositions to be made.

Detailed discussion of the chemistry of $Al(NO_3)_3$ and HNO_3 is beyond the scope of this paper. The subject (HNO_3) has been extensively covered in the literature; a somewhat popularized historical account of HNO_3 manufacture and chemistry, Strong Water by Thomas H. Chilton (6), serves as a good introduction to the subject.

ANALYSES

Fluidization and calcination tests were initiated using 46-mesh Ottawa sand--a clean, uniformly sized, rounded, granular quartz. Chemical material balances for aluminum and nitrogen were greatly simplified by a starting bed low in these elements. Although quartz-cored Al_2O_3 grains would eventually be eliminated by overflow of product from the bed, in practice no test was continued long enough to accomplish this result.

Aluminum analyses were performed by ethylenediaminetetracetic acid (EDTA) titration. Reagent-grade ANN, used in this work, contained no interfering elements.

Nitric acid and residual nitrate in calcined Al_2O_3 were determined by Kjeldahl analysis using Raney nickel reductant.

Gas analyses for N_2O and N_2 were performed by onstream gas chromatography of noncondensable gases exiting the condenser. Nitrogen was separated by means of a 1/8-in-OD by 10-ft-long Linde[5] 5A column operated at 25° C. Nitrous oxide (N_2O) was separated with a 1/4-in-OD by 10-ft-long Chromasorb 102 column, operated at 25° C.

Precautions were necessary to avoid contamination with atmospheric nitrogen during analysis for the nitrogen formed by decomposition of nitrogen compounds. The entire calcining system was operated above atmospheric pressure to eliminate contamination with air. During steam fluidization, preboiled water, stored under argon, was used as boiler feedwater to minimize contamination with dissolved nitrogen. The atomizing gas was argon. During the measurements of N_2 and N_2O, air fluidization was simulated with a mixture containing 80 pct Ar and 20 pct O_2. The considerable quantity of pure argon required was supplied from a cryogenic liquid argon tank.

The argon-oxygen mixture is a chemically acceptable substitute for air because nitrogen gas is not in equilibrium with other nitrogen compounds; therefore, the presence or absence of nitrogen should have no effect on formation or stability of nitrogen compounds. A comparable situation exists in HNO_3 manufacture where nitrogen is considered to be a chemically inert species (6, p. 55). The nitrogen blank analysis was reduced to a barely detectable trace, and N_2O to nondetectable amounts, within less than 30 min. Blank analyses were subtracted from nitrogen values obtained during calcining of ANN. Steady state N_2 and N_2O values were attained within 30 min after spraying of ANN began.

Measurement of the NO_2 and NO contents of offgas by means of a commercial benchtop NO_x analyzer were not especially successful. Although considerable effort was directed toward accurate NO_2 and NO analyses, results were considered to be relatively unreliable, partly because the indicated NO_2 analysis of offgas in many cases exceeded 3,000 ppm, beyond which the instrument departs from linearity and partly because of instrument instability.

RESULTS

Distribution of Aluminum and Nitrogen During Typical Tests

Distribution of aluminum and nitrogen through the calcining system, during two typical tests at 300° C using steam or air fluidization is illustrated in figure 3. Ideally, all the Al_2O_3 should be retained in the fluidized bed and all the HNO_3 should be recovered in the condenser. Departures from this ideal illustrate some of the problem areas in this route from ANN to Al_2O_3.

During steam fluidization (fig. 3, numbers not in parentheses), Al_2O_3 retention

[5]Reference to specific brand names does not imply endorsement by the Bureau of Mines.

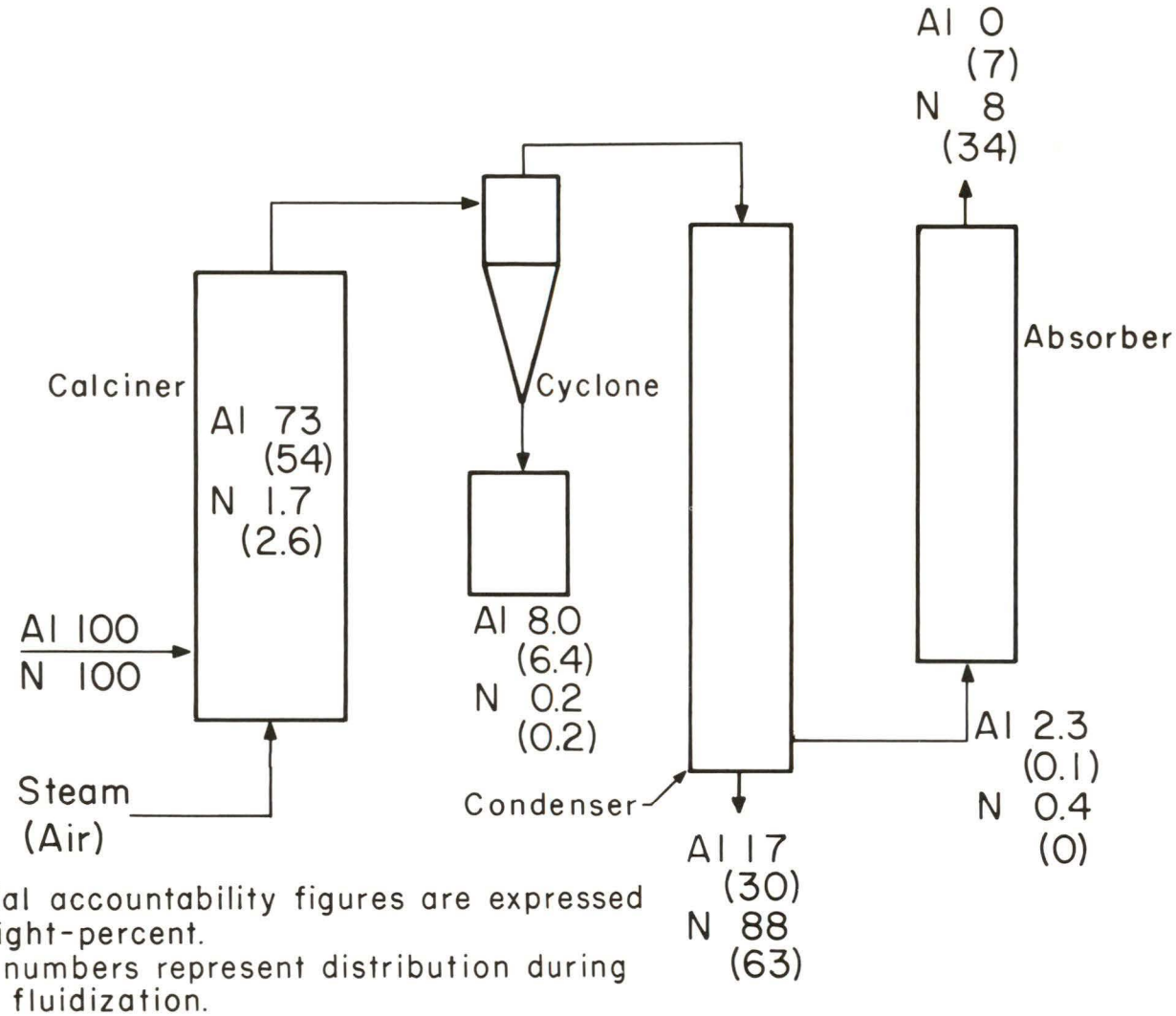

FIGURE 3. - Aluminum and nitrogen distribution throughout the calcining system during steam and air fluidization.

in the fluidized bed was 73 pct, and most of the remainder was retained in the dilute HNO_3 condensate. Nitrogen recovery as HNO_3 was 88 pct. During air fluidization (fig. 3, numbers in parentheses) Al_2O_3 retention in the fluidized bed was 54 pct, and nitrogen recovery as HNO_3 was only 63 pct.

Steam fluidization, although providing higher recovery of Al_2O_3 and HNO_3, is energy intensive, both for generation of fluidizing steam and for concentration of the weak (~10-pct) HNO_3 recovered. Air fluidization, in contrast, caused an increase in dust loss from the fluidized bed, a decrease in HNO_3 recovery, and an increase in losses of NO_x and Al_2O_3 to the atmosphere.

Alumina Retention in the Bed

During early tests, attempts were made to improve retention of Al_2O_3 in the fluidized bed. Samples of fluidized solids, taken at timed intervals during a series of tests, provided data on both the rate of Al_2O_3 accumulation on fluidized solids in the bed, and on the distribution of Al_2O_3 throughout the calcining system versus time. The rate of Al_2O_3 accumulation in the bed became linear within an

hour (fig. 4). A postulated difference in Al_2O_3 accumulation rate, caused by a difference between the two mechanisms; cohesion to clean quartz surfaces versus adhesion to the alumina-coated surfaces, had disappeared within an hour. Presumably the quartz surfaces had been coated with Al_2O_3 within that time interval. The weight fraction of Al_2O_3 retained, based on material balance calculations, reached a constant value within 200 min of test initiation (fig. 5). Therefore, dynamic steady state was achieved throughout the calcining system within 200 min of test initiation.

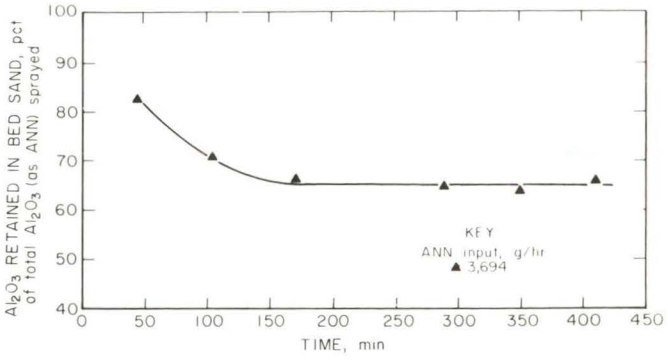

FIGURE 5. - Weight fraction of Al_2O_3 retained on fluidized solids in the fluidized bed during a typical test.

The relationship between rate of ANN input and Al_2O_3 retention in the fluidized bed has significance for this process. Although the highest input rate causes the highest rate of Al_2O_3 accumulation in the bed (fig. 4), material balance calculations indicated that the highest input rate also causes the greatest Al_2O_3 loss from the bed. Alumina lost from the bed is carried into the condenser in the form of fine dust. Sensitivity to input rate was determined quantitatively by four tests in which the independent variable was ANN feedrate, with other conditions held constant (300° C bed temperature, steam fluidization, 40 psig atomizing air). The resulting steep negative correlation curve relating input feed rate to Al_2O_3 retention in the bed demonstrates that small increases in feed rate, through a spray nozzle, will cause substantial additional loss of Al_2O_3 (fig. 6).

Physical evidence documenting the mechanism of Al_2O_3 loss from the bed was obtained by scanning electron microscopy (SEM). Frothy pumicelike layers of Al_2O_3 form where ANN is thickly applied to hot particle surfaces. This physically weak Al_2O_3 forms by evolution of gases from viscous molten, basic $Al(NO_3)_3$ during the very rapid transition from ANN to Al_2O_3. In contrast, application of thin layers

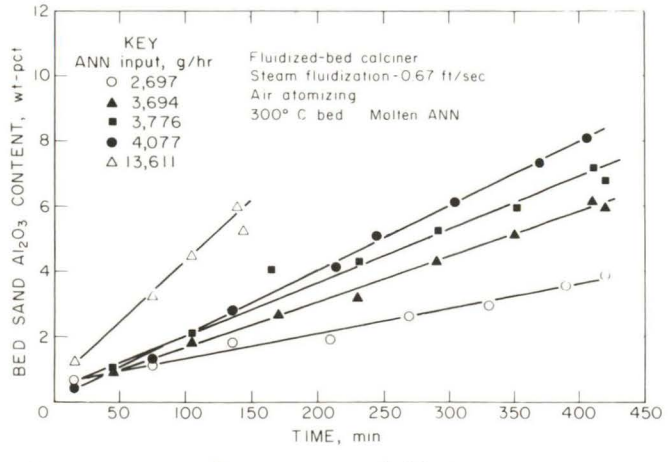

FIGURE 4. - Comparison of Al_2O_3 accumulation rate on fluidized solids in the fluidized bed.

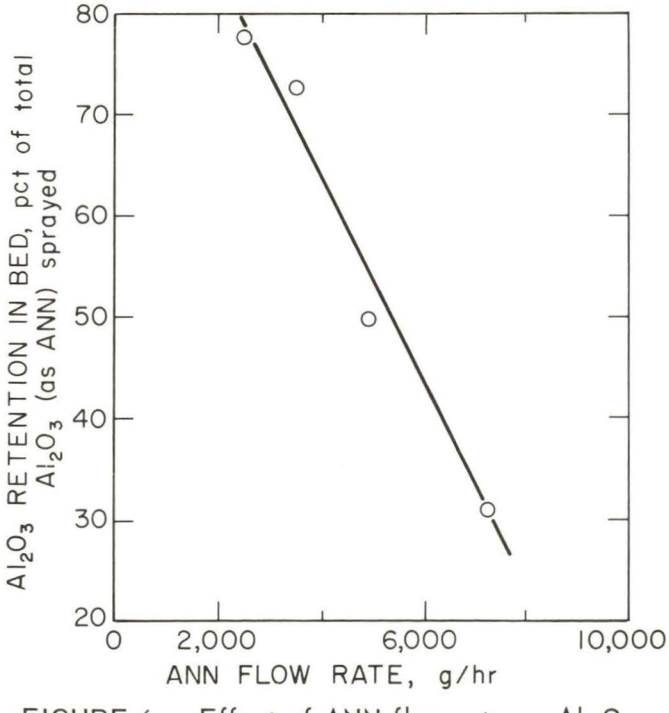

FIGURE 6. - Effect of ANN flow rate on Al_2O_3 retention in bed.

presumably allows escape of gases, forming a more cohesive coating. Frothy Al_2O_3 surfaces are readily worn away by attrition of solids during fluidization.

Atomizing air pressure also exerted a significant influence on Al_2O_3 retention in the bed. Atomizing air at 40 psig provided the highest retention. At lower pressures, larger droplet size and lower droplet velocity presumably formed thicker layers. Some confirming evidence was obtained by SEM. At 60 psig the spray plume penetrated the bed, causing impingement of particles and possibly of the spray as well, on the back wall of the calcining vessel, as determined by the sandblast pattern there. Optimum retention appears to be a balance between coating thinness and violence done to the particles by excessive atomizing pressure (fig. 7).

Additional evidence relating coating thickness to Al_2O_3 retention is provided by tests wherein $Al(NO_3)_3$ solution concentration was the independent variable. Alumina retention of 81 pct and 86 pct was achieved when spraying 40 pct $Al(NO_3)_3$ solution during air and steam fluidization, respectively. In contrast, during spraying of molten ANN [57 pct $Al(NO_3)_3$], Al_2O_3 retention was significantly lower: 54 pct and 73 pct during air and steam fluidization, respectively (fig. 8). Presumably thinner coatings formed by the dilute solutions were the cause of improved Al_2O_3 retention. Spraying such dilute solutions would, of course, substantially increase energy requirements.

Nitric Acid Recovery

Recovery of HNO_3 in the condensate is affected by bed temperature, fluidizing gas composition, and atomizing gas flowrate. As expected, recovery of HNO_3 is higher at lower temperatures; 93 pct at 250° C versus 78 pct at 400° C during steam fluidization (fig. 9). Volume flow

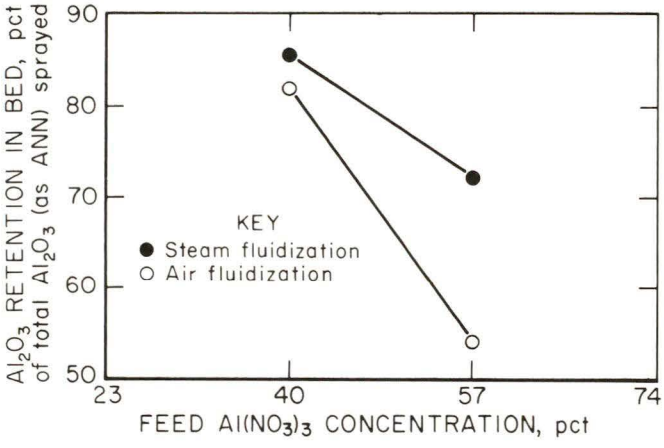

FIGURE 8. - Effect of feed $Al(NO_3)_3$ concentration on Al_2O_3 retention in bed.

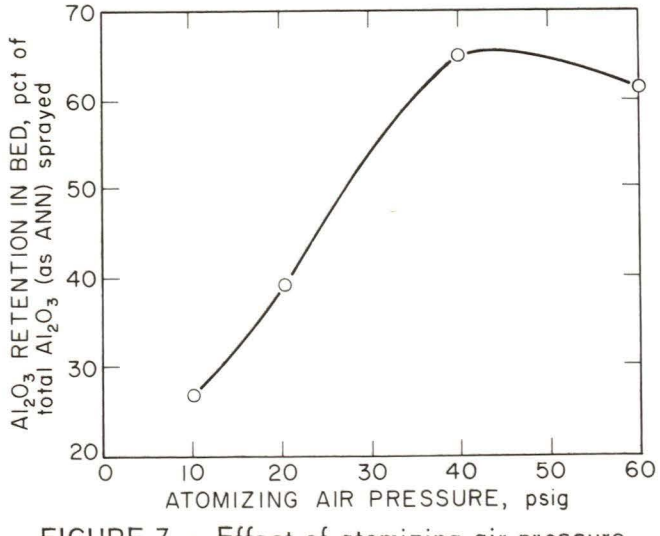

FIGURE 7. - Effect of atomizing air pressure on Al_2O_3 retention in bed.

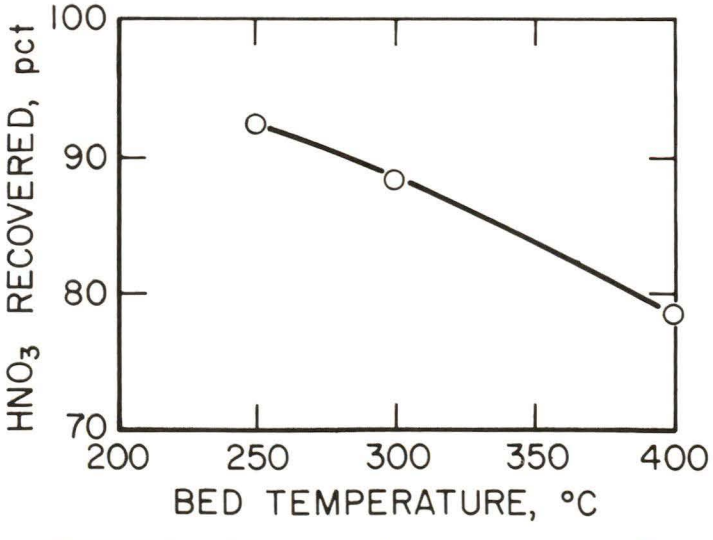

FIGURE 9. - Effect of bed temperature on HNO_3 recovery.

rate of noncondensable gas (air) had an adverse effect on HNO_3 recovery. A series of tests were made with different air-steam fluidizing gas mixtures to determine the effect of fluidizing gas composition on HNO_3 recovery (parameters held constant were bed temperature, 300° C; atomizing air pressure, 40 psig; ANN pressure, 7.5 psig; with the 0.016-in liquid orifice). Recovery of nitrate as HNO_3 ranged from approximately 88 pct during 100-pct steam fluidization to 63 pct during 100-pct air fluidization. The decrease in HNO_3 recovery was linear with respect to increasing air content (fig. 10).

Recovery of HNO_3 during steam fluidization also diminishes as atomizing gas pressure is increased. The significant independent variable is atomizing air flowrate, which in turn is a function of air pressure. Recovery of HNO_3 was 96 pct at 10 psig atomizing air pressure versus 87 pct at 60 psig (fig. 11). Noncondensable gases are deleterious in part because they sweep NO_x rapidly through the condenser. The condenser acts as an inefficient HNO_3 absorption system wherein NO_x is oxidized and absorbed, forming additional HNO_3 condensate. Because this overall reaction is slow, sweeping NO_x rapidly through the condenser adversely affects the formation of HNO_3 from NO_x.

Ideally, steam should be used for atomization of ANN; however, tests utilizing steam atomization were not successful. Formation of aggregates of particles in the bed forced premature shutdown. Presumably the steam contained excessive amounts of water that causes agglomeration of particles.

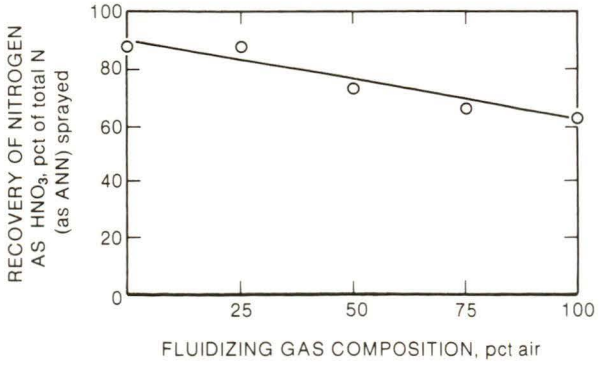

FIGURE 10. - Effect of fluidizing gas composition (steam-air) on recovery of nitrogen as HNO_3.

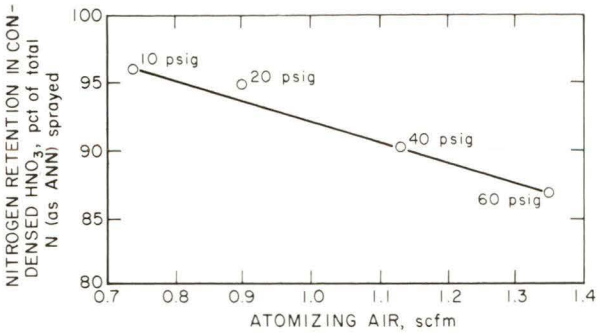

FIGURE 11. - Effect of atomizing air rate on nitrogen retention as condensed HNO_3.

Residual nitrogen in product Al_2O_3 was determined as a function of temperature during steam fluidization. The nitrogen content of calcined ANN was 5.3 pct at 250° C, decreasing to 2.3 pct at 300° C and 1.6 pct at 400° C (fig. 12). The level of nitrogen in calcined ANN from which HNO_3 cannot be recovered either directly or indirectly (as NO_x) was not determined, but it is believed to be in the 1- to 2-pct range. The nitrogen content of calcined ANN is also affected by fluidizing gas composition. Nitrogen content in calcined ANN is approximately

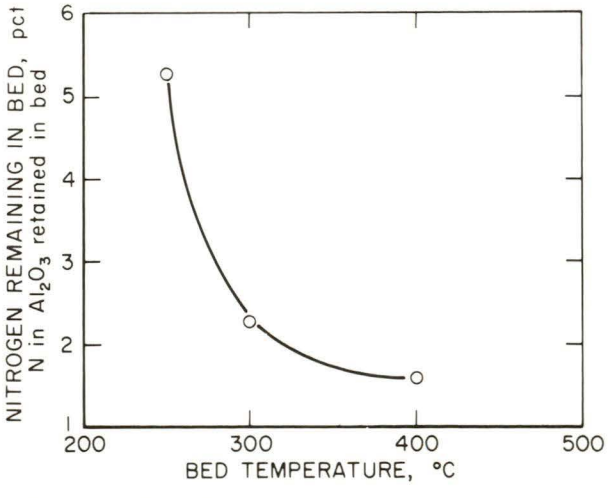

FIGURE 12. - Effect of temperature on nitrogen retained in Al_2O_3 in the fluidized bed.

2.2 pct when calcining with a fluidizing steam content ranging from 100 pct to 50 pct, whereas it increases to 3.7 pct when ANN is calcined in air (fig. 13). Test temperatures were 300° C.

Decomposition of Nitrate to N_2 or N_2O

As previously noted, decomposition of nitrate to NO or NO_2 may be reversed by reoxidation-absorption in an HNO_3 plant, whereas decomposition to N_2O or N_2 is, for practical purposes, irreversible with respect to HNO_3 production. Data on decomposition of the nitrate to N_2O and N_2, which is essential for a cost analysis of the clay-HNO_3 process, was determined by onstream gas chromatography of offgas from the condenser.

Decomposition of ANN to N_2 was minimal during steam fluidization, amounting to only a few tenths of a percent of the chemically combined nitrogen fed to the system, whereas N_2 produced during simulated air fluidization is 0.7 and 1.5 pct at 300° and 400° C, respectively. Decomposition to nitrogen was more sensitive to temperature change during simulated air fluidization than during steam fluidization (fig. 14).

Decomposition to N_2O was about 5.3 pct during simulated air fluidization whereas only 0.7- to 1.3-pct decomposition to N_2O was measured during steam fluidization (fig. 15). Nitrous oxide (N_2O), however, is relatively water soluble, indicating that appreciable N_2O could be dissolved in condensate, which would cause large errors in N_2O analysis by means of gas chromatography during steam fluidization. Condensate was not analyzed for N_2O because no method was available.

Analysis for NO_2 and NO at the exit port of the condenser was attempted during many tests. Results were considered to be unreliable because of instrumental instability and the fact that NO_2 content was above the calibrated range of the

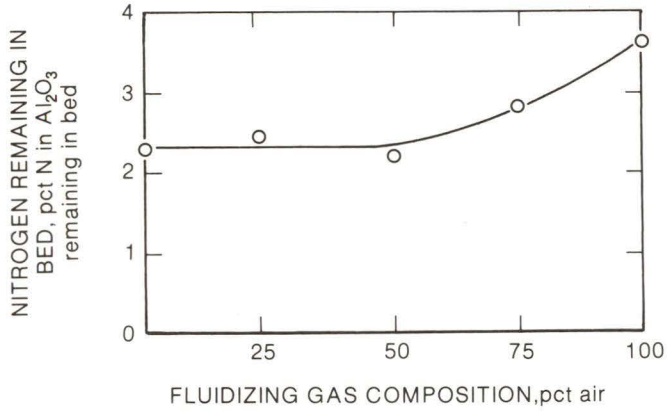

FIGURE 13. - Effect of fluidizing gas composition (steam-air) on nitrogen retained in Al_2O_3 in the fluidized bed.

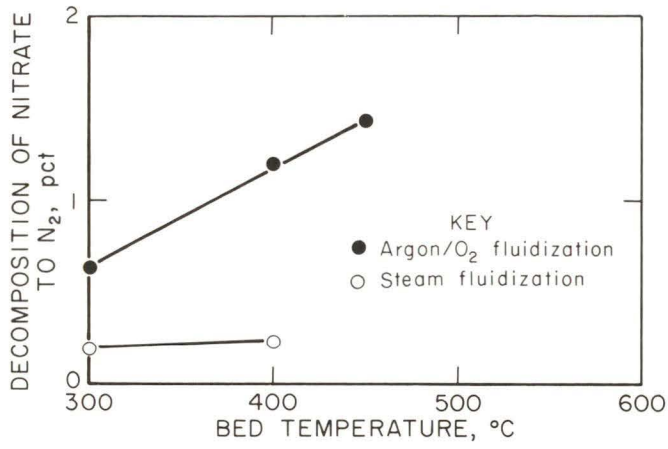

FIGURE 14. - Effect of bed temperature and fluidizing gas composition on decomposition of ANN to N_2.

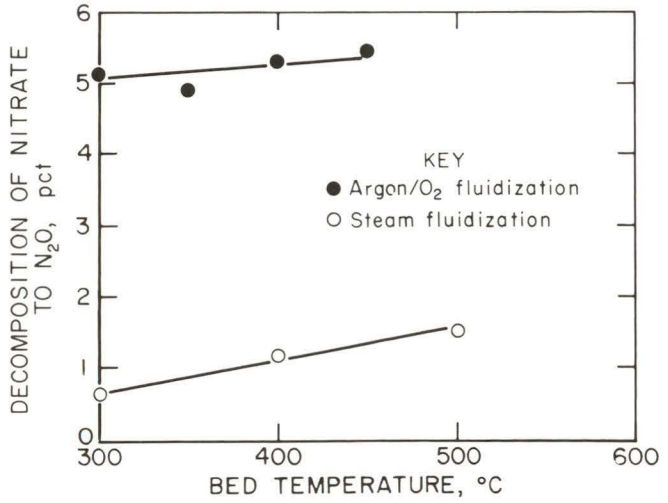

FIGURE 15. - Effect of bed temperature and fluidizing gas composition on decomposition of ANN to N_2O.

optical absorption instrument in use. Offgas generally exceeded 3,000 ppm NO_2 during most tests.

Total decomposition of ANN to unrecoverable nitrogen-containing products may be calculated from the decomposition data (table 2). Assumptions made in the calcalculation are that--

1. All NO and NO_2 would be recovered in an HNO_2 plant.

2. Nitrogen remaining in product Al_2O_3 is unrecoverable.

3. N_2O values determined during steam fluidization are correct.

TABLE 2. - Decomposition of ANN

Fluidizing gas	Temp., ° C	Gas as N		Residual N in Al_2O_3, wt-pct	Total N loss,[1] pct
		N_2, wt-pct	N_2O, wt-pct		
Steam.....	300	0.2	0.7	3.0	3.9
Steam.....	400	.2	1.3	2.1	3.6
Air.....	300	.6	5.2	4.9	10.7
Air.....	400	1.2	5.4	3	9.6

[1]Percent of chemically combined nitrogen fed to the calciner as ANN.

Total decomposition of ANN to unrecoverable nitrogen products is about 10 pct during air fluidization and nearly 4 pct during steam fluidization. Decomposition would, of course, be higher than these values in proportion to the amount of N_2O absorbed in the condenser.

DISCUSSION

Neither air fluidization nor steam fluidization appear to be acceptable for a single-pass operation.

During air fluidization, NO_x content of offgas exceeded 3,000 ppm, and the volume of noncondensable offgas was high. Removal of NO_x from large gas volumes by scrubbing and catalytic destruction is expensive. A manufacturer of NO_x cleanup equipment suggested that recirculation of fluidizing gas may be economically advantageous because of the high cost of NO_x removal. The assumption may be made that recirculating fluidizing gas would attain high levels of NO_x, and that a bleed stream high in NO_x could be successfully treated in an HNO_3 plant. A potential disadvantage of recycling fluidizing gas is that repeated exposure of NO_x gases to the high-temperature environment of the fluidized bed could cause additional decomposition to N_2O or N_2. Information along these lines can only be determined experimentally and may have a significant impact on overall cost of the process.

During steam fluidization, improved HNO_3 recovery was offset by the higher energy input required for generation of the fluidizing steam. During normal operation, 55×10^6 Btu per ton of product Al_2O_3 was required to generate fluidizing steam, compared with 8×10^6 Btu per ton of Al_2O_3 required to preheat fluidizing air. Additional energy would be required to concentrate the dilute HNO_3 produced during steam fluidization. Series arrangement of beds and utilization of waste heat would undoubtedly reduce these heat requirements. Recycling of fluidizing gas would also substantially reduce these energy costs, but with the additional costs of compressor equipment and the energy required to operate the compressors.

Because of fundamental difficulties with the approach to ANN calcination described in this report, detailed data on heat requirements for this unit operation were not determined.

An additional significant problem area is the necessarily low feed rate through a single spray nozzle in the fluidized bed. No effective means to improve feed rate, while spraying ANN, is foreseen. The problem should be sidestepped by a different feed introduction method.

CONCLUSION

Decomposition of nitrate to N_2O and N_2, which are unrecoverable in an HNO_3 plant, has been determined quantitatively for a single-stage, single-pass dense fluidized bed calciner. Loss as N_2O ranges from 0.7 to 5.4 pct and loss as N_2 ranges from 0.2 to 1.2 pct, depending upon the temperature and fluidizing gas composition. Total nitrogen loss, including the residual nitrogen in the fluidized-bed Al_2O_3 product ranges from 3.6 to 10.7 pct.

In addition to nitrogen losses through nitrate decomposition, other problems are found to exist in a single-stage, single-pass fluidized bed decomposer:

Alumina retention in the fluidized bed ranges between 54 and 73 pct, with 6.4 to 8.0 pct appearing in the cyclone and the balance in the condenser and absorber. Retention is inversely related to the feed input rate; this relationship appears to be a fundamental property of $Al(NO_3)_3$.

Energy requirements for the generation of fluidizing steam and that for concentrating the dilute HNO_3 product are excessive for a viable process.

Unsolved problems indicate that an alternate processing strategy is required. Presumably, staged lower temperature removal of HNO_3 would minimize nitrate decomposition, and preparation of solid basic $Al(NO_3)_3$ feed for the fluidized bed would eliminate the need to spray molten ANN into the fluidized bed.

A convergence of evidence indicates that the proposed calcining unit operation as reported here is not technically or economically feasible for high-tonnage production of Al_2O_3 from ANN.

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APPENDIX

This appendix presents a detailed account of the design, construction, and operation of the calcining system. Hopefully, this information will save future workers in this field considerable time and frustration.

Fluidizing gas generation and handling equipment was sized on the basis of a maximum 2 ft/sec superficial fluidizing velocity over a temperature range of 200° to 400° C (94 and 67 lb/hr of steam, respectively, at 2 ft/sec). Equipment capacities required to meet these conditions were--

1. Steam generator: 100 lb/hr at 80 psig.

2. Steam superheater: 12-kw circulation heater.

3. Throttling value: C_v = 1.2.

4. Cyclone: 1-1/2-in-diam.

5. Condenser: tube-in-shell with 15 ft^2 of cooling surface area.

6. Coalescer: 4-1/2-in-diam by 6-1/2-in-long, packed with stainless steel wire mesh.

7. NO_x absorption column: 10-in-diam by 10-ft-long. (See flow diagram, fig. 1.)

Generation and Heating of Fluidizing Gases

Steam, required for fluidization of solids, was provided by an electric steam generator capable of producing 100 lb of steam per hour at 80 psig. Superheating of fluidizing steam and preheating of fluidizing air was accomplished by means of a 12-kw, thermostatically controlled circulation heater, operated at 80 psig. Fluidizing gases were preheated, approximately to fluidized bed operating temperature, normally 300° C, to minimize the heat load on the fluidized bed heaters and to minimize temperature gradients in the bed (fig. 1). Installation of a drain, fitted with a steam trap, was necessary to prevent accumulation of water in the circulation heater.

When fluidizing with steam-air mixtures, steam was superheated in a circulation heater and air was preheated in a separate circulation heater. The two gases were heated at 80 psig, throttled to the process pressure of 2.5 psig, and mixed in a tee prior to introduction into the plenum chamber.

Calcining Vessel

A plenum chamber supplied fluidizing gas to the overlying nonsifting support plate (fig. 2). Twelve gas ports, mounted in threaded 1/2-in holes in the support plate, provided even distribution of fluidizing gas. The ports consisted of 1/2- by 1-in type 316 SS (stainless steel) bolts drilled lengthwise with 3/16-in holes. The slotted bolt heads with attached coverplates provided the nonsifting feature. (See detail, fig. 2.) Samples of fluidized solids were withdrawn during operation through a central drainpipe and ball valve assembly. System overpressure was relieved by means of a pressure relief valve connected to the plenum chamber.

The calcining vessel, 8 in square by 36 in high, normally contained a working depth of 18 in (0.67 ft^3) of fluidized solids. The vessel was fitted on one side with a gasketed rectangular plate, through which electrically heated, finned tubes were mounted in bore-through fittings. The spray nozzle was mounted in a separate, circular, gasketed plate within the rectangular plate, which greatly facilitated removal, inspection, and cleaning of the nozzle (fig. 2). The nozzle tip was mounted flush with the vessel's inside wall. Two sight glasses were mounted on opposite sides of the vessel, above the level of fluidized solids, to allow visual inspection of fluidization and the interaction between fluidized solid and finned tubes. Initially, a

rectangular plexiglass plate, with mounted finned tubes and spray nozzle, was used as one wall of the calcining vessel to allow visual observation of fluidization and spray nozzle action during air fluidization of sand at ambient temperature. Visual observation proved valuable in understanding and controlling bed and spray nozzle operation.

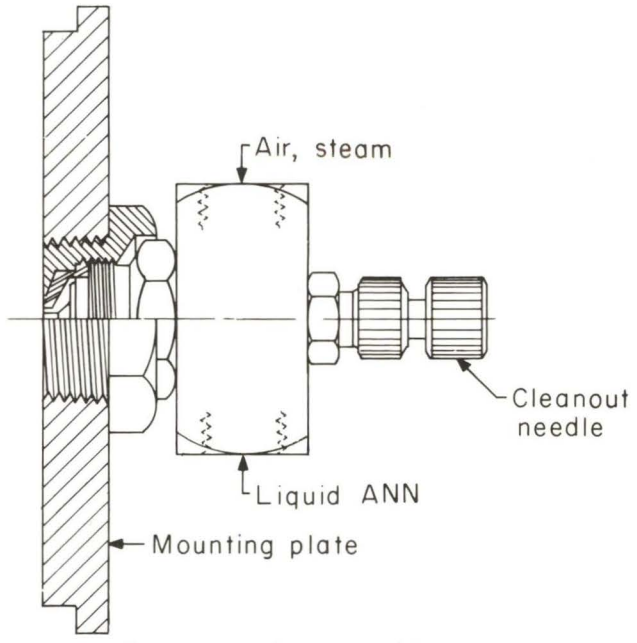
A disengagement column 10 in square by 36 in high, mounted above the calcining vessel, provided for retention of coarse solids in the bed by virtue of reduced gas velocity.

The plenum chamber and calcining vessel were fabricated of 1/4-in plate, whereas 16-gage sheet was used for the disengagement column. The plenum chamber, calcining vessel, and disengagement column were welded to 3/8-in-thick by 12-in-square bolted flanges and sealed with 1/8-in asbestos gaskets. Carefully machined flange surfaces provided leak-free operation.

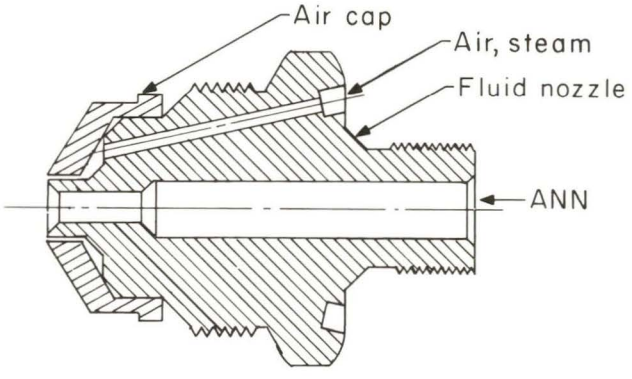
Spray Nozzle

The strategy of spray nozzle operation is to propel droplets of molten ANN into the fluidized bed, where contact with hot, fluidized solids causes buildup of calcined ANN on the surfaces of the fluidized particles. Conditions that cause spray drying, formation of physically weak layers of calcined ANN, or excessive attrition should be avoided.

Spray nozzle configuration and operating conditions are critical to optimum retention of calcined ANN on fluidized solids. After experimentation, it was found that a "siphon spray setup" supplied by Spraying Systems Inc.[1] is the most satisfactory (fig. A-1). The "setup" or front end of the spray nozzle consisted of an air cap and a fluid cap mounted on a spray body, all fabricated of type 316 SS. Atomizing gas flowed through the air cap annulus surrounding the fluid cap orifice. A cleanout needle assembly at the rear of the spray body provided for cleanout of the liquid orifice during operation. Although the spray system was designed for siphon operation, this application utilized pressurized liquid to control ANN input rate. Therefore, changes in atomizing gas pressure exerted little influence on ANN feed rate. Optimum operation was achieved with a 0.016-in liquid orifice and a 0.050 by 0.078-in atomizing gas annulus. Additional variations were made by substituting a liquid cap with a larger orifice or by drilling the air cap to provide a larger atomizing-gas annulus.



Spray nozzle assembly



Siphon spray setup

FIGURE A-1. - Spray nozzle assembly.

[1]Reference to specific manufacturers does not imply endorsement by the Bureau of Mines.

Mounting the nozzle tip flush with the calciner inside wall is essential to prevent solids buildup around the nozzle. Sharp corners or annular grooves near the nozzle tip provide sites for accumulation of calcined ANN-sand aggregates. These aggregates destroy the spray pattern, in turn causing formation of more ANN-sand aggregates within the fluidized bed. The spray nozzle was mounted beneath the finned heating tubes.

Heat Input

The strategy of heat input is to minimize exposure of HNO_3 vapor to excessively hot surfaces, where decomposition to lower oxides of nitrogen may occur. Therefore, heating elements were designed with large surface areas to provide operation at relatively low temperature differentials.

Thirteen spiral-finned tubes, closed at one end, were mounted horizontally, within the fluidized solids region in the calciner (fig. 2). Fins, welded to 5/8-in-OD by 1/2-in-ID tubes, are the interrupted type, spaced 6 per inch, 3/8 in deep and 0.023 in thick. Replaceable electrical cartridge heating elements (each 8 in-long, 1/2-in-diam, 1,500-w, 240-v) supplied heat to the finned tubes. Clearance of a few thousandths of an inch between the outside diameter of the cartridges and the inside diameter of finned tubes provided good heat transfer while allowing replacement of heating elements. Electrical leads were insulated with Al_2O_3 beads to prevent short circuits caused by embrittlement of silicone rubber insulation.

Heat Loss

Insulation of the calcining system and cyclone was necessary to prevent condensation of steam with the attendant buildup of fine solids on moist surfaces. Receiving vessels, both for coarse solids and cyclone underflow, were covered with electrical heat tape and insulated to provide a temperature above the dew point of fluidizing steam.

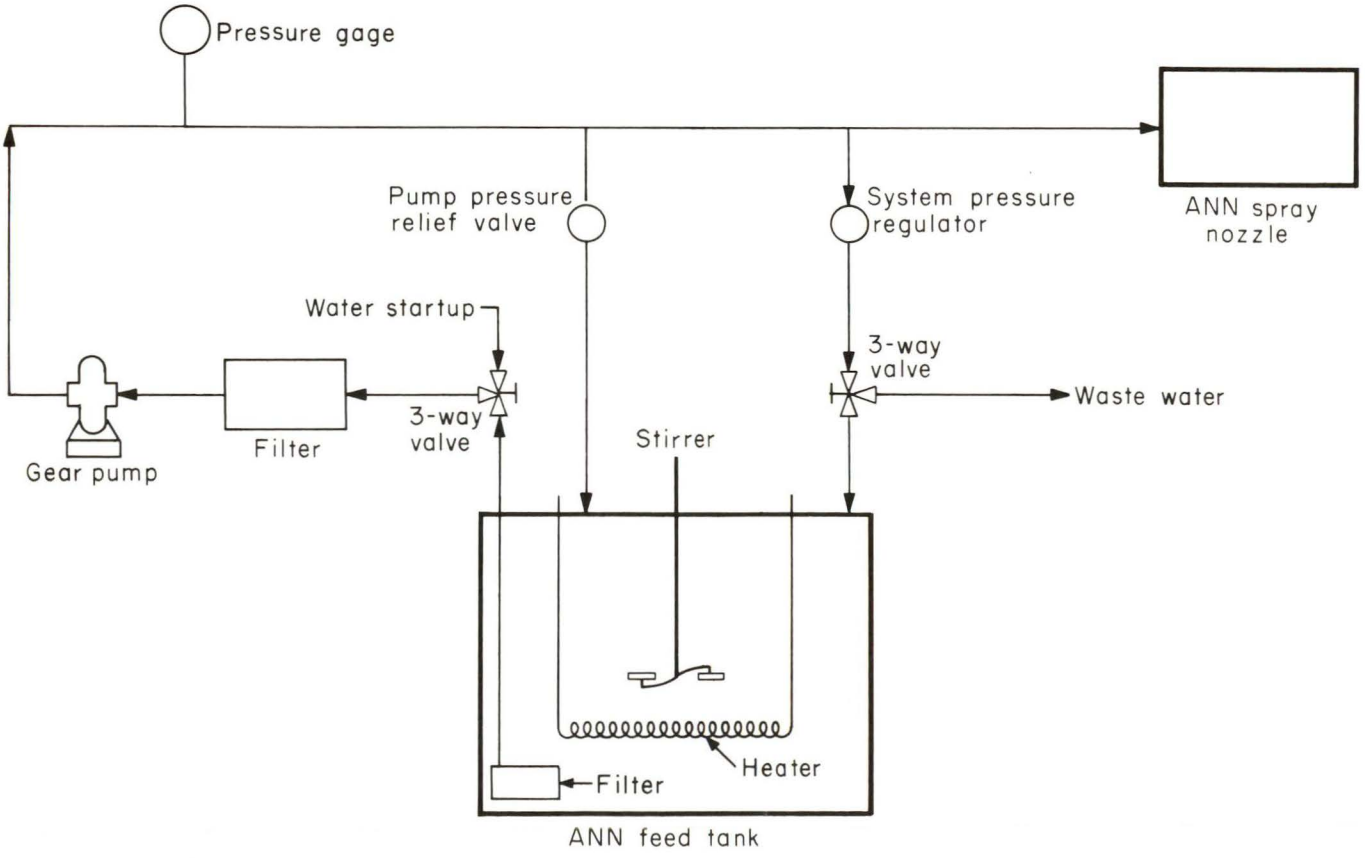


FIGURE A-2. - Gear pump system for delivery of molten ANN to spray nozzle.

Feed Introduction

Initial melting of ANN feed (melting temperature, 73° C) was done in a stainless steel vessel fitted with 20 ft of coiled, 1/4-in SS tubing heated with 80 psig steam. During the first 31 tests, molten ANN feed was transferred to and held at atmospheric pressure in a closed, electrically heated, thermostatically controlled, agitated vessel (fig. A-2). A recirculating feed stream was pressurized by means of a gear pump with a 4-gal/min capacity. Pump startup was accomplished by priming the pump with hot water which was then discarded ("water startup" and "waste water," fig. A-2). The two 3-way valves were then switched simultaneously to begin pumping of molten ANN. During shutdown, lines were washed out by reversing this procedure. Operating pressure in the recirculating feed line was set by adjusting the spring loading on a pressure-regulating valve, providing a constant supply of filtered, pressurized ANN to the spray nozzle. The quantity of ANN fed was controlled by ANN pressure versus resistance at the spray nozzle orifice.

Difficulties with this system included (1) pump wear, that introduced a fine dispersion of carbon from wear plates and face seal into the molten ANN, (2) leakage of molten ANN at the face seal, and (3) freezeup of lines with subsequent plugging of the in-line filter. Because of these difficulties, a pressure tank system was designed and installed to replace the gear pump system.

The pressure tank was a standard, type 316 SS, 20-gal Pfaudler-type reactor (fig. A-3). It was steam-jacketed and the hinged cover was fitted with five

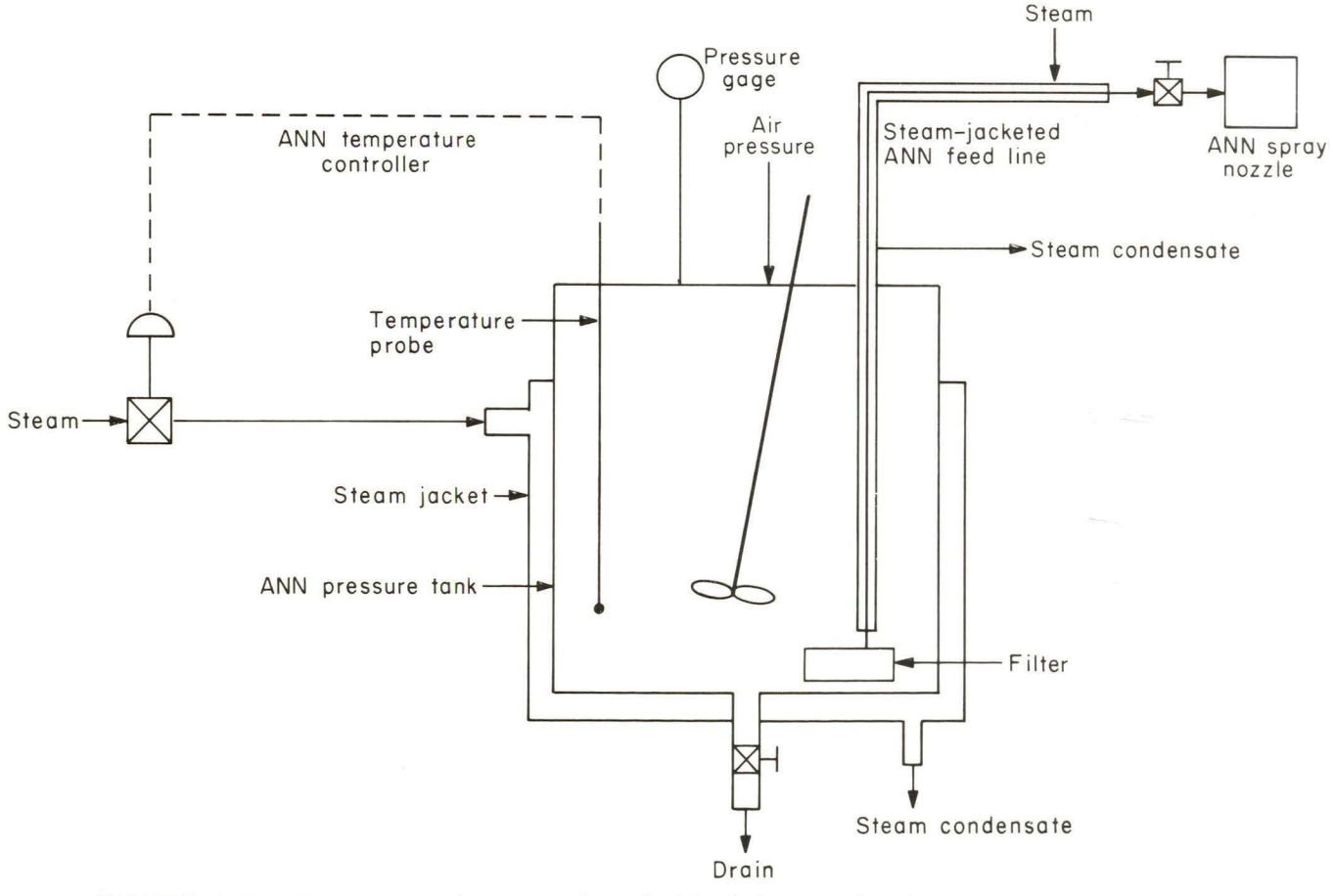


FIGURE A-3. - Pressure tank system for reliable delivery of molten ANN to spray nozzle.

flanged ports, two for observation and three for access. Working pressure was 60 psig maximum. Agitation was provided by a variable speed, 1/4-hp mixer with packing gland seal. Temperature control was provided by means of a standard steam-line temperature control unit. Molten ANN, pressurized by compressed air, was supplied to the spray nozzle through steam-jacketed lines (fig. A-3). Inherent simplicity of the pressure tank system improved system reliability.

Alumina Recovery

Coarse solids may be removed by overflow into a heated vessel, however, during tests of less than 8-hr duration, solids were retained in the bed. All of the data were taken without overflow of coarse solids.

The disengagement column above the fluidized bed prevented carryover of coarse granular solids to the cyclone. Smaller particles were carried through the disengagement column and into the cyclone by the combined fluidizing gas, atomizing gas, and offgas, where intermediate sized dust, larger than a few micrometers in diameter, was collected in a closed, heated, receiving vessel at the cyclone apex. The finest dust was carried through the cyclone. The exact particle size of cyclone separation was not determined, but would, of course, vary in response to gas velocity through the cyclone.

Nitric Acid Recovery

Nitric acid vapor and fluidizing gas with entrained, fine solids flowed into the condenser, a 15-ft^2 surface area tube-in-shell design with cooling water on the tube side. There, HNO_3 and fluidizing steam were condensed, and fine Al_2O_3 dust was entrained within and partially dissolved in the HNO_3 condensate. During air fluidization or when greater amounts of ANN were sprayed, the accumulation of solids in the condenser caused plugging of the liquid seal valve and gas exit port. A recirculating condenser washdown system utilizing product acid was installed to prevent plugging (fig. A-4).

Offgas Treatment and Analysis

The stream of noncondensable offgases from the condenser consisted principally of atomizing air during steam fluidization or atomizing and fluidizing air during air fluidization. A small fraction of the product HNO_3 was present as spray entrained within the stream of noncondensable gases. The HNO_3 spray was recovered by means of a coalescer, 4-1/2-in-diam by 6-1/2-in-long, packed with woven wire mesh, attached to the condenser outlet.

From the coalescer, the noncondensable gases flowed through the NO_2 absorption column. This column was intended to remove NO_2 gas from other noncondensable offgases, by reaction with sulfamic acid solution. Reacted NO_2 was determined by analysis of the absorption solution; thus the column served the double function of improving nitrogen accountability in the system and prevention of release of NO_2 to the atmosphere.

The gas absorption column, 10-in-ID by 10-ft-long, contained 7 ft of 5/8-in polypylene Flexirings, and was supplied with 2.5 gal/min of 8- to 10 pct sulfamic acid solution. Although the column was designed to physically handle the volume of air required for air fluidization of the bed, no absorption data were available from which an efficient column length could be calculated.

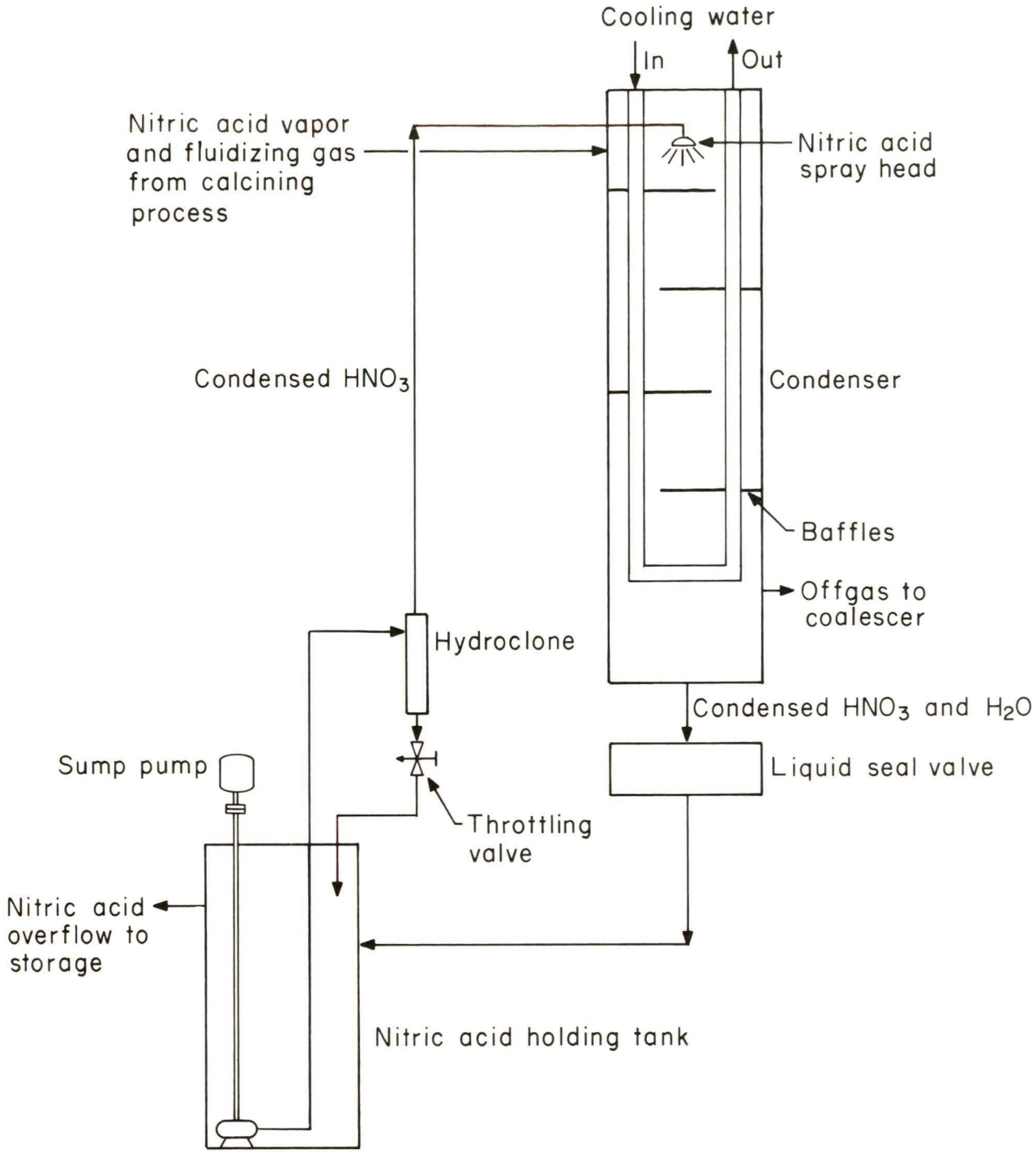


FIGURE A-4. - Condenser washdown system.

Instrumentation and Control

Temperatures were measured by means of iron-constantan thermocouples sheathed in stainless steel, connected to a 12-point-temperature chart recorder as follows:

1. Superheater output.
2. Plenum chamber.
3. Fluidized bed, bottom.
4. Fluidized bed, top.

5. Gas above fluidized bed.

6. Condenser, gas inlet.

7. Molten ANN in pressure tank.

8. Molten ANN at spray nozzle inlet.

9. Condenser, water output.

Bed temperature was controlled by manual adjustment of three autotransformers; each controlled four heating elements in the finned tubes. Heat input rate to finned tubes was determined by individual ammeters and voltmeters on each of the three autotransformers. Temperature was held within a few degrees of the desired value.

Fluidizing gas flow rate was indicated by a high-pressure rotameter on the pressure side (80 psig) of a throttling valve. Both steam and air fluidization rates were monitored and controlled by reference to calibration curves. Pressures of fluidizing gas, atomizing gas, and molten ANN in the pressure tank were indicated by Helicoid stainless steel pressure gages.

Melting and Handling Aluminum Nitrate Nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$]

Reagent-grade ANN was used during this test work. This material, received in 300-lb drums, cakes badly and must be mined from the drums. Melting was most easily accomplished with the steam coil previously described. Melting on a hotplate was impractical because of poor heat transfer and local overheating of the ANN, which causes some decomposition to NO_2. The vapors, constantly evolved during melting, are high in HNO_3, causing a change in composition throughout the melting operation. Therefore, proper sampling of molten ANN fed after the melting operation was essential to accurate material balances. Fortunately, molten ANN exposed to air forms a crystalline surface skin that retards evaporation.

The melted ANN was weighed, and transferred to the pressure tank, where, at 220° F, any remaining solid phase ANN melted. When no solid phase remained, spraying was begun without danger of plugging the inline filter.

Of serious consequence during ANN transfer and after system shutdown was the expansion of ANN during crystallization, which causes breakage of glassware used for its containment. The expansion once caused rupture of a weld in the stainless steel melting vessel. Because of this expansion characteristic, glass-lined equipment is inappropriate for containment of ANN.

Safety

The toxic nature of the NO_x gases cannot be overemphasized to workers in this field (6). Molten ANN is a serious health hazard because copious evolution of fumes high in HNO_3 occurs during melting and transfer of this material. Nitrogen oxide gases evolved during calcination are also hazardous, as are NO and NO_2 evolved from the product acid. Because exposure to NO_x fumes must be avoided, any person involved in transferring or handling molten ANN is required to wear chemical respirators with full face protection.

Operation and Startup

Continuous operation of the system can be difficult if cold spots occur anywhere in the ANN delivery system. Steam jacketing of the 1/4-in ANN lines by means of annular 1/2-in copper tubing with steam pressure set at 20 psig provided adequate temperature for reliable operation. ANN sprayed above its boiling point, however, can cause flashing of vapor at the nozzle tip, upsetting normal spraying.

The liquid orifice and atomizing gas annulus of the spray nozzle will plug with quartz sand unless purge air at 4 to 5 psig is flowing continuously

during filling of the bed with sand and during startup operations. In addition a steam purge line was connected to the ANN line to allow steam purging of both the liquid side of the nozzle and the ANN line to the tank. Purging with steam provided preheating and cleanout of the ANN line, and melting of ANN crystals in the ANN line during operation, a feature that saved several tests from premature shutdown.

Fluidization with superheated steam presented little difficulty if the calcining system was properly insulated, dead-ended exit ports were heated to above the dew point, and the system was preheated before introducing steam. Startup was accomplished by fluidizing with air, preheated in the circulation heater, while fluidized solids were heated to operating temperature with the finned tubes. (The system may be heated from room temperature to 300° C in 1 h). When operating temperature was reached, fluidizing steam was substituted for the fluidizing air.

Materials of Construction

The least expensive and most commonly recommended alloy materials for HNO_3 containment under these conditions are types 316 and 304 SS. The system was constructed of type 316L SS, except for the fins on the finned tubes, which were type 304 SS. High-temperature gaskets were asbestos and low-temperature seals for confining molten ANN were made of Teflon.

The combination of 304 with 316 SS is not acceptable where galvanic corrosion can occur, but no problem was encountered with the finned tubes where type 304 fins were welded to type 316 tubes. The finned tubes were not immersed in an electrolytic solution. Severe galvanic corrosion of type 304 SS occurred when this combination of materials was unintentionally used in the pressure tank.

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