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THE COMPOSITION OF OFF-GAS
FROM BATCH URANIUM-ALUMINUM DISSOLUTION

December 15, 1955

M. D. Martin

J. A. Buckham

AEC RESEARCH AND DEVELOPMENT REPORT

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For The Atomic Energy Commission

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by

M. D. Martin
J. A. Buckham

Chemical Engineering Development Section
CPP Technical Branch

December 15, 1955

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division

Under Contract
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THE COMPOSITION OF OFF-GAS
FROM BATCH URANIUM-ALUMINUM DISSOLUTIONABSTRACT

Full scale pilot plant studies of the mercury-catalyzed nitric acid dissolution of unirradiated 7.5 percent uranium-92.5 percent aluminum alloy slugs were carried out in a batch dissolver. Cast and extruded slugs were used in the experimental work.

The cast slug dissolutions were conducted under process conditions similar to those used in regular plant operation. The extruded slugs were dissolved similarly using less catalyst. All dissolutions were continued until the reaction rate was very low so that off-gas composition could be measured under widely varying dissolver solution composition.

The extruded slug dissolutions required much less catalyst than for the cast slugs. With only one-half the amount of catalyst as used for cast slug dissolutions, the dissolver solution was acid deficient in 15 minutes as compared to 5 hours required for dissolution of cast slugs to a similar point.

Nitrogen dioxide concentration in the dissolver is high during the early part of dissolution but decreases to a low value as the dissolver solution becomes neutral or acid deficient. Virtually all of the nitrogen dioxide is absorbed in the condensate at the condenser. The hydrogen content is nearly constant for acidic dissolver solutions, averaging about 4 percent for extruded slugs and 2 percent for cast slugs. In extruded slug dissolution, the hydrogen in the off-gas increases rapidly to about 23 percent when the dissolver solution becomes acid-deficient. This hydrogen increase is accompanied by a decrease in nitric oxide.

The data and correlations developed in these studies will permit the determination of the off-gas explosive hazards which may exist under various conditions of dissolution.

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I. INTRODUCTION

A. General Considerations

This report provides data and correlations related to the composition of off-gases and general stoichiometry involved in the mercury-catalyzed nitric acid batch dissolution of unirradiated uranium-aluminum alloy slugs. The work was undertaken because very little information has been obtained as to the range of composition of off-gases involved under various dissolution conditions. Special interest is found in the possible hydrogen content of off-gases and explosive hazards which might be encountered with mixtures of hydrogen and various oxides of nitrogen. It was also desirable to obtain more knowledge of the general stoichiometry involved under unusual conditions of dissolver operation such as with highly acid-deficient dissolver solutions. The data contained in this report may be found useful for application to other types of uranium-aluminum alloy slugs and dissolution processes.

B. Batch Dissolution Process

The batch dissolution process consists of charging a given number of uranium-aluminum alloy fuel elements to a large diameter cylindrical dissolver through a slug charging chute attached to the upper side of the dissolver. The charging chute extends to approximately the center of the dissolver. The uranium-aluminum slugs lie near the bottom of the dissolver on a perforated plate. The slug charging chute is then closed by a blind flange. A given volume of nitric acid feed, usually of approximately 4.75M strength, is charged to the dissolver. The nitric acid feed also contains mercury catalyst in the form of mercuric nitrate. The recommended⁽¹⁾ amount of catalyst for the batch-wise dissolution of cast uranium-aluminum slugs is 5 percent of the alloy weight as mercuric nitrate (0.005M mercuric nitrate in a 1.2M aluminum product), while 2 percent is stated to be sufficient for extruded slugs.

The dissolver is then heated with steam admitted to a jacket on the dissolver. The reaction usually starts at temperatures ranging from 50°C to 80°C depending upon the particular material to be dissolved. Cast slugs require a higher temperature to start the reaction than do extruded slugs. As soon as the reaction starts, large volumes of off-gas consisting of oxides of nitrogen and hydrogen are evolved. This off-gas is passed through the tube side of a large shell-and-tube condenser to remove water vapor which is returned to the dissolver. The condenser is cooled with water passed upwards and countercurrent to the flow of off-gas. The essentially dry off-gases are then sent through the off-gas vent system to a unit for further processing if required and are then vented to the atmosphere. At the beginning of the dissolution reaction the large heat of reaction evolved is sufficient to sustain the dissolution so that the steam is cut off. However, as the reaction progresses the heat from the reaction diminishes and it is necessary to apply more steam to the dissolver jacket to complete the reaction. When a suitable product is obtained,

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usually around 1M nitric acid in strength, it is pumped or jetted to a hold tank for subsequent extraction. A heel of undissolved slugs remains in the dissolver. For the next dissolving operation a quantity of slugs is charged sufficient to make up a total weight of alloy in the dissolver (undissolved heel plus fresh slugs) approximately equal to the original weight charged.

C. Dissolution Chemistry

Some of the reactions which may occur in the mercury-catalyzed dissolution of uranium-aluminum alloy in dilute nitric acid are as follows:

1. $\text{Al} + 6 \text{HNO}_3 = \text{Al}(\text{NO}_3)_3 + 3 \text{NO}_2 + 3 \text{H}_2\text{O}$
2. $\text{Al} + 4 \text{HNO}_3 = \text{Al}(\text{NO}_3)_3 + \text{NO} + 2 \text{H}_2\text{O}$
3. $8 \text{Al} + 30 \text{HNO}_3 = 8 \text{Al}(\text{NO}_3)_3 + 3 \text{N}_2\text{O} + 15 \text{H}_2\text{O}$
4. $2 \text{Al} + 6 \text{HNO}_3 = 2 \text{Al}(\text{NO}_3)_3 + 3 \text{H}_2$
5. $\text{U} + 8 \text{HNO}_3 = \text{UO}_2(\text{NO}_3)_2 + 6 \text{NO}_2 + 4 \text{H}_2\text{O}$
6. $\text{U} + 4 \text{HNO}_3 = \text{UO}_2(\text{NO}_3)_2 + 2 \text{NO} + 2 \text{H}_2\text{O}$
7. $4 \text{U} + 14 \text{HNO}_3 = 4 \text{UO}_2(\text{NO}_3)_2 + 3 \text{N}_2\text{O} + 7 \text{H}_2\text{O}$
8. $\text{U} + 2 \text{HNO}_3 + 2 \text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 + 3 \text{H}_2$

From the above reactions it is then seen that the gases evolved contain nitrogen dioxide, nitric oxide, nitrous oxide, and hydrogen. In addition to these gases it may be postulated that an additional reaction with aluminum might possibly produce nitrogen but evidence obtained in the present work seems to show that very little, if any, nitrogen is generated. To simplify calculations for data contained in this report only the first four reactions were considered since the uranium contained in the fuel element is small compared to the aluminum (less than 1 mole percent).

It is found^{(1),(2)} that the dissolution process can continue after all the hydrogen ions present in the original nitric acid are consumed, giving products deficient in acidity as compared to aluminum nitrate solutions. The additional hydrogen ions necessary for further dissolution are supplied by the hydrolysis of aluminum and uranyl nitrates. For example, the aluminum nitrate may hydrolyze as follows:

9. $\text{Al}(\text{NO}_3)_3 + \text{H}_2\text{O} = \text{Al}(\text{OH})(\text{NO}_3)_2 + \text{HNO}_3$
10. $\text{Al}(\text{OH})(\text{NO}_3)_2 + \text{H}_2\text{O} = \text{Al}(\text{OH})_2 + \text{NO}_3 + \text{HNO}_3$

As the newly-formed nitric acid is consumed in the dissolution of metal more hydrolysis occurs and the product solution is then considered "acid-deficient", although the pH is less than seven. The amount of acid-deficiency is measured by the concentration of hydroxyl ions in the complex ions formed as a result of hydrolysis. Acid-deficiency as referred to in this report is designated by the use of a minus sign to distinguish it from acidic dissolver solutions.

It has been stated that as the off-gases pass through the condenser, the water vapor is condensed and returned to the dissolver. A large amount of the nitrogen dioxide is dissolved in and reacts with this condensed vapor to form nitric and nitrous acids. The reactions involved are as follows:

so that the overall reaction may be considered to be

Therefore, the off-gases after the condenser contain little or no nitrogen dioxide and a larger amount of nitric oxide than that originally produced by the metal dissolution.

II. SUMMARY AND CONCLUSIONS

Full scale pilot plant studies of the mercury-catalyzed nitric acid dissolution of unirradiated 7.5 percent uranium-92.5 percent aluminum alloy slugs have been conducted in a typical plant batch dissolver. Both cast and extruded slugs were dissolved. The work was aimed at determining the off-gas composition, especially hydrogen content, and the dissolution stoichiometry which is encountered under various process conditions.

All of the cast slug dissolutions were made according to regular plant procedure except that the dissolver was operated until little or no off-gas flow was observed. In general, dissolver products from cast slug dissolution were nearly neutral in acidity. The extruded slug dissolutions were made with varying amounts of mercuric nitrate catalyst so as to vary the dissolution rates and product composition. Dissolver products ranged from slightly acid-deficient to highly acid-deficient.

The maximum effective catalyst concentration (0.02M) was used for all cast slug dissolution but was varied from 0.01M to 0.001M for extruded slugs. The higher concentration used in the extruded slug dissolution produced a product of over 2M acid-deficiency and caused the dissolver solution to become neutral in acidity within a half hour after the start of dissolution. The lower concentration produced a product of only slight acid-deficiency.

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The total off-gas flow rate after the condenser is higher for extruded than for cast slugs during the early part of a dissolution. The maximum flow rate to be expected near the beginning of dissolution is 7-8 scfm (0°C and 14.7 psia) and 4-5 scfm for extruded and cast slugs, respectively. The flow rate drops to below 0.15 scfm within 3 to 4 hours for both extruded and cast slugs.

The dissolution reaction rate decreases slowly as the dissolver solution molarity decreases but drops sharply at or near the neutral dissolver solution region after which the rate decreases slowly again. This is shown by the sharp drop in off-gas flow rate in these regions. For extruded slug dissolution this sharp decrease occurs at the neutral point but for cast slugs it occurs at approximately 0.75 molar acidity. Although the off-gas composition is changing throughout a dissolution, a sharp change in composition seems to occur in these regions as shown by a marked decrease in nitrogen dioxide concentration.

The off-gases from batch dissolution contain hydrogen, nitrogen dioxide, nitric oxide, and nitrous oxide in varying concentrations depending on the dissolving conditions. In addition a small amount of water vapor is present in the off-gases after the condenser.

The average hydrogen concentration in the off-gas after the condenser for cast slug dissolution is 2 percent. The maximum hydrogen to be expected for normal cast slug dissolutions (product acid concentration around 1M) is about 8 percent. Hydrogen concentration in extruded slug dissolution is about 4 percent for 1-2M acidic dissolver solutions and increases rapidly for acid-deficient solutions reaching a maximum of 23 percent at approximately 2M acid-deficiency.

The concentration of nitrogen dioxide is high in the dissolver during the early part of an extruded slug dissolution, but drops as the reaction proceeds. There is a sharp drop in the region of neutral dissolver solution. The average concentration was 0.57 moles of nitrogen dioxide per mole of dry gas obtained after the condenser. The dry gas after the condenser is considered to be nitrogen dioxide-free since this constituent is almost completely dissolved in the condensate (less than 0-2 percent by actual analysis). Crude estimates of the nitrogen dioxide concentrations in the dissolver for cast slug dissolutions indicate that this constituent is present in the same order-of-magnitude as for extruded slug dissolutions.

The nitric oxide concentration in the off-gas after the condenser for acidic dissolver solutions averages 72 percent for extruded slugs and 82 percent for cast slugs. It decreases to 50 percent at 2M acid-deficiency for extruded slugs and 74 percent at 0.4M acid-deficiency for cast slugs.

The concentration of nitrous oxide in the off-gas after the condenser for acidic dissolver solutions averages 24 percent for extruded slugs and 16 percent for cast slugs. It increases to 28 percent at 1.6M acid-deficiency for extruded slugs and 23 percent at 0.4M acid-deficiency for cast slugs.

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It may be concluded that the stoichiometry of dissolution is such that the reaction producing nitrogen dioxide diminishes in favor of the other reactions as the dissolution proceeds.

The acid consumption for both cast and extruded slugs is similar. The average acid consumption for either slug dissolution is 4.0-4.1 moles of nitric acid consumed per mole of aluminum dissolved. The acid consumption decreases as the dissolver solution becomes acid-deficient because the stoichiometry shifts to that reaction consuming the least acid and producing hydrogen. The lowest acid consumption encountered was 3.8 at 2M acid-deficient dissolver solutions in extruded slug dissolution.

III. TEST EQUIPMENT AND MATERIALS

A. Materials

Commercial grade 60 percent (13M) nitric acid and demineralized water were used in preparing the acid feed solutions. A chemically pure grade of mercuric nitrate monohydrate crystals was used as catalyst.

Unirradiated uranium-aluminum alloy slugs of cast and extruded types were used in the experimental work. These slugs were cylinders approximately 1-1/2 inches in diameter and nine inches long and were not jacketed.

B. Dissolver and Condenser

The batch dissolver system is shown in Figure 1. The dissolver and condenser were surplus plant equipment removed from the ICPP and installed at the Chemical Engineering Laboratory.

The stainless steel batch dissolver is cylindrical with a diameter of approximately three feet and about six feet in height. The lower third of the dissolver is jacketed for steam heating. The slug chute is stainless steel pipe, six inches in diameter. It enters the dissolver at an approximate angle of 45 degrees and about two-thirds of the distance from the bottom to the top. It extends from about 2-1/2 feet outside to the center of the dissolver and is provided with a blind flange and gasket for closure after changing the slugs. The dissolver is provided with various nozzles on the top for charging feed, instrumentation, etc. A six-inch pipe connected to the top of the dissolver is provided for removal of off-gases. The usual plant procedure is to jet the product out of the dissolver via a nozzle extending from the top to the bottom; however, for the present experimental work a special nozzle was extended through the bottom steam jacket to the dissolver wall and welded in place. Product was then pumped out with a centrifugal pump.

FIG. 1

DIAGRAM OF BATCH DISSOLVER SYSTEM

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The stainless steel condenser is a shell-and-tube type with the off-gases passing through the tubes and the cooling water through the shell side. It is approximately 16 inches in diameter, 20 feet long, and contains 475 square feet of heat transfer area. The off-gases enter the condenser through a 6-inch diameter stainless steel riser and exit through a 2-inch stainless steel pipe. The condensate is returned to the dissolver through a one-inch stainless steel pipe.

C. Instrumentation

The off-gases from the condenser passed through an orifice manifold containing three orifices of varying size so that the range of off-gas flow could be measured. The flow was continuously recorded by a Brown circular chart recorder.

A rotameter manifold was provided in the condensate return line to measure flow; however, this was not used due to widely fluctuating flows and plugging caused by pipe scale, etc.

Thermocouples were used to measure the following temperatures:

1. Dissolver solution
2. Condensate
3. Cooling water before and after condenser
4. Off-gas at the orifice manifold
5. Off-gas before and after condenser

The thermocouples for measuring off-gas temperature before and after the condenser were not added until later in the experimental work. All thermocouples were connected to a Minneapolis-Honeywell multiple-point indicator.

Additional lines were installed for later experimental work so that the cooling water from the condenser could be diverted to a measuring tank to determine the flow rate.

Off-gas pressure at the orifice manifold was indicated by a pressure gage and manometer.

D. Sampling

Off-gas sampling was provided at the dissolver, before the condenser, and at the orifice manifold after the condenser. The off-gas sampling point at the dissolver was not added until later in the experimental work. Off-gas samples were taken in standard, 125 ml glass sample tubes constructed with a stop cock at each end. A vacuum pump was used to evacuate and flush off-gas through the sample tubes.

Dissolver solution samples were taken at the product pump out line directly under the dissolver.

Condensate samples were taken from the condensate return line directly under the condenser.

IV. EXPERIMENTAL PROCEDURE

Table 1 shows the process conditions used for each of the seven runs. Four runs were made with cast slugs and three with extruded slugs.

The procedure for all runs was similar. The required number of slugs were charged to the dissolver and the slug charging chute was closed. Cooling water was started to the condenser and the orifice manifold set to divert the off-gas through the largest orifice. The required volume of feed was pumped to the dissolver. Steam was admitted to the dissolver jacket and the contents heated. As soon as the reaction started, as indicated by a rapidly rising dissolver temperature and off-gas rate, the steam was cut off. In most runs the off-gas meter indicated off scale reading for 5-15 minutes after the start of the reaction. As soon as the reaction began to diminish (as shown by a rapid lowering of off-gas rate) the steam was again admitted to the dissolver jacket and kept on for the remainder of the run. All runs were continued for at least 8 hours at which time the off-gas rate had fallen to a very low value. The run was concluded by shutting off the steam and admitting cooling water to the dissolver jacket. When the dissolver product had cooled to 40-50°C the product was pumped out to storage and sampled.

Dissolver temperatures averaged about 95-100°C with the off-gas entering the condenser at about 96°C and leaving at 20-25°C during each run.

Off-gas samples were collected every 15 to 30 minutes during the first two to three hours of each run when the off-gas rate was high; the interval was increased to 30 to 60 minutes during the last part of each run. Each sample was obtained by intermittently evacuating the collecting tube with a vacuum pump and then allowing off-gas to flow into the tube. This was repeated four to six times. In general, it became more difficult to obtain samples with little or no air contamination as the off-gas flow rate decreased. Samples directly from the dissolver were not taken in Runs 1 and 2. Due to low off-gas rates in the latter part of each run, a relatively long period of time elapsed during which a particular increment of off-gas traveled from the dissolver to the condenser or the orifice manifold. It was decided that samples taken directly from the dissolver for all subsequent runs would be more representative of the dissolution reaction at the particular time the sample was taken.

Dissolver solution and condensate samples were collected every 30 to 60 minutes throughout the run except in Runs 1 and 2 in which only three condensate samples were collected.

Condenser cooling water flows were measured by collecting a measured volume of water over a short period of time in Runs 6 and 7. From these measured flows the condensate flow could be calculated indirectly from a heat balance around the condenser.

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Table 1

Process Conditions For Experimental Work

<u>Run Number</u>	<u>Fuel Element</u>	<u>Number of Slugs Charged</u>	<u>Slug Weight Pounds</u>	<u>Heel Weight From Previous Run, Pounds</u>	<u>Feed Composition</u>		<u>Feed Volume, Liters</u>	<u>Dissolution Time Hours</u>
					<u>Nitric Acid Molarity</u>	<u>Mercury Catalyst Molarity</u>		
1	Cast	66	88	None	4.79	0.02	566 ¹	8.0
2	Cast	51	68	22	4.71	0.02	566	8.5
3	Cast	31	41	45	4.87	0.02	566	8.6
4	Cast	0 ²	0	43 ²	4.75	0.02	566	7.75
5	Extruded	66	79	None	4.75	0.01	324	8.5
6	Extruded	34	41	33	4.81	0.003	566	7.0
7	Extruded	66	79	None ³	4.79	0.001	566	10.0

1. Approximately 180 liters of 5.60M nitric acid feed containing no catalyst was accidentally pumped into the dissolver with the regular feed at the start of the run.
2. This was a heel cleanout run, therefore, no new slugs were charged.
3. This run was made with new slugs. The heel from the previous run was cleaned out before the start of the run.

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V. CALCULATION PROCEDURESA. Analyses of Off-Gases

The analyses of off-gases as reported by the analytical laboratory were on a dry basis. Although a number of analyses showed the presence of nitrogen and oxygen, many contained little or none of these constituents. No trend in nitrogen concentration appeared in any runs. Those containing nitrogen and oxygen showed these constituents in approximately the same ratio as that for air. All samples which contained nitrogen also contained oxygen. In addition, some argon was detected in samples containing large concentrations of nitrogen and oxygen. It was therefore considered justifiable to assume that no nitrogen was generated by the dissolving reaction but that its presence in the samples was due to air contamination in the sample bottles. Those analyses which showed less than 25-30 percent nitrogen were corrected to an air-free basis; those with higher nitrogen content were considered unreliable and were thrown out. The condensate analyses showed that acid was present but no aluminum. Since entrainment from the dissolver would carry aluminum into the condensate it was assumed that the acidity was produced by the dissolution of nitrogen dioxide (generated in the dissolver) in the condensed water. The analyses were corrected to a nitrogen dioxide-free basis since very few samples showed greater than 0-2 percent of this constituent to be present. The air-free and nitrogen dioxide-free analysis was obtained by first correcting the nitric oxide to account for the part of this constituent which combined with oxygen from air contamination and then totaling the constituents, exclusive of nitrogen, oxygen, and nitrogen dioxide. The percent of each constituent (nitrous oxide, corrected nitric oxide and hydrogen) was divided by the total to obtain the corrected analysis. This resultant air-free and nitrogen-free gas was arbitrarily defined as dry gas for use in subsequent calculations. Since reported analyses showed that most of the nitrogen dioxide was absorbed in condensed water in the sample tube for those samples taken before the condenser, samples taken before and after the condenser are analogous when calculated on a nitrogen dioxide-free basis. The calculated dry gas is actually very similar to the off-gas as it leaves the condenser.

The approximate lag time or time elapsed during which a particular increment of off-gas sample taken after the condenser flows from the dissolver to the sample point was estimated by making a trial-and-error graphical integration of the off-gas flow to determine the time spent in filling up the holdup volume. These lag times were then used to determine the dissolver solution molarity at the time these samples left the dissolver. The graphs of off-gas composition vs dissolver solution molarity were plotted using these corresponding dissolver solution molarities.

B. Condensate Flow Rates

Condensate flow rates for Runs 6 and 7 were calculated from a heat balance around the condenser. The heat removed from the condenser was obtained from the cooling water flow rate and the temperature difference.

Since all variables in the heat balance are known except the condensate flow, the flow was obtained by equating the heat removed from the system to the sum of the heats generated in the system (i.e., the heat of cooling off-gas, heat of condensing water vapor, heat of dissolution of nitrogen dioxide in the condensate, and the heat of cooling the condensate to the outlet temperature). The heat of condensation is the major item in the heat balance. The heat of dissolution of nitrogen dioxide in water was obtained by assuming reaction (13) given in Section I-C.

C. Nitrogen Dioxide Produced During Metal Dissolution

Since the nitrogen dioxide generated in the dissolver could not be directly measured due to its dissolution in condensed water vapor, it was calculated for Runs 6 and 7 indirectly. The condensate analyses were reported as moles of nitric acid per liter. Assuming reaction (13) to be valid, the rate of nitrogen dioxide dissolution (as moles per minute) is obtained from the condensate analysis and flow rate. The dry gas flow rate (as moles per minute) was obtained from the metered off-gas flow rate and the corrected off-gas analysis calculated as described in Section A. The rate of nitrogen dioxide dissolution was then divided by the dry gas rate to obtain the moles of nitrogen dioxide generated per mole of dry gas. This dry gas is essentially the gas flowing from the condenser. The nitrogen dioxide generated in earlier runs in which cooling water flows were not measured was crudely estimated by assuming that at equal off-gas flow rates (comparing the early run with Runs 6 and 7) the compositions were similar and condensate flow rates were equal.

D. Weighted Acid Consumption Based on Off-Gas Composition

Weighted acid consumptions were calculated for Runs 6 and 7 by the use of reactions (1) through (4). The small amount of uranium dissolved was neglected. From these reactions it may be seen that the moles of aluminum dissolved per mole of the particular gas evolved is 0.333 for nitrogen dioxide, 1.0 for nitric oxide, 2.67 for nitrous oxide, and 0.667 for hydrogen. The moles of aluminum dissolved per mole of dissolver off-gas (nitrogen dioxide as calculated in Section C plus dry gas) for each reaction was obtained from the above figures, the nitrogen dioxide content, and the dry gas composition. These were then added to obtain the total moles of aluminum dissolved per mole of dissolver off-gas. Dividing each of these by the total gives the percent of aluminum dissolved by each reaction. From reactions (1) through (4) it may be seen that the moles of acid consumed per mole of aluminum dissolved is 6.00 for evolution of nitrogen dioxide, 4.00 for evolution of nitric oxide, 3.75 for evolution of nitrous oxide, and 3.00 for evolution of hydrogen. The acid consumption for each reaction was obtained by multiplying each of the above figures by the percent of aluminum dissolved by that reaction. The total of these figures gives the weighted acid consumption.

E. Acid Consumption Based on Material Balance

These acid consumptions were obtained from the feed and product analyses. The moles of nitric acid consumed for each mole of aluminum dissolved were calculated by dividing the moles of acid in the feed minus the moles of acid in the product, by the moles of aluminum in the product (or moles dissolved). In the case of acid-deficient product, the moles of acid deficiency were added to the moles of acid in the feed and the total was divided by the moles of aluminum in the product.

VI. DISCUSSION OF RESULTS

A. General

The off-gas flow rates, off-gas compositions, and acid consumptions are correlated with the type of slug dissolved (i.e., cast or extruded slug). In correlating these results, dissolver solution molarity has been used as the major process parameter. This quantity has been selected because the dissolution reagent should be expected to influence the extent to which the specific reactions occur and enable one to make general conclusions as to the dissolution stoichiometry of other uranium-aluminum alloy types (such as the MTR fuel element).

Tables 2 and 3 show a summary of results for cast and extruded slug dissolutions, respectively. The dry off-gas analyses after the condenser were for samples taken at the times given in the table; however, the corresponding dissolver solution compositions shown are for dissolver solution at the time the particular increment of off-gas sample left the dissolver. In this way, lag time between the dissolver and the sample point is accounted for. Run Number 1 may not be considered as typical of the regular plant process for dissolving cast slugs since an excess amount of acid feed was pumped to the dissolver accidentally. The first extruded slug dissolution (Run 5) was made with less acid feed than for cast slugs and with more catalyst than used in subsequent extruded slug dissolutions (recommended by F. M. Warzel in private communication). The dissolver solution was highly acid deficient within one-half hour after the start of dissolution. The subsequent extruded slug dissolutions were made with the same volume and strength of feed as for cast slugs, only the catalyst concentration was decreased.

Table 4 shows a summary of off-gas compositions encountered during the runs. Table 5 shows the dissolver product composition for each run.

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Table 2
Summary of Results for Cast Slug Dissolution

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Run No.	Time (Hours From Start of Run)	Condensate Composition (Acid Molarity)	Dissolver Solution Composition (Acid Molarity)	Dry Off-Gas Analysis - Nitrogen Dioxide Free (Mole Percent)			Acid Consumption Based on Material Balance (Moles Acid/Mole Al Dissolved)		
				Before Condenser	After Condenser		Before Condenser	After Condenser	
				NO	N ₂ O	H ₂	NO	N ₂ O	H ₂
1	0.08		4.70				78.5	18.3	3.2
	0.17		4.19	81.3	16.7	2.0			
	0.58		3.10				74.5	22.2	3.3
	0.58		2.82	76.4	20.4	3.2			
	0.83		2.20				75.0	21.7	3.3
	0.83		1.89	78.3	18.6	3.1			
	1.08		1.48				78.9	17.9	3.2
	1.08		1.34	80.6	15.9	3.5			
	1.33	1.73							
	1.83		0.61	77.0	19.8	3.2			
	2.33		0.62				69.9	25.3	4.8
	2.33		0.37	72.0	23.7	4.3			
	2.83		0.23				64.1	29.4	6.5
	3.33		0.54				64.1	28.3	7.6
	3.33		0.13	72.2	22.2	5.6			
	3.83	0.24	0.06	67.0	27.5	5.5			
	4.83		0.32				70.1	24.1	5.8
	5.33		0.24				75.5	18.9	5.6
	5.33		0.07	80.2	16.5	3.3			
		Averages		76.1	20.1	3.8	72.3	22.3	4.8
									3.89
2	0.50		1.60	77.0	21.9	1.9			
	2.75		0.06	70.7	24.0	5.3			
	4.75	0.10							
	5.25		-0.09				73.5	23.0	3.5
	5.75		-0.11				75.0	21.8	3.2
	6.75		-0.18				75.1	21.5	3.4
	7.25		-0.20				71.0	24.4	4.6
	7.25		-0.37	82.6	15.7	1.7			
	8.25		-0.25				75.0	21.6	3.4
	8.25		-0.40						
		Averages		78.5	19.1	2.4			
				77.2	20.0	2.8	73.9	22.5	3.6
									4.18
3	0.37		2.78				78.5	20.3	1.2
	0.37		2.60	81.7	17.0	1.3			
	0.62	1.77	1.81	80.2	18.4	1.4			
	0.87		1.40				75.9	22.8	1.3
	0.87		1.34	78.1	19.5	2.4			
	2.62	0.12							
	2.87		0.05	80.4	16.4	3.2			
	3.62	0.08	0.16				75.9	21.3	2.8
	4.62	0.08	0.02				77.2	20.3	2.5
	5.37		-0.28	85.0	13.4	1.6			
	5.62	0.08	-0.05				78.4	19.4	2.2
	6.62	0.07	-0.05				78.7	19.1	2.2
		Averages		81.1	16.9	2.0	77.4	20.6	2.0
									4.08
4	0.25		3.28				83.5	15.4	1.1
	0.25		3.20	87.6	12.4	0			
	0.50	2.37	2.70	87.9	11.0	1.1			
	0.75		2.52				82.3	16.5	1.2
	1.00	1.79	2.25	86.5	12.4	1.1			
	1.25		2.11				83.1	15.6	1.3
	1.25		2.06	86.9	12.0	1.1			
	2.50		1.55				83.0	15.7	1.3
	2.50		1.47	86.6	12.4	1.0			
	2.75	0.97					81.9	16.8	1.3
	3.00		1.45						
	3.00		1.35	87.8	11.2	1.0			
	3.50		1.26	86.2	12.3	1.5			
	3.75	0.61					83.1	15.5	1.4
	4.00		1.33						
	4.50		1.20	90.9	7.9	1.2			
	4.75	0.34					84.1	14.3	1.1
	5.50		1.24						
	5.50		1.18	92.3	6.6	1.1			
		Averages		88.1	10.9	1.0	83.0	15.8	1.2
									4.13

1. Negative values of acid molarity indicate acid-deficient dissolver solution.

NOTE: The average nitrogen dioxide in off-gas for all runs is estimated to be 0.5 moles/mole dry gas.

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Table 3

Summary of Results for Extruded Slug Dissolution

Run No.	Time (Hours From Start of Run)	Condensate Composition (Acid Molarity)	Dissolver Solution Composition (Acid Molarity) ¹	Dry Off-Gas Analysis - Nitrogen Dioxide Free (Mole Percent)						Nitrogen Dioxide in Dissolver (Moles/Mole Dry-Gas)	Acid Consumption (Moles Acid/Mole Al Dissolved)		
				Before Condenser			After Condenser				Based on Off Gas Composition	Based on Material Balance	
				NO	NO ₂	H ₂	NO	NO ₂	H ₂				
5	0.05		2.5				63.5	32.4	4.1				
	0.05		2.0	61.0	31.9	7.1							
	0.25	0.18	-1.12	47.8	36.5	15.7							
	0.50		-1.62				53.7	32.3	14.0				
	0.50		-1.66	49.7	27.2	23.1							
	0.75	0.11	-1.97	55.7	27.0	17.3							
	1.00		-2.08				57.6	30.1	12.3				
	1.00		-2.10	59.4	24.3	16.3							
	1.25	0.21	-2.22	69.3	20.5	10.2							
	1.50		-2.28				65.0	25.6	9.4				
	1.50		-2.32	66.7	21.1	12.2							
	2.25		-2.39				68.4	19.9	11.7				
			Averages		58.5	26.9	14.6	61.6	28.1	10.3			5.23
6	0.25		4.25	70.1	26.7	3.2							
	0.50	1.49	1.19	67.5	27.3	5.2			0.516		4.04		
	0.75		-0.05	55.5	31.5	13.0							
	1.00	0.23	-0.61	52.9	30.0	17.1			0.048		3.80		
	1.25		-0.78				48.2	29.9	21.9				
	1.25		-0.81	53.5	29.2	17.3							
	1.50	0.17	-0.94	54.2	27.9	17.9			.049		3.80		
	1.75		-1.20	55.6	27.3	17.1							
	2.00		-1.40	55.4	25.2	19.4							
	2.25		-1.38				54.3	25.8	19.9				
	3.00	0.08	-1.58				60.2	20.5	19.3				
			Averages		58.1	28.1	13.8	54.2	25.4	20.4	0.204	3.88	4.22
	7	0.42		3.40	73.6	22.2	4.2						
0.50		2.34	3.17							1.14	4.33		
0.75			2.54				69.6	26.3	4.1				
0.75		2.16	2.52							1.08	4.31		
1.00			2.10	73.1	22.9	4.0							
1.25			1.69				69.1	26.5	4.4				
1.25			1.62	73.3	22.8	3.9							
1.50		1.46	1.19	72.2	23.7	4.1				0.82	4.29		
1.75			0.66				68.5	26.6	4.9				
1.75			0.60	73.5	22.6	3.9							
2.25		0.64	0.02	66.6	26.7	6.7				0.60	4.22		
2.75			-0.01				69.2	24.2	6.6				
2.75			-0.05	72.8	21.7	5.5							
3.25			-0.09	79.7	17.2	3.1							
3.50			-0.10	78.1	17.3	4.6							
4.25			-0.05				75.4	20.0	4.6				
4.25		.05	-0.14							0.26	4.01		
4.75			-0.07				78.8	16.8	4.4				
5.25		.06	-0.15							0.20	3.99		
5.25			-0.08				79.8	16.0	4.2				
5.75			-0.09				77.5	18.3	4.2				
6.25			-0.10				80.8	15.1	4.1				
6.75			-0.12				82.9	13.6	3.5				
7.75			-0.51				52.4	34.0	13.6				
7.75		1.25	-0.53	65.2	28.5	6.3				0.11	3.84		
8.00			-0.57				64.8	26.1	9.1				
8.00			-0.63	69.4	24.0	6.6							
9.75			-0.82				66.6	23.9	9.5				
			Averages		72.5	22.7	4.8	72.0	22.1	5.9	0.60	4.14	4.00

1. Negative values of acid molarity indicate acid deficient dissolver solution.

Table 4Off-Gas Composition

	<u>Cast Slugs</u>		<u>Extruded Slugs</u>	
	<u>Range</u>	<u>Average</u>	<u>Range</u>	<u>Average</u>
H ₂	1-8%	2%	3-23%	10%
NO	64-92%	79%	48-83%	65%
N ₂ O	15-29%	19%	14-36%	25%
NO ₂			0.05-1.14 $\frac{\text{moles}}{\text{mole dry gas}}$	0.57 $\frac{\text{moles}}{\text{mole dry gas}}$

Table 5Dissolver Product Composition

<u>Run No.</u>	<u>Al (g/l)</u>	<u>Acid Molarity</u>
1	36.8	-0.21
2	35.1	-0.41
3	36.8	-0.39
4	24.5	1.19
5	39.9	-2.49
6	46.1	-1.93
7	40.9	-0.90

B. Off-Gas Flow Rates

Figures 2 and 3 show the dry off-gas flow rates for a typical cast and extruded slug dissolution at various dissolving times and dissolver solution compositions. This off-gas may be considered to be dry gas as defined in the calculation procedures since it is practically water and nitrogen dioxide-free. The flow rate was higher during the first three hours for the extruded slug dissolution, thereafter flows were so low as to appear similar. The effect of injecting additional catalyst in the extruded slug dissolution was to cause a sharp increase in the flow rate for a short period of time after which the rate decreased rapidly. From Figure 3 it may seem that in the extruded slug dissolution the flow rate dropped sharply in the region of neutral dissolver solution but in the cast slug dissolution this sharp drop occurred in the region of 0.75 molar acidity. Although the dissolution reaction rate is decreasing continually as shown by the decreasing off-gas flow rate, the sharp drop in these regions indicates an abrupt decrease in the reaction rate at these points after which the reaction rate then decreases slowly again. The composition of

FIG.2

TYPICAL DRY OFF GAS FLOW RATES

FIG.3
VARIATION OF DRY OFF GAS FLOW RATE
WITH DISSOLVER SOLUTION COMPOSITION

the off-gas is changing continually as indicated by the decrease in nitrogen dioxide content of the off-gas (Run 7, Table 3). However the major change in composition seems to occur in the region of sharp drop in reaction rate as shown by a sharp drop in nitrogen dioxide during this time. The flow rates for both dissolutions were very low after the dissolver solution reached an acid-deficiency of about 0.1 molar (-0.1 acid molarity) except for the sharp increase in the extruded slug dissolution due to adding extra catalyst.

C. Hydrogen Content of the Dry Off-Gas

Figure 4 shows the percent of hydrogen in the off-gas on a nitrogen dioxide-free basis. The trend in hydrogen content and for all other constituents of the off-gas is shown by means of straight lines because it would be difficult to predict an exact smooth curve through the points. The hydrogen content is nearly constant for acidic dissolver solutions, averaging about 4 percent for extruded slugs and 2 percent for cast slugs. The hydrogen sharply increased for neutral and acid-deficient dissolver solution in extruded slug dissolution. The maximum was 23 percent at an acid-deficiency of 1.7 molar (-1.7 acid molarity). The possible downward trend in hydrogen above an acid-deficiency of 1.7 molar is only speculative since most of the off-gas samples which these eight points represent showed rather high (25 to 35 percent) nitrogen due to air contamination and therefore may not be accurate.

D. Nitric Oxide Content of the Dry Off-Gas

Figure 5 shows the percent of nitric oxide in the off-gas on a nitrogen dioxide-free basis. The average nitric oxide content is nearly constant for acidic dissolver solutions, about 72 percent for extruded slugs and 82 percent for cast slugs. As the dissolver solution becomes neutral or acid-deficient the nitric oxide content decreases to an average of 50 percent at 1.6M acid-deficient for extruded slugs and 74 percent at 0.5M acid-deficient for cast slugs. This decrease appeared to begin at about 1.0M acid molarity for cast slugs and at neutrality for extruded slugs. Most of the off-gas samples taken after the dissolver solution reached 1.7M acid-deficiency showed rather high air contamination and the analyses are therefore questionable.

E. Nitrous Oxide Content of the Dry Off-Gas

Figure 6 shows the percent of nitrous oxide in the off-gas on a nitrogen dioxide-free basis. The average nitrous oxide content is nearly constant for acidic dissolver solutions, about 24 percent for extruded slugs and 16 percent for cast slugs. As the dissolver solution becomes neutral or acid-deficient the nitrous oxide content increases to an average of 28 percent at 1.6M acid-deficiency for extruded slugs and 23 percent at 0.4M acid-deficiency for cast slugs. This increase appeared to begin at about 1.0M acid molarity for cast slugs and at neutrality for extruded slugs.

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F. Nitrogen Dioxide Content of Dissolver Off-Gas

Figure 7 shows the moles of nitrogen dioxide per mole of dry gas for extruded slug dissolution. It is indicative of the nitrogen dioxide present in the off-gas at the dissolver before it is absorbed in water. It decreases from a maximum of approximately 1.1 moles of nitrogen dioxide per mole of dry gas at 3.2 molar acidity to 0.05 moles at 1 molar acid-deficiency. It drops sharply in the region of neutral acidity. The average nitrogen dioxide content was 0.57 moles per mole of dry gas. Estimates of the nitrogen dioxide generated during cast slug dissolution showed an average of 0.5 moles per mole of dry gas.

The original analysis of off-gas after the condenser showed that 0-2 percent nitrogen dioxide is present. Occasionally as much as 8 percent was encountered, especially in the early part of dissolution when the concentration was high in the dissolver.

G. General Off-Gas Composition Trends

Figures 8 and 9 show a summary of the various constituents in the dry off-gas for cast and extruded slug dissolutions, respectively. From Figure 8 it may be seen that as the dissolver solution approaches zero acid molarity in cast slug dissolution, the nitric oxide decreases. There is very little change in hydrogen. From Figure 9 it may be seen that as the dissolver solution becomes acid deficient during extruded slug dissolution nitric oxide decreases and both hydrogen and nitrous oxide increase.

Nitrogen dioxide is a predominate constituent of the off-gas in the dissolver early in the dissolution but decreases as the dissolver acid molarity decreases. In general, when the dissolver solution is strongly acid, the predominate off-gas constituent in the dissolver is nitrogen dioxide but when the dissolver solution is acid-deficient, the predominate constituent is nitric oxide.

There is some general agreement between off-gas compositions for the batch dissolutions reported herein and off-gas compositions obtained during recent continuous dissolutions of cast and extruded uranium-aluminum slugs.³

H. Acid Consumption

Acid consumptions calculated by both methods were in good agreement. The high value in Run 5 based on a material balance around the dissolver is due to a questionable low analysis for aluminum in the product (throughout this run, aluminum concentration was higher for dissolver solutions than for the product). The average acid consumptions for extruded and cast slugs were 4.0 (neglecting the high value in Run 5) and 4.1 moles of acid per mole of aluminum dissolved, respectively. These values compare favorably with the average for continuous dissolution which was 4.0 moles of acid per mole of aluminum dissolved.⁴ The acid consumption decreases as the dissolver solution becomes more acid-deficient. This is due to the increased production of hydrogen with its attendant low acid consumption.

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FIGURE 7
VARIATION OF NITROGEN DIOXIDE IN DISSOLVER OFF GAS
WITH DISSOLVER SOLUTION COMPOSITION

FIGURE 8

VARIATION OF DRY OFF GAS COMPOSITION WITH
DISSOLVER SOLUTION COMPOSITION FOR

CAST SLUG DISSOLUTION

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FIGURE 9

VARIATION OF DRY OFF GAS COMPOSITION WITH
DISSOLVER SOLUTION COMPOSITION FOR
EXTRUDED SLUG DISSOLUTION

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