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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	in	inch
°C/min	degree Celsius per minute	min	minute
cm	centimeter	μm	micrometer
cm^3	cubic centimeter	nm	nanometer
cm^3/min	cubic centimeter per minute	pct	percent
g	gram	torr	millimeter of mercury

ANALYTICAL METHODS FOR DETERMINING PRODUCTS FROM THERMAL DECOMPOSITION OF ALUMINUM NITRATE NONAHYDRATE

By A. Adams[1] and P. A. Romans[2]

ABSTRACT

The Bureau of Mines determined the composition of the vapors liberated during thermal decomposition of aluminium nitrate nonahydrate. Small samples were heated from room temperature to 550° C with initial heating rates from 50° to 200° C/min. Gases were rapidly swept away from the heated chamber with Ar and subjected to immediate analysis in order to minimize reaction between the components. In addition to H_2O, four N-containing compounds were identified: HNO_3, NO_2, NO, and N_2O. N_2 could not be determined in the presence of the nitrogen oxides, and attempted separation from the oxides led to the formation of more nitrogen. Relative amounts of each component were found to vary over a period of time; however, total amounts measured with different heating rates were reasonably constant and were typically as follows: 84.2 pct HNO_3, 7.1 pct NO_2, 4.3 pct NO, and 4.2 pct N_2O. HNO_3 and NO were determined from chemical reactions with a permanganate solution, N_2O was measured with a mass spectrometer, and NO_2 was measured with a spectrophotometer. Details of the methods used are described. Since NO_2 and NO can readily be converted to HNO_3, about 96 pct of the N from the decomposition can be recovered as HNO_3.

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INTRODUCTION

Research reported here is part of the work conducted at the Albany Research Center in support of the Bureau of Mines alumina mini-plant project. The goal was to develop processes using domestic raw materials to produce alumina for reduction to metal by established industrial methods; although the project has been shut down, the analytical methods should have validity for other workers. The work described herein relates to the HNO_3 leaching of kaolinitic clay. The leach solution is purified and aluminium nitrate is crystallized as the nonahydrate (1-4).[3] Aluminium nitrate nonahydrate (ANN) is then calcined to cell-grade alumina; costly HNO_3 is recovered from the offgas (5). A study of the gaseous products from the thermal decomposition was undertaken to determine how much of the various N-containing compounds is initially released. With this information at hand, procedures may be devised to maximize recovery of HNO_3.

GENERAL APPROACH

SOME PRELIMINARY OBSERVATIONS

When ANN is decomposed at 500° C, N is liberated predominantly as HNO_3 with smaller amounts of NO_2, NO, and N_2O. Other oxides such as N_2O_3, N_2O_5, and N_2O_4 along with HNO_2 are all unstable at this temperature (6). Decomposition of the ANN was followed in our laboratory by taking periodic scans of offgas from a sample heated in a tube furnace swept with Ar. Initially H_2O and HNO_3 are released in large quantities, but as the reaction continues measurable amounts of NO_2 and NO are evolved, and in the final stages some N_2O is produced.

PRELIMINARY STUDIES

A sample of ANN was heated to 150° C and held at that temperature for 35 min; then the temperature was raised to 270° C over the next 25 min. The decomposition products were then analyzed in a mass spectrometer in which both HNO_3 and NO_2 were fragmented by the ionizing field into positive ions NO_2^+ and NO^+. The curve shown in figure 1 is a plot of the intensity ratio of these two ions as a function of time after introduction of the above sample into the heated decomposition tube. Intensity ratios, $I(NO_2^+)/I(NO^+)$, observed for the pure compounds HNO_3 and NO_2, are also indicated. It can be seen that, at the beginning of the decomposition reaction, observed intensities approach those for HNO_3, but at 55 min the ratios are what would be expected for NO_2. Liberation of NO during the decomposition prevents quantifying the analyses for HNO_3 and NO_2 from these data, but the shift in composition of gases with time is well demonstrated. The first appearance of N_2O^+ is also noted on the graph. N_2O ion at 44 mass units is unique to N_2O; it cannot come from the other three N-containing compounds. HNO_3 could be measured from the peak at 63 mass units, but we chose an alternate method for subsequent quantitative analysis.

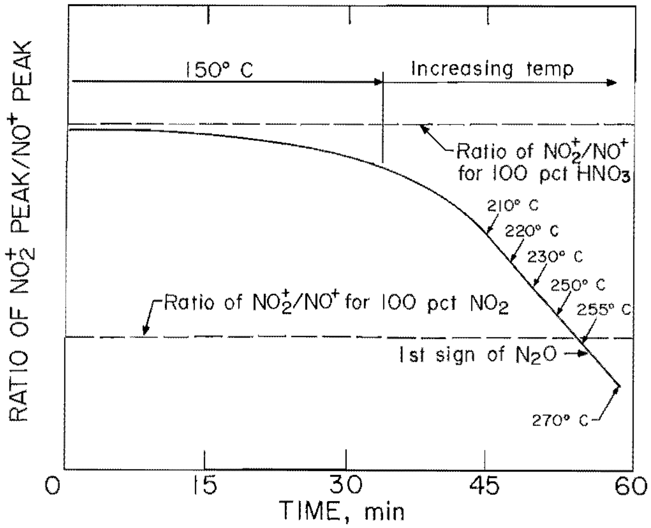

FIGURE 1.—Mass spectrometer data for N_2O and NO.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ANN introduced into a fluidized-bed calciner will undergo the same decomposition as observed here; however, interaction between the gases will occur for two reasons. First, because the nitrate is introduced continuously, products from all stages of decomposition will contribute to the offgas. Thus, water vapor and all N compounds mentioned previously will be present simultaneously. Second, the gaseous components will remain in the heated zone for a matter of minutes, sufficient time for reactions to proceed significantly (7). The steady state condition depends upon the feed rate, heat conduction, depth of bed, etc., and will be different for each unit. With this in mind, it was decided not to attempt analysis of the gas from a calcination unit but instead to measure individual components of total gas evolved from a small sample of ANN heated in a tube furnace swept with Ar. This should relate directly to the thermal decomposition products intitally produced in a calciner.

EXPERIMENTAL PROCEDURES AND RESULTS

DECOMPOSITION APPARATUS

The decomposition apparatus shown in figure 2 was constructed to simulate heating rates found in a fluidized-bed reactor. Thick-walled stainless steel tubing was used for the internal tube because it stored the energy needed for heating the sample rapidly (5 to 6 min) from room temperature to 550° C. The initial fast heating rate of 200° C/min for the sample changed to 50° C/min between 125° and 250° C owing to the high energy needed for dehydration and decomposition of ANN. The fast heating rate during the final stages of heating provided measurable concentrations of decomposition products in the flush gas without having to reduce the Ar flow rate. The thick-walled stainless steel tubing remained near 500° C during the entire decomposition test. Efficient transfer of heat to the sample was accomplished by using a 1- by 3-cm Pt boat to contain the 1-g sample inside the tube.

The flow rate of the flush gas used, Ar, was maintained at 75 cm^3/min and was checked at the beginning and end of a run using a bubble tube flowmeter. The 1-g sample, spread evenly in the Pt boat, was kept in the cool portion of the stainless steel tube until the furnace and reaction chamber had reached thermal equilibrium; then the sample and boat were pushed into the hot zone and the test started.

The flush gas passed from the reaction tube to one of the three detection devices through 1/8-in-OD stainless steel connector tubes; tube length was kept as short as possible, usually less than 6 in, to minimize heat loss. The 1/8-in connecting tubes were initially heated to 150° C but did get hotter as the higher temperature flush gas passed through the lines.

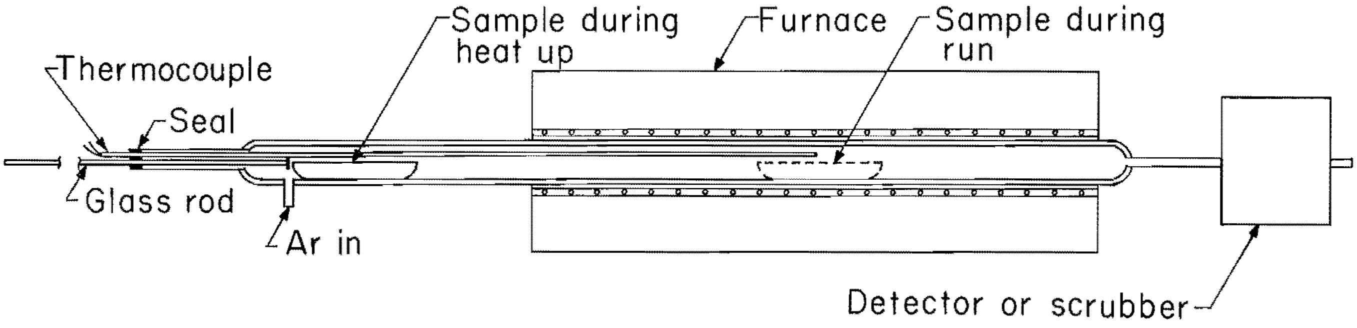

FIGURE 2.—Detail of decomposition apparatus.

One-half of sample used for each decomposition test was used to determine the total ANN content of the sample by measuring the Al content. This determination of ANN was used to calculate the total N present during decomposition.

ANALYTICAL PROCEDURES

As mentioned previously, it is not possible to simultaneously analyze for HNO_3, NO_2, NO, and N_2O when all are contained in the same mixture. Consequently, NO_2 and N_2O were measured independently and the values for HNO_3 and NO were calculated.

NO_2 was determined spectrophotometrically, and N_2O was determined by measuring the peak height at mass 44 using the mass spectrometer method previously described. HNO_3 and NO were determined by collecting the decomposition gases in permanganate scrubber solutions and calculating their values. The details of the determinations follow below.

Nitrogen Dioxide (NO_2) Analysis

A spectrophotometer specifically designed for HNO_3 manufacturing plants was modified for this study. The original instrument had a large-volume sample cell with a path length of 12 in. The instrument was modified for this study by fitting it with a low-volume (30-cm^3) cell with a shorter path length (2 cm). Using this modification, the largest amount of NO_2 obtained for a 1-g sample of ANN was 80 pct of the full-scale value, and the minimum detection limit was 1 pct NO_2 in the sweep gas.

NO_2 was determined by measuring the absorbance at 436 nm. The system was calibrated statically with synthetic mixtures of Ar and NO_2. Ten-cubic-centimeter samples of standards containing various percentages of NO_2 were injected into the Ar flush gas line, and the peak areas for the concentrations injected were recorded. These represent instantaneous concentrations versus time and, when compared with actual number of grams of NO_2 injected, the values always agreed to within 10 pct of the injected amount.

As stated previously, all connecting lines were heated to 150° C, sufficient temperature to prevent the dimer of NO_2, i.e., N_2O_4, from forming.

Nitrous Oxide (N_2O) Analysis

N_2O was determined using a mass spectrometer and measuring the mass peak at 44 mass units corresponding to N_2O^+. The mass spectrometer inlet system was modified as shown in figure 3 to allow the flush gas containing N_2O to enter the mass spectrometer. The 1-g sample contained in the Pt boat inside the quartz

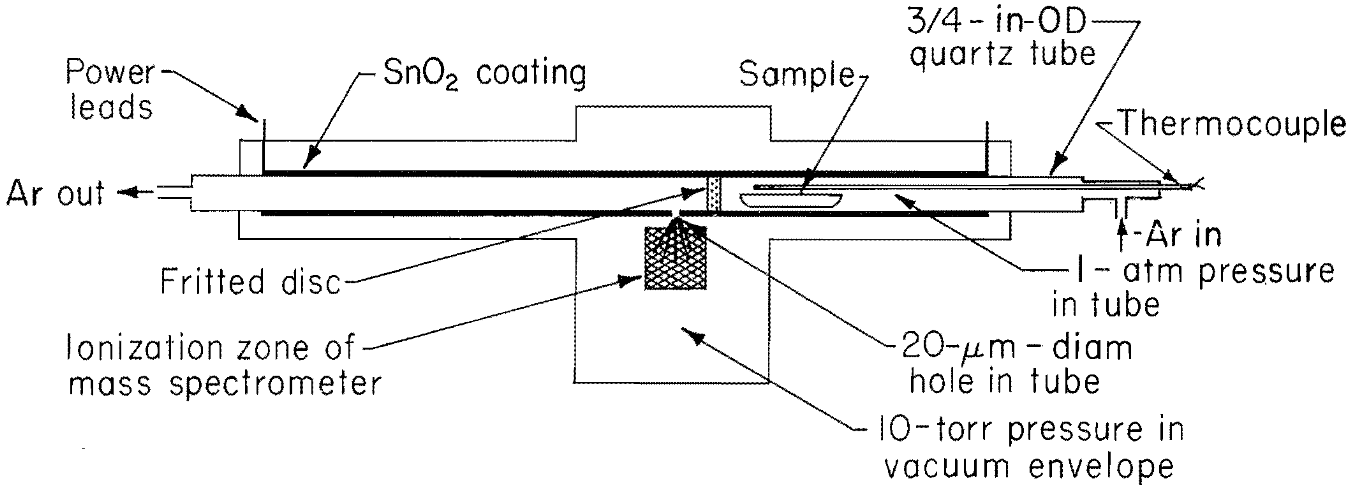

FIGURE 3.—Mass spectrometer inlet system.

tube was heated rapidly to 550° C. A laser-drilled 20-µm hole in the side of the quartz tube was the point through which the flush gas containing N_2O entered the mass spectrometer. The 20-µm hole served as a leak from the decomposition reaction carried out at atmospheric pressure to the high vacuum required in the mass spectrometer (8). A constant, measured flow of Ar was passed over the sample during the decomposition. The system was calibrated using standard mixtures of N_2O in Ar.

In addition to the mass peak at 44 mass units for N_2O^+, the mass peak for HNO_3 at 63 mass units was monitored. It was found that the amount of HNO_3 determined by monitoring this peak was equal to the amount of HNO_3 present after subtracting the other NO_x contents from the total N content. This additional information served as a check for HNO_3 content determined by the permanganate scrubber solutions.

The volume of N_2O formed during a run was determined by comparing the area under the curve formed when the Ar-N_2O ratio was plotted versus time with the area under a similar curve for the constant Ar flow. For example, if the area under the Ar-N_2O curve is 5 pct of the area under the Ar curve, then the volume of N_2O is 5 pct of the total Ar flow for that time period.

Nitric Oxide (NO) and Nitric Acid (HNO_3) Analysis

The HNO_3 and NO were determined indirectly by calculation after determining the values for NO_2 and N_2O. This was accomplished by introducing the decomposition gases from the decomposition apparatus mentioned in the "Experimental Procedures and Results" section into H_2SO_4-$KMnO_4$ scrubber solutions.

Both NO_2 and NO react with the scrubber solution according to the following equations:

$$5\ NO + 3\ MnO_4^- + 4\ H^+ = 5\ NO_3^- + 3\ Mn^{2+} + 2\ H_2O; \qquad (1)$$

$$5\ NO_2 + MnO_4^- + H_2O = 5\ NO_3^- + Mn^{2+} + 2\ H^+. \qquad (2)$$

The scrubber solutions were back-titrated according to the technique described by Kolthoff and Sandell (9). Three scrubber bottles in series were used to ensure that all the incoming gases were trapped. It was found that the first scrubber accounted for 95 pct of the gases liberated during decomposition. By using a known amount of permanganate and knowing the amount of NO_2 liberated using the spectophotometric results, it is possible to calculate the amount of NO liberated using equations 1 and 2.

The amount of N as HNO_3 can be calculated by first totaling the equivalent N in NO_2, N_2O, and NO as analyzed. This amount is subtracted from the total N based on the ANN analysis; see "Decomposition Apparatus" section. These calculated values for the HNO_3 content agreed well with values obtained from the mass spectral studies.

RESULTS AND DISCUSSION

A total of 15 runs were made, and the various NO_x were analyzed by the techniques previously described. These results are summarized and presented in table 1. The average values in the first three columns were used to calculate the HNO_3 by difference. As can be seen from the results, most of the N is convertible to HNO_3. Since NO_2 and NO can readily be converted to HNO_3 by known techniques, the HNO_3 recovery could increase from 84 pct to 96 pct.

Owing to equilibrium conditions the relative amounts of the various NO_x in

TABLE 1. - Decomposition products, percent

N as NO_2	N as N_2O	N as NO[1]	N as HNO_3[2]
7.1	3.9	4.6	NAp
7.5	4.4	4.4	NAp
7.4	4.4	4.1	NAp
7.0	3.8	4.3	NAp
6.6	4.3	3.9	NAp
7.1 (av)	4.2 (av)	4.3 (av)	84.2

NAp Not applicable.

[1] Based on total $KMnO_4$ reacted minus $KMnO_4$ reacted with NO_2.

[2] 100 pct minus pct NO_2, minus pct NO, minus pct N_2O.

NOTE.--0.2 pct of the N remains in the residue after decomposition.

the decomposition gas will change as the offgas is condensed and the HNO_3 recovered. Conditions to maximize oxidation will tend to favor formation of more HNO_3 and less NO_x. These techniques have been well established in the HNO_3 industry. Conditions to maximize recovery of HNO_3 could be achieved by a two-stage recovery process. In the first stage, approximately two-thirds of the N could be converted to HNO_3. In the second stage, conditions that favor the conversion of NO_2 and NO to HNO_3 could be used.

Presented in table 2 are the values for the decomposition tests for total N. It can be seen by an examination of the data that greater than 99 pct of the total N was liberated during the ANN decomposition.

TABLE 2. - Nitrogen in sample and residue

Sample			Residue			N
wt, g	N, pct	N wt, g	wt, g	N, pct	N wt, g	liberated, pct
1.0684	11.2	0.1196	0.1453	0.48	0.0007	99.4
.8687	11.3	.0982	.1192	.53	.0006	99.4
1.1249	11.0	.1237	.1503	.39	.0006	99.5
1.1295	11.4	.1288	.1566	.45	.0007	99.5
.8042	11.6	.0933	.1133	.51	.0006	99.4

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