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MEASUREMENT OF HAZARDOUS COMPONENTS OF DAREX PROCESS OFF-GAS

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ORNL-3022

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

CHEMICAL DEVELOPMENT SECTION B

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DATE ISSUED

APR 17 1961

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ABSTRACT

The hydrogen in the off-gas from batch Darex dissolutions of 304L stainless steel in refluxing nitric-hydrochloric acid mixtures where the hydrogen ion concentration was constant at 7 M (20 cc of acid per gram of stainless steel) increased from about 0.15 vol % in 2 M HCl to 2 vol % in 6 M HCl. In 2 and 3 M HCl the hydrogen concentration was maximum, 0.35-0.5 vol %, when 30-50% of the total dissolving time had elapsed. In 6 M HCl the hydrogen concentration remained in the 1.5-3.5 vol % range throughout the dissolution. The maximum nitrous oxide content of the off-gas increased from 0.7 to 10 vol % as the hydrochloric acid concentration was increased from 2 to 6 M. With a smaller volume of 5 M HNO_3-2 M HCl the hydrogen content of the off-gas decreased and the nitrous oxide content increased.

CONTENTS

1.0 INTRODUCTION

A series of laboratory experiments was performed to measure the amount of hydrogen and nitrous oxide evolved in Darex (1-5) dissolutions of stainless steel under various conditions that might occur in processing of power reactor fuels. The composition of the Darex off-gas is of major concern because of the explosive potential of some of the component gases, especially hydrogen and nitrous oxide (N_2O), which cannot be removed by scrubbing with caustic solution (6). The concentrations of these gases in the off-gas from the Darex pilot plant must be known fairly accurately so that a safe gas-handling system can be designed. Experiments were performed to determine the volume percent hydrogen and nitrous oxide in the off-gas from Darex dissolutions as a function of the total gas evolved throughout dissolution, the fraction of total dissolving time, the relative nitrate and chloride content of 7 M acid, and the fraction of the flowsheet volume of acid used.

Laboratory work was performed by D. M. Helton and E. R. Johns. The off-gases were analyzed by gas-chromatographic methods by A. D. Horton of the Analytical Chemistry Division.

2.0 RESULTS

2.1 Hydrogen in Batch Darex Off-gas

The hydrogen concentration of the off-gas from Darex dissolutions of 304L stainless steel increased from about 0.15 to 2 vol % as the chloride content of mixed nitric-hydrochloric acid (hydrogen ion concentration constant at 7 M) was increased from 2 to 6 M (Fig. 1a). The hydrogen volumes were measured experimentally, but the total volume of off-gas was calculated in each case by assuming that each mole of dissolved stainless steel produced 1.5 moles of gas. This assumption was used to permit graphic comparisons between the different acid concentrations, and was considered a close approximation of the actual off-gas volume only in the case of 5 M nitric acid—2 M hydrochloric acid, where previous observations (3) indicated evolution of nearly equal volumes of nitric oxide and nitrogen dioxide. Work done later (Sect. 2.4) indicated that more nitric oxide than nitrogen dioxide is evolved with this reagent but the nitric oxide to nitrogen dioxide ratio assumed does not affect the volume percent calculations greatly since the total volume of gas evolved per mole of dissolved stainless steel must fall in the range 1-3 moles, the limiting values being those calculated for pure nitric oxide or nitrogen dioxide, respectively. For example, the results of Table 1 (Sect. 2.4) indicate that each mole of dissolved stainless steel would produce 1.2-1.5 moles of gas. Volume percent hydrogen values read from Fig. 1 may be converted to millimoles of hydrogen per gram of stainless steel by multiplying by 26.8 millimoles, the assumed total gas evolution per gram of stainless steel dissolved. For example, the measured hydrogen values of 0.15 and 2 vol % correspond to 0.04 and 0.54 millimole of hydrogen gas per gram of stainless steel dissolved in 2 M hydrochloric acid—5 M nitric acid and 6 M hydrochloric acid—1 M nitric acid, respectively. These results indicate that careful

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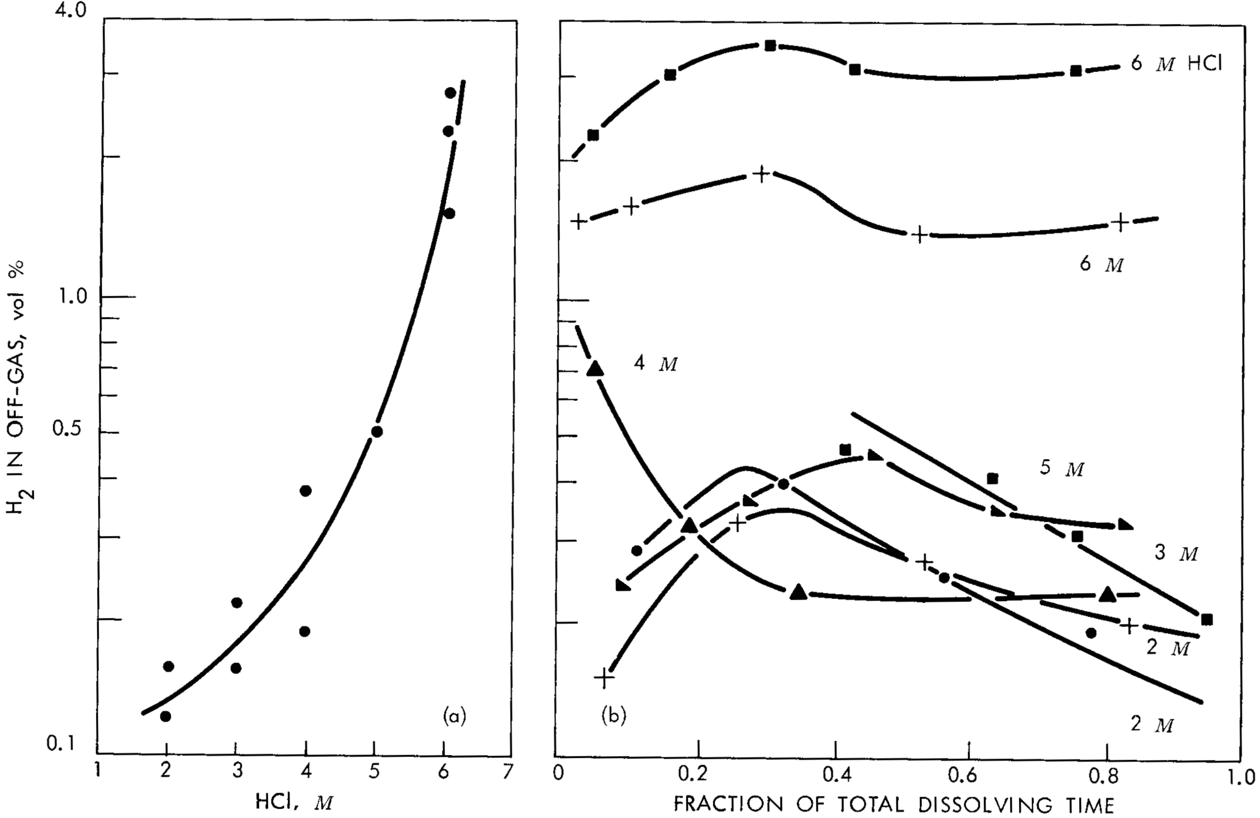

Fig. 1. Hydrogen in Darex off-gas on dissolution of stainless steel as a function of (a) HCl concentration, and (b) dissolving time. Reflux temperature; samples, 2-3 g of 304L stainless steel (40 mils thick); 20 cc of reagent per gram of stainless steel; total HCl + HNO_3, 7 *M*; total dissolution time, 5 min (2 *M* HCl) to 22 min (6 *M* HCl).

control of reagent concentration may be necessary to ensure very low hydrogen concentration in the Darex off-gas. If it should be necessary to increase the chloride concentration in the dissolvent to prevent passivation (5), special provisions may have to be made for handling the increased hydrogen concentration in the off-gas.

In experiments in which the volume percent hydrogen was determined as a function of the fraction of total dissolution time, the hydrogen concentration of the off-gas did not vary greatly during the dissolution. At hydrochloric acid concentrations less than 3 M in mixed 7 M nitric-hydrochloric acid, the hydrogen concentration was maximum when between 30 and 50% of the total dissolution time had elapsed (Fig. 1b). Maximum hydrogen concentrations were about three times the average for the same dissolvent (Fig. 1a). With 4 M hydrochloric acid, the hydrogen concentration was maximum when dissolution started, and with 6 M hydrochloric acid the hydrogen concentration remained nearly constant at approximately 2 vol % throughout dissolution. Close reproducibility was not achieved in the 6 M hydrochloric acid experiments, where nearly twice as high a hydrogen concentration was found in the off-gas in the first experiment as in the second. The reason for this lack of close reproducibility is not known, but results in 6 M hydrochloric acid—1 M nitric acid were in close enough agreement to satisfactorily define the shape of the curve in Fig. 1a.

These hydrogen concentrations are encouragingly low in comparison to those in mercury-catalyzed dissolution of uranium-aluminum alloys, where the hydrogen concentration was 2-4 vol % throughout dissolution (7) under process flowsheet acidity (4.5 to 0 M nitric acid) but increased to as much as 23% when the acidity decreased to 1.7 M acid deficiency.

2.2 Nitrous Oxide in Batch Darex Off-gas

The nitrous oxide concentration of the Darex off-gas was about twice the hydrogen concentration when the dissolvent was 5 M nitric acid—2 M hydrochloric acid and increased more rapidly than the hydrogen as the amount of chloride in mixed 7 M nitric-hydrochloric acid was increased (Fig. 2). Nitrous oxide concentrations were maximum after approximately 30% of the total dissolution time had elapsed in all runs. These maximums were about 0.7, 5.5, and 10 vol % in 2 M hydrochloric acid, 3 M hydrochloric acid, and 4-6 M hydrochloric acid, respectively. In 2 M hydrochloric acid the nitrous oxide concentrations were below detectable limits (about 0.1 vol %) after 50% of the total dissolution time had elapsed. These results indicate that careful control of reagent concentration is necessary to prevent high concentrations of nitrous oxide, as well as hydrogen, in the Darex off-gas.

2.3 Effect of Decreasing the Amount of Acid Used

In all runs discussed above, the flowsheet (Fig. 6, Appendix) volume of acid was used. Experiments were made to determine if the concentration of hydrogen or nitrous oxide in the off-gas was increased by using less than the flowsheet volumes of acid.

With both 5 M nitric acid—2 M hydrochloric acid (Fig. 3a) and 3 M nitric acid—4 M hydrochloric acid (Fig. 3b), the hydrogen concentration of the off-gas decreased when

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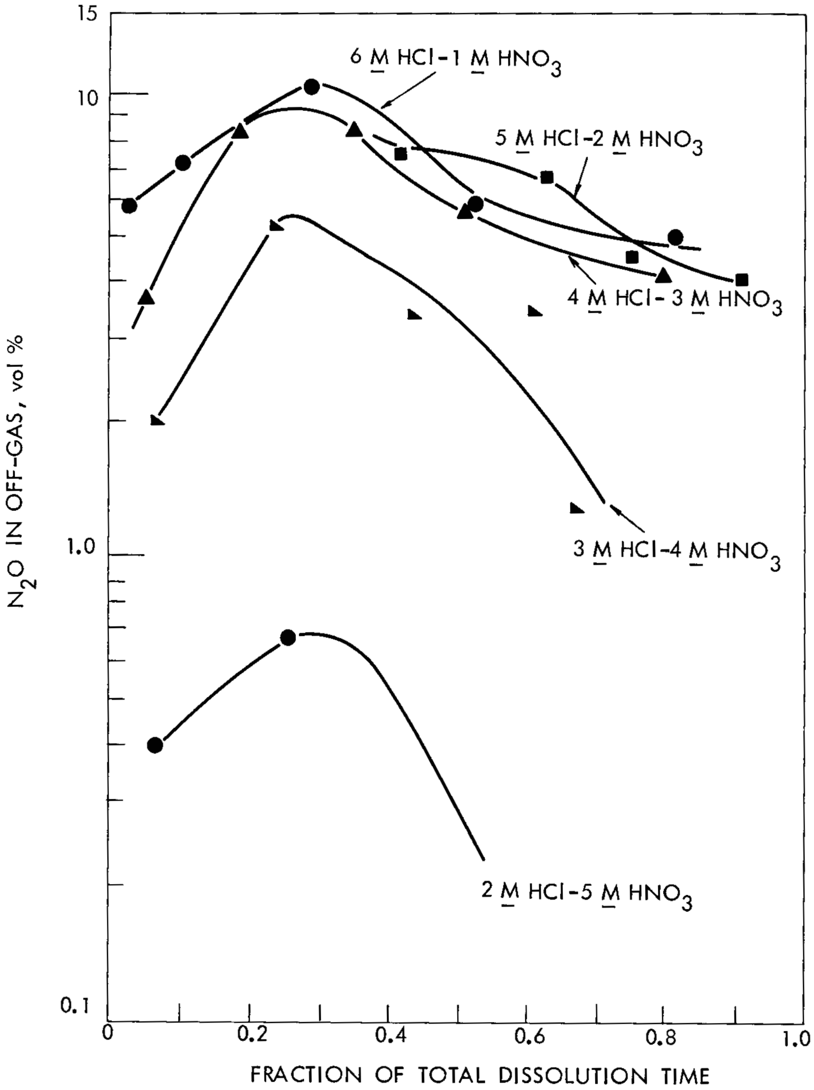

Fig. 2. Nitrous oxide in batch Darex off-gas as a function of stainless steel dissolving time. Reflux temperature; samples, 2-3 g of 304 L stainless steel (40 mils thick); 20 cc of reagent/g of stainless steel; total HCl + HNO_3 7 *M*; total dissolution time, 5 min (2 *M* HCl) to 22 min (6 *M* HCl).

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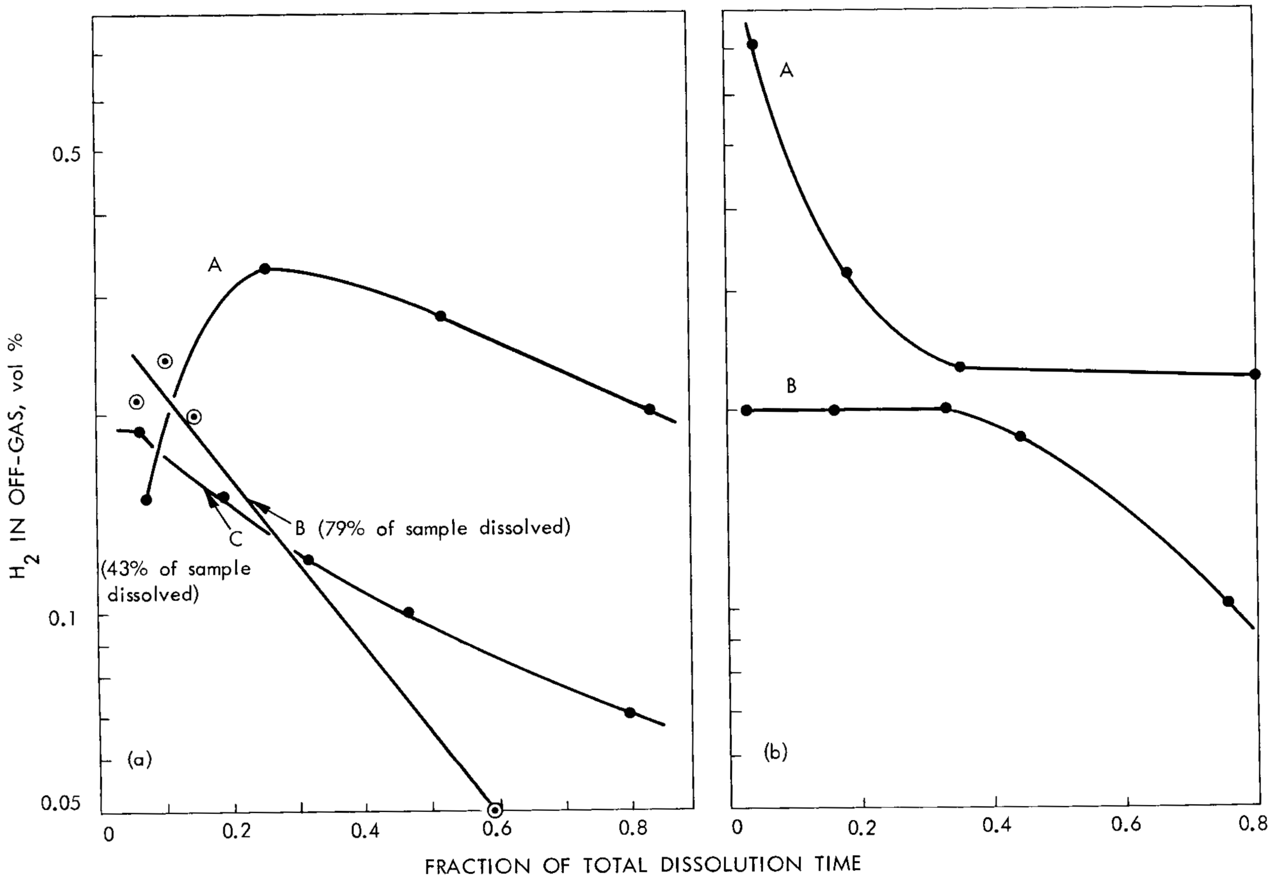

Fig. 3. Hydrogen in batch Darex off-gas as a function of volume of (a) 5 *M* HNO_3 - 2 *M* HCl and (b) 3 *M* HNO_3 - 4 *M* HCl used. Reflux temperature. Curves A, flowsheet volume of reagent (20 ml/g of stainless steel); curves B, half flowsheet volume; curve C, quarter flowsheet volume.

the volume of acid was decreased. In 5 M nitric acid—2 M hydrochloric acid, the maximum hydrogen concentration in the off-gas was about 0.3, 0.25, and 0.2 vol % with the flowsheet volume, half-volume, and quarter-volume of acid, respectively. The amounts of type 304 stainless steel dissolved were 100, 79, and 43% (50, 79, and 86 g/liter) respectively, and the total amounts of hydrogen evolved were equivalent to 0.12, 0.09, and 0.07 vol % of the off-gas, based on the assumption that a total of 1.5 moles of off-gas was produced per mole of dissolved stainless steel. In 3 M nitric acid—4 M hydrochloric acid, the maximum hydrogen concentrations of the off-gas were about 0.7 and 0.2 vol % at the flowsheet volume and half-volume, respectively. All the stainless steel dissolved in both the latter runs. The total amounts of hydrogen evolved were equivalent to 0.19 and 0.17 vol % of the off-gas, respectively.

The nitrous oxide concentration of the off-gas gave a less consistent pattern, increasing rapidly from a maximum of 0.7 to 7 vol % as the volume of 5 M nitric acid—2 M hydrochloric acid was decreased from the flowsheet volume to one-quarter the flowsheet volume (Fig. 4a), and decreasing from a maximum of 10 to 3.4 vol % as the volume of 3 M nitric acid—4 M hydrochloric acid was decreased from the flowsheet volume to half the flowsheet volume (Fig. 4b).

There appears to be little hazard associated with using too small a quantity of dissolvent, regardless of the relative nitric-hydrochloric acid concentrations, with regard to evolution of hydrogen. However, in the currently favored dissolvent, 5 M nitric acid—2 M hydrochloric acid (5), nitrous oxide evolution increases rapidly as the volume of dissolvent is decreased. If a dissolvent containing relatively less nitric and more hydrochloric acid is used, decreasing the volume of dissolvent used would lead to a smaller increase (or even a decrease) in the nitrous oxide evolution. These observations also indicate that, if a continuous dissolution process should be used, the concentration of nitrous oxide in the off-gas would be highly dependent on the flow rate of the dissolvent and the extent of loading of the dissolvent with dissolution products. In all cases, the hydrogen concentration of the off-gas should be relatively low.

2.4 Complete Analysis of the Darex Off-gas

If mixed with a reducing gas such as hydrogen, chlorine and all the oxides of nitrogen found in the Darex off-gas can react explosively under certain conditions (6,8). It had been thought previously (3) that the Darex off-gas would contain mostly nitric oxide and nitrogen dioxide in nearly equal amounts, but analysis of the off-gas from the dissolution of type 304 stainless steel in refluxing 5 M nitric acid—2 M hydrochloric acid (flowsheet volumes) with air excluded showed 65% nitric oxide and a significant amount of nitrogen (4%) and probably nitrosyl chloride (Table 1).

The gas-chromatographic analytical technique used did not permit either very accurate analyses for nitrogen dioxide or nitrosyl chloride or separation of these two gases. The sum of the nitrogen dioxide and nitrosyl chloride concentrations was 15 ±10%, indicating a nitrogen dioxide evolution less than one-third that of nitric oxide. For efficient removal of the oxides of nitrogen it will be necessary to add air or oxygen

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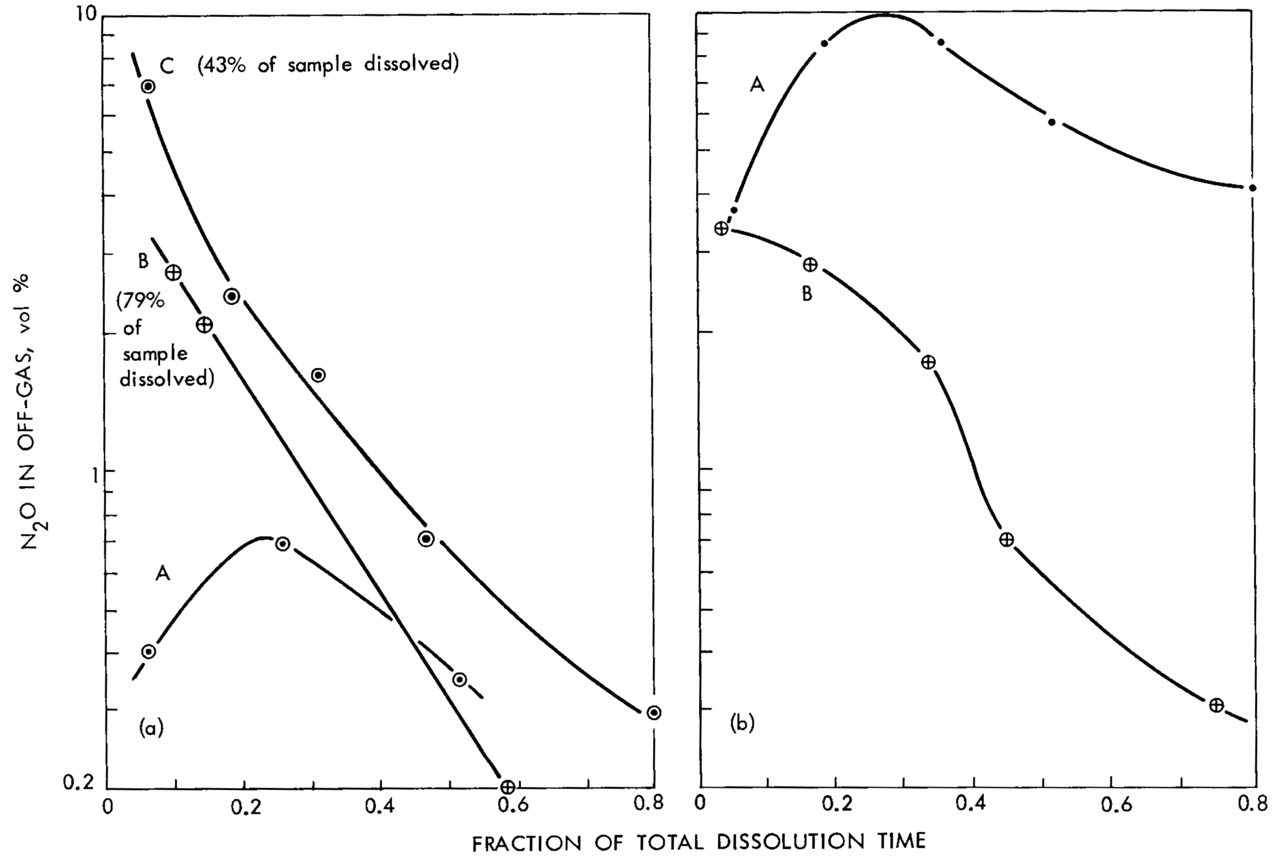

Fig. 4. Nitrous oxide in batch Darex off-gas as a function of volume of (a) 5 *M* HNO_3 - 2 *M* HCl and (b) 3 *M* HNO_3 - 4 *M* HCl used. Reflux temperature. Curves A, flowsheet volume of reagent (20 ml/g of stainless steel); curves B, half flowsheet volume; curve C, quarter flowsheet volume.

before the off-gas passes through the caustic scrubber, since the nitric oxide has to be converted to nitrogen dioxide or sesquioxide for efficient removal by caustic solution.

Table 1. Analysis of Darex Off-gas

Sample wt: 4 g
Dissolvent: 5 M HNO_3--2 M HCl (80 ml)
Temperature: reflux

Component	Amount, vol %
H_2	0.1
NO	65.4
N_2	4.3
NO_2 + NOCl	15
Cl_2	0.5
N_2O	0.4
Other	14

3.0 EXPERIMENTAL PROCEDURE

Twenty milliliters of mixed 7 M nitric-hydrochloric acid, containing 2-6 M hydrochloric acid, per gram of type 304L stainless steel in a weighed sample was placed in the dissolver (Fig. 5). This is the volume recommended in the Darex flowsheet (Fig. 6). The apparatus, including the manifold and traps, was swept with a large volume of argon to remove air. The acid was brought to the boiling point and the 304L stainless steel sample was introduced. Between 200 and 400 ml of off-gas was allowed to pass through the first trap (26 ml volume) and into the off-gas collector before the next trap was switched into the off-gas line. This procedure was repeated until five samples were collected in the traps, the last trap being left in line until dissolution was complete. After dissolution, the dissolver, condenser, and gas-sampling manifold were swept with argon, which was collected in the calibrated gas collector. The gas in each trap plus that in the gas collector was analyzed by gas-chromatographic techniques for hydrogen and nitrous oxide. The traps were occasionally analyzed for argon, and contained as much as 2% argon. Analyses of the gas in the traps provided average values of the hydrogen and nitrous oxide concentrations during the time a particular trap was in the off-gas line. The sum of the values for each trap and the gas collector gave the total amount of hydrogen produced. It was not

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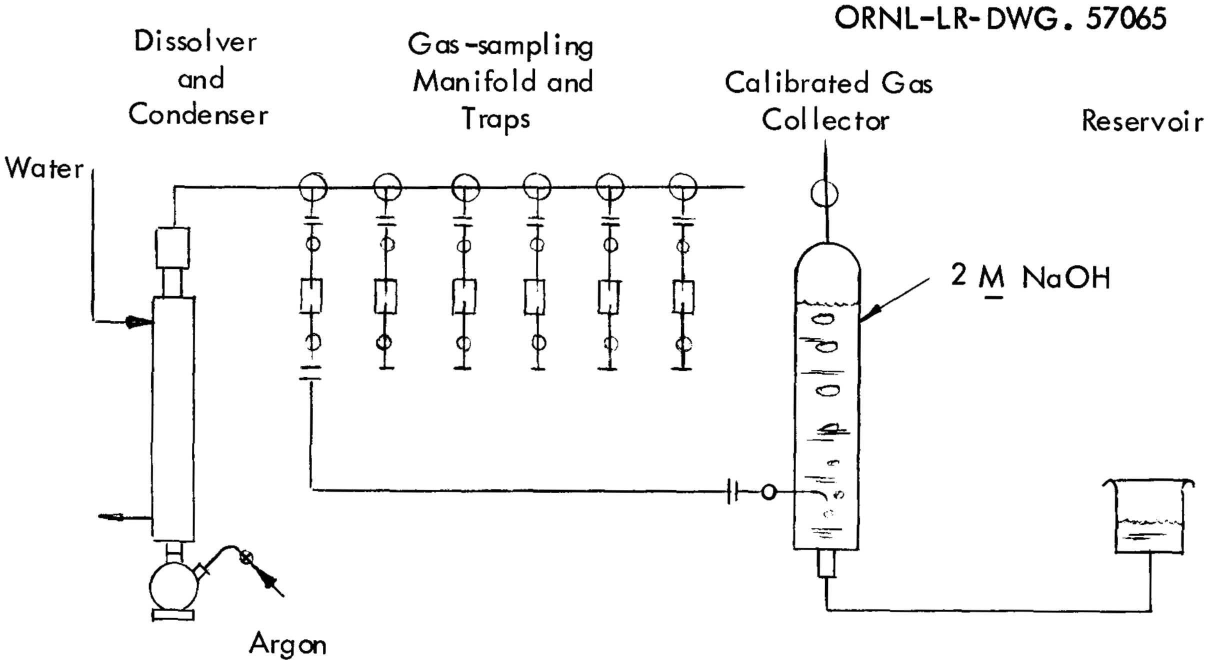

Fig. 5. Darex off-gas sampling apparatus.

possible by these techniques to accurately determine the total amount of nitrous oxide produced, since nitrous oxide is slightly soluble in the 2 M sodium hydroxide used in the gas collector. The reabsorption of a small amount of nitrogen dioxide and sesquioxide in the water condensed from the refluxing dissolvent by the short (8-in.) water-cooled condenser could not be avoided.

These techniques permitted obtaining pure samples of off-gas uncontaminated by any sweep gas other than a small amount of argon or contacting any liquids other than water in the condenser, and without changing the pressure from 1 atm or otherwise disturbing the reactions that occur during dissolution.

In the gas-chromatographic analyses hydrogen was determined by the use of a molecular sieve (Linde 5A) packing at 25°C with argon carrier gas. The minimum detectable concentration was about 0.02 vol % and the estimated accuracy at a concentration of 0.05 vol % was ±5%. Nitrous oxide was determined by use of silica gel packing at 80°C with helium carrier gas. The minimum detectable concentration was about 0.1 vol % and the estimated accuracy at a concentration of 0.2 vol % was ±5%.

4.0 REFERENCES

1. W. E. Clark, M. L. Hyman, A. H. Kibbey, F. G. Kitts, and J. J. Perona, "Stainless Steel Fuel Processing (Darex)," in AEC Research and Development Report, ORNL-2265, pp. 28-38 (March 1957).

2. J. E. Savolainen and R. E. Blanco, Chem. Eng. Prog., 53: 78F (1957).

3. J. J. Shefcik and A. M. Platt, "Preliminary Darex Flowsheet," HW-58600 (December 1958).

4. B. C. Finney and F. G. Kitts, "Darex Processing of APPR Fuel: Effect of Acidity and Gas Sparging on Rate of Chloride Removal from Dissolver Product During Refluxing," ORNL-2753 (July 1959).

5. L. M. Ferris and A. H. Kibbey, "Sulfex-Thorex and Darex-Thorex Processes for the Dissolution of Consolidated Edison Power Reactor Fuel: Laboratory Development," ORNL-2934 (Oct. 26, 1960).

6. J. M. Holmes, "Dissolver Off-gas and Rare Gas Plant Hazards," ORNL-CF-59-11-133 (November 1959).

7. M. D. Martin and J. A. Buckham, "The Composition of Off-gas from Batch Uranium-Aluminum Dissolution," IDO-14361 (December 1955).

8. K. S. Warren, "A Survey of Potential Vapor Phase Explosions in Darex and Sulfex Processes," ORNL-2937 (Dec. 27, 1960).

5.0 APPENDIX

A Darex flowsheet is shown in Fig. 6.

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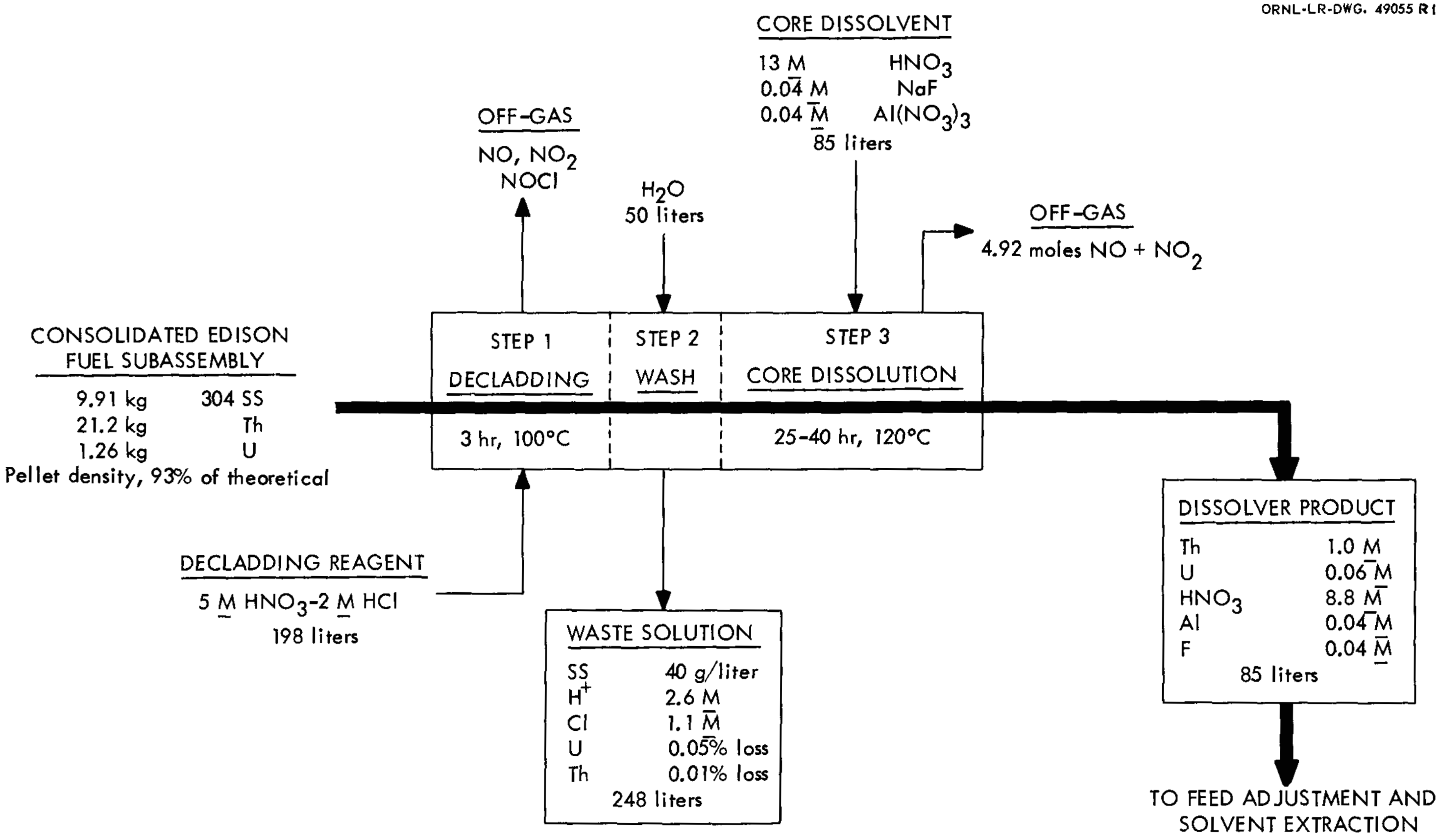

Fig. 6. Decladding and dissolution of Consolidated Edison reactor fuel by the Darex-Thorex process.[5]

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