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CHEMICAL EFFECTS IN MICROMOLAR NITRIC ACID FROM GAMMA RADIATION AND HEATED ALUMINUM

A LABORATORY STUDY WITH APPLICATION TO SRP REACTORS

E. W. BAUMANN

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A LABORATORY STUDY WITH APPLICATION TO SRP REACTORS

by

Elizabeth W. Baumann

Approved by

R. L. Folger, Research Manager
Analytical Chemistry

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E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

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ABSTRACT

The effects of gamma radiation and heated aluminum on 20μM HNO_3 were studied to determine the causes of occasional pD instability in the D_2O moderator of the Savannah River reactors. At doses of 5×10^6 rad, 70% of the initial concentration of the nitric acid (helium-saturated) was maintained. When hydrogen or organic reducing agents were present, all the nitric acid was lost at doses below 2×10^5 rad. Freshly cleaned aluminum at 100°C, contacted with stirred air-free solutions at 75°C, caused a loss of >80% of the H^+ and 50% of the NO_3^- in one hour. Treating the aluminum with lithium silicate solution reduced these acidity losses to 30%.

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INTRODUCTION

In the nuclear reactors of the Savannah River Plant (SRP), nitric acid is added to the D_2O coolant-moderator to maintain the pD of 5 required for minimum corrosion of aluminum fuel cladding.[1] Aluminum corrosion must be effectively controlled to prevent excessive reduction of heat transfer from fuel tubes and penetration of the cladding.

Decomposition of the nitric acid, or loss of acidity, has been encountered frequently during the initial ascension to power and, less frequently during full-power operation. Although addition of oxygen to the moderator generally will stabilize the nitrate, excess oxygen in the system may aggravate corrosion of other parts of the reactor.

Better understanding of the phenomena involved in these acidity losses was needed for more consistent control, but little information was available. Existing data on radiolytic and chemical reactions were used by Jenks[2] to predict conditions required in the High Flux Isotope Reactor to maintain 10μM H^+ near the fuel element surfaces. To provide reasonable assurance of stability against radiolysis, a concentration of 10^{-3}M O_2 was estimated to be required. A test in the Engineering Test Reactor (presumably with no additives) showed establishment of a steady state in the bulk solution, with about 10% of the 10μM HNO_3 converted to HNO_2.[2] Studies of radiolysis of nitrates in neutral and alkaline solutions at higher concentrations[3] suggest the probable interactions between reduction products of nitrate and the radiolysis products of water.

In-reactor experiments are difficult to perform and control, but many aspects of the chemical conditions in the reactor can be reproduced in the laboratory. Therefore the separate effects of gamma radiation and heated aluminum on 20μM HNO_3 were studied in the laboratory under chemical conditions that simulate those in the Savannah River reactors.

SUMMARY

The separate chemical effects of gamma radiation and heated aluminum on oxygen-free 20μM HNO_3 were determined in laboratory experiments intended to elucidate the causes of occasional periods of pD instability in the D_2O moderator of the Savannah River reactors.

Closed static systems were irradiated by ^{60}Co to a maximum dose of 5×10^6 rad. In helium-saturated solution, a steady state was attained in which about 70% of the initial nitric acid was maintained. In the presence of hydrogen or easily oxidizable organics, all nitric acid was lost at doses below 2×10^5 rad.

The surface reaction was studied by contacting stirred, air-free solutions at ∿75°C with aluminum heated to ∿100°C (thermal conditions close to high-flux reactor operating conditions).[4] Freshly cleaned aluminum caused a loss of more than 80% of the acidity and about 50% of the nitrate within one hour. Acidity losses were reduced to 30% when the cleaned aluminum surface had been treated with lithium silicate before exposure to the simulated operating conditions.

It was concluded that loss of nitric acid in the reactor is propagated by radiolysis combined with low acidity and/or reducing agents in the system such as organics or deuterium released by aluminum corrosion.

DISCUSSION

BACKGROUND

Description of Reactor Conditions

The reactor system consists of an array of aluminum-clad fuel elements and other components in a stainless steel tank. The heat produced within the fuel elements is removed by heavy water recirculated through heat exchangers. A small bypass stream flows through a filter-deionizer combination to control the heavy water purity. A gas space above the heavy water contains primarily helium; a catalytic recombiner removes the deuterium gas formed by radiolysis and corrosion, and a slight excess of oxygen is maintained. The water is kept at a nominal pD of 5 ($10\mu M\ D^+$) by injection of nitric acid from time to time. The water is always below its normal boiling point.

The chemical composition of the moderator is routinely monitored by in-line electrometric pD and electrical conductivity measurements and by laboratory determinations of pD and NO_3^- on samples withdrawn from the system. These routine analyses permit the detection of changes in solute concentrations in the moderator, and assure that acceptable conditions are maintained during operation.

As part of the present program, more precise determinations of pD and NO_3^- were made on samples taken from the reactor at specified times during the startup process for several cycles. These analyses revealed that for some new fuel charges the acidity was almost depleted ($D^+ << NO_3^-$) before nuclear startup. During one observation, a period of pD instability occurred after criticality, during which no nitrate or nitrite was detected in the moderator. These studies were useful in confirming the interpretation of the laboratory experiments described below.

Chemistry of the Nitrogen Compounds

Nitric acid, the acidifier used because it is compatible with reactor materials, is the source of a multitude of reduction

products; compounds of every nitrogen valence state from +5 to -3 are possible:

+5: N_2O_5, HNO_3
+4: NO_2
+3: N_2O_3, HNO_2
+2: NO
+1: N_2O, $H_2N_2O_2$
0: N_2
-1: NH_2OH
-2: NH_2NH_2
-3: NH_3, NH_4OH

The acid or base anhydrides will be retained in the aqueous phase of the reactor, but other gaseous compounds (NO, N_2O, N_2) could escape from the solution, especially at higher temperatures or with the evolution of gases produced by radiolysis or corrosion.

The interactions of these reduction products depend upon their relative concentrations and the acidity of the system. Two reactions are:

- Reaction of low concentrations of NO_2 with water:

$$2\ NO_2 + H_2O \rightleftarrows HNO_2 + H^+ + NO_3^- \qquad k = 10^5 \qquad (1)$$

  Thus, one-electron reduction of NO_3^- to NO_2 would be unlikely to result in nitrogen losses via escape of gaseous NO_2 because the relative equilibrium concentration of NO_2 in these dilute solutions is very small.

- Decomposition of nitrous acid:

$$3\ HNO_2 \rightleftarrows H^+ + NO_3^- + 2\ NO + H_2O \qquad k = 30 \qquad (2)$$

  This equilibrium is comparatively slow in cold dilute solutions and is rather easily reversed; at higher temperatures, evolution of NO comprises a possible escape route for nitrogen compounds.

In dilute solutions, the radiolysis of nitric acid can be described simply in terms of reactions with the products of the radiolysis of water, particularly:

H, H_2 (reducing agents)

OH, H_2O_2 (oxidizing agents)

The initial reaction would be reduction of nitric acid by the reducing agents

$$H + NO_3^- \rightarrow OH^- + NO_2 \quad (3)$$

followed by disproportionation of the NO_2 according to Equation (1). As radiolysis products build up, secondary reactions involving these products can occur. In acid solution the HNO_2 produced is oxidized back to HNO_3 by peroxide and OH.

$$NO_2^- + 2\ OH \rightarrow NO_3^- + H_2O \quad (4)$$

The presence of oxidizing or reducing impurities in the system would be expected to upset the steady state between the nitrogen compounds and the water radiolysis products. Oxidizable compounds such as organic material or hydrogen (e.g., from aluminum corrosion) would deplete oxidizing agents, and favor continuing reduction with loss of nitrogen compounds from the system. Excess oxygen or peroxide would result in a net oxidizing atmosphere, with subsequent stabilization of nitric acid.

The acidity of the system, which is the primary concern, will be only slightly affected if reduction proceeds to nitrous acid. Although nitrous acid is a weak acid, the fraction dissociated at reactor concentrations of 10μM is greater than 75%.

GAMMA RADIOLYSIS

Experimental

The apparatus and experimental procedures were designed to obtain sets of nine identical, oxygen-free solutions of 10 to 20μM HNO_3, free from impurities that would interfere with the radiolytic process. Two or three solutions of each set were kept as unirradiated controls, and the others were irradiated in duplicate to three different doses by ^{60}Co. All were irradiated in "Pyrex"* glass tubes with ground glass caps. No pressure buildup or air inleakage was detected in the irradiated tubes.

The apparatus for preparing sample sets is shown in Figure 1. Glassware was cleaned from time to time with chromic acid cleaning solution, rinsed thoroughly, and air-dried. Where essential to the integrity of the system, "Kel-F"** stopcock grease was used on the lower half of the ground glass joints. Delivery tubes were constructed so that liquid did not contact the joint. The system was entirely of glass, except for "Excelon"*** tubing that connected the helium cylinder to the molecular sieve trap.

* Registered tradename of Corning Glassware.
** Registered tradename of Minnesota Mining & Mfg. Co.
*** Registered tradename of Armstrong Cork Co.

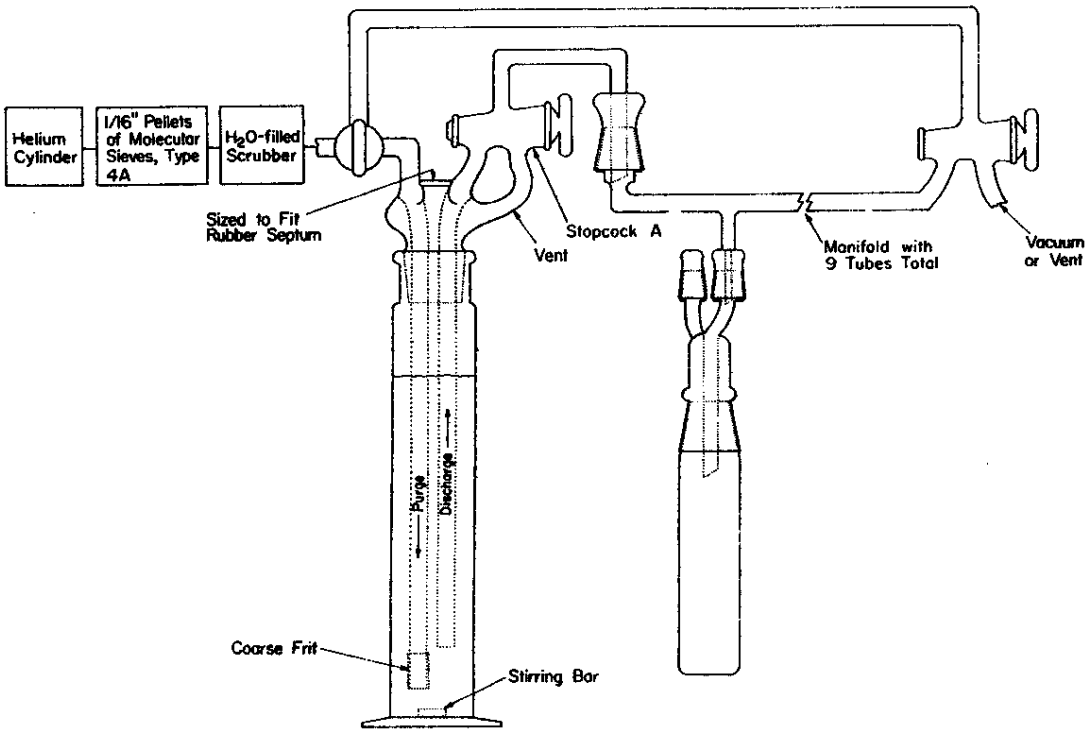

FIG. 1 APPARATUS FOR PREPARATION OF SOLUTIONS FOR IRRADIATION

Solutions of 10 to 20μM HNO_3 were prepared by dilution of 0.01M HNO_3 in the specially prepared water described in the Appendix. About 200 ml of solution was bubbled with helium in the main container with stirring for 30 to 60 minutes. By this treatment, the dissolved oxygen was reduced to less than 3μM, as determined by Winkler tests, described in the Appendix.

The empty sample tubes were evacuated and flushed with helium four to eight times (stopcock A closed) to remove air prior to filling them.

Then, with stopcock A open, solution was forced into each tube in turn by helium pressure. Each tube was removed from the manifold in a stream of helium and closed at once with ground glass caps that had been flushed with helium.

The tubes were irradiated within a cylindrical ^{60}Co source at a dose rate of 10^6 rad/hr. The irradiated solutions were analyzed for H^+, NO_3^-, NO_2^-, and H_2O_2 by methods described in the Appendix.

Results

Figures 2 and 3 give the results of the irradiation tests. H^+ and NO_3^- were determined in the solutions irradiated in duplicate. The data points are average concentrations and the vertical lines indicate the range of the duplicate analyses. Nitrate concentration includes nitrite, which was found by intermittent determinations to be less than 10% of the total. The molar concentration of H_2O_2 was less than 10% of the original nitrate. Peroxide concentration did not increase with radiation dose, nor did it vary with time (>15 minutes) after removal from the radiation field.

Figure 2 shows that a steady state is established in helium-saturated, triply distilled water after an early loss of about 30% HNO_3. No explanation is offered for the apparent rise in hydrogen ion concentration with irradiation dose; the free acidity of this dilute unbuffered solution is easily altered.

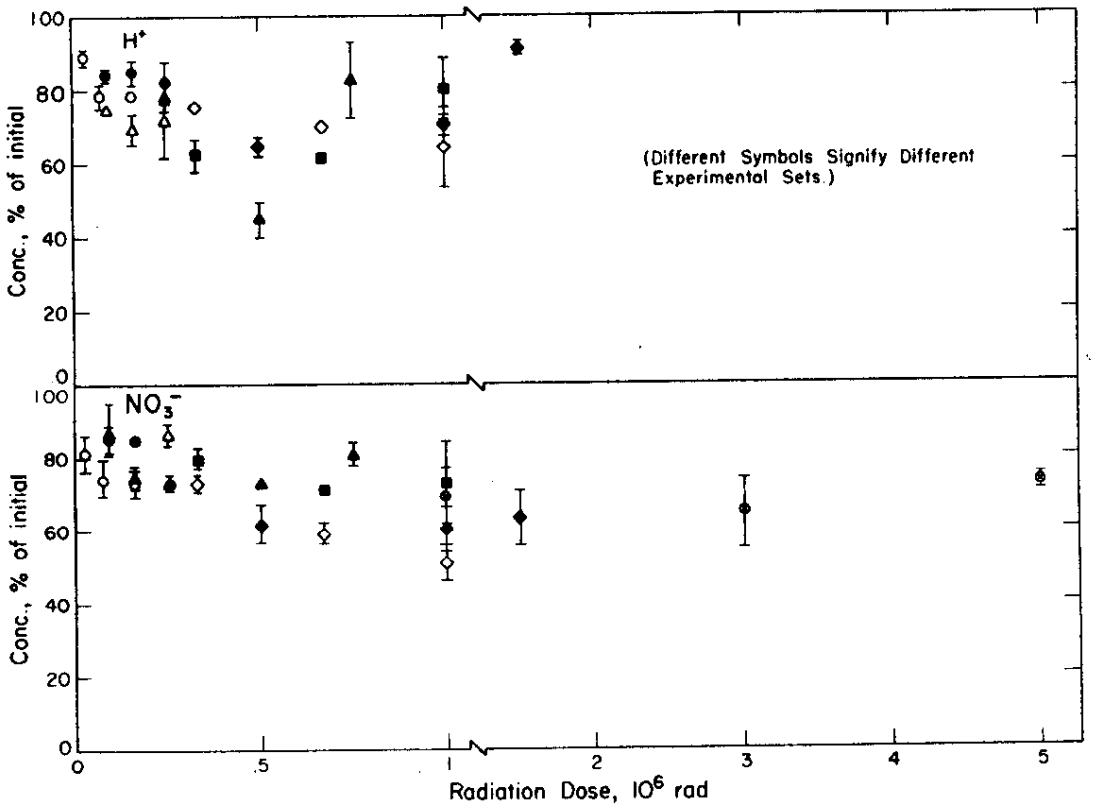

FIG. 2 EFFECT OF GAMMA RADIATION ON H^+ AND NO_3^- IN ~15μM HNO_3 IN He-SATURATED TRIPLY DISTILLED WATER

Figure 3 shows similar results with helium-saturated, deionized water from a seasoned resin column of "Amberlite"* MB-1. Water from a column of new resin caused immediate loss of all nitrate and hydrogen ion. The effluent from the seasoned column apparently contains few easily oxidizable organics, as indicated by the Fricke dosimeter tests mentioned in the Appendix.

Figure 3 also shows that in triply distilled water the presence of hydrogen, reducing agent that can scavenge OH radicals and prevent the back-reaction [Equation (4)], causes rapid and complete loss of nitric acid on irradiation.

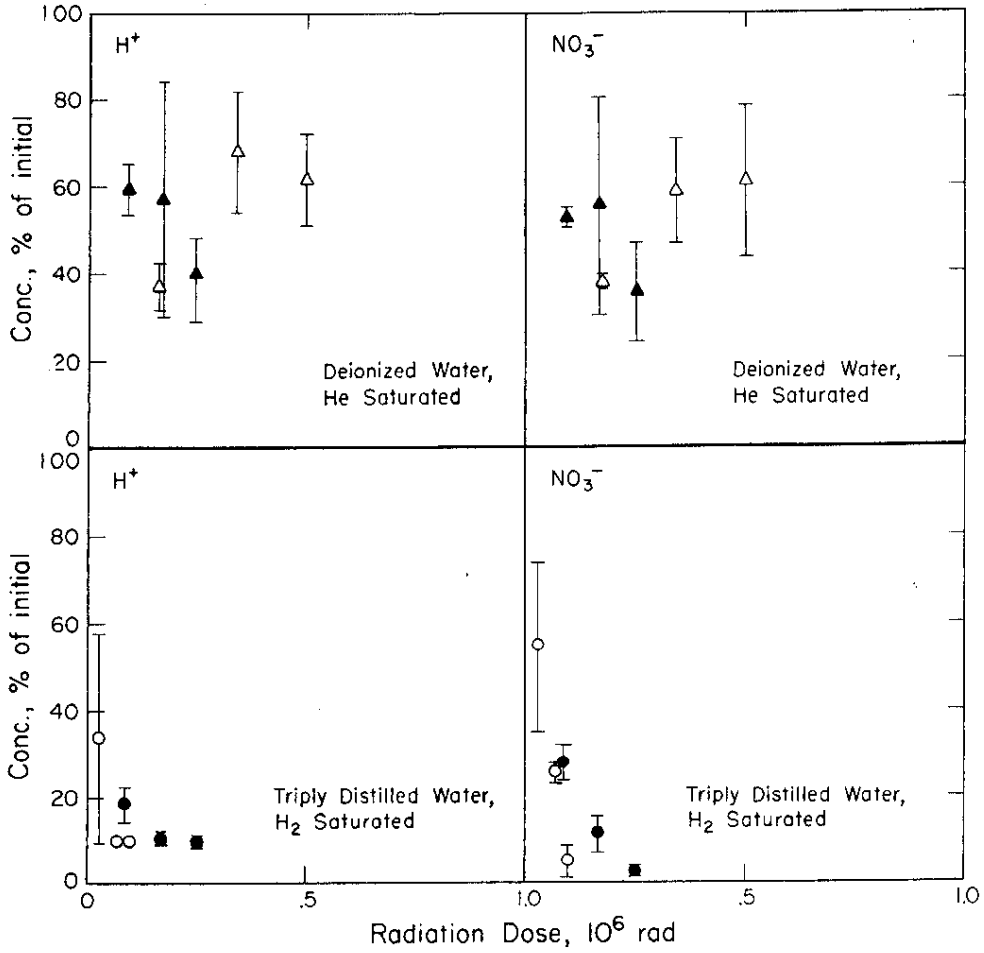

FIG. 3 EFFECT OF GAMMA RADIATION ON H^+ AND NO_3^- IN ~15μM HNO_3

* Registered tradename of Rohm and Haas Co.

HEATED ALUMINUM

Experimental

Apparatus and Procedure. The apparatus shown in Figure 4 was designed to heat an aluminum sheath from within (representing a fuel element in the reactor) in a stirred air-free solution (representing reactor coolant) to attain a steady-state solution temperature below boiling. The relative temperatures of the solution and the aluminum were adjusted by the flow of cooling water through the jacket of the vessel. The temperature of the aluminum was determined by a chromel-alumel thermocouple in the aluminum wall, and a thermometer in the solution determined the solution temperature.

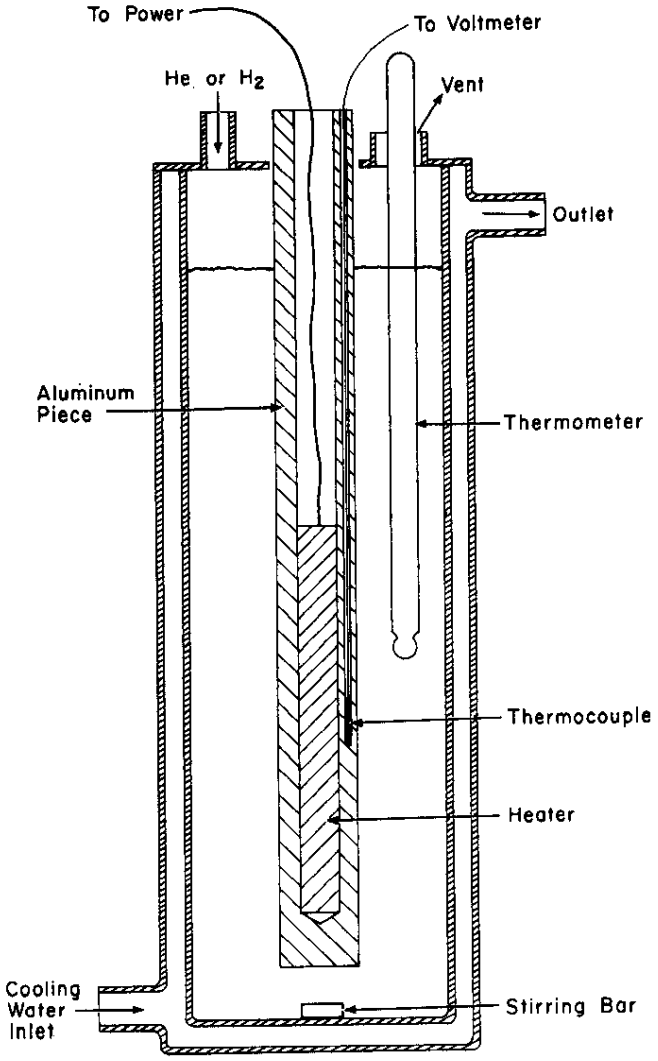

FIG. 4 APPARATUS FOR EXPERIMENTS WITH HEATED ALUMINUM

A final purge of the solution with helium was made in the vessel in the absence of the aluminum piece. Then, with helium flowing over the liquid surface, the aluminum sheath was inserted and heated at once. Either the helium flow was continued or hydrogen was slowly bubbled through the solution. The 4-in.-long, 525-watt resistance heater within the sheath was run at full power. Buildup of gas bubbles on the sheath was minimized by vigorously stirring the solution with a magnetic stirring bar. At intervals, ~10 ml solution was withdrawn by pipet for determination of H^+ and NO_3^-. Total volume was ~500 ml.

Preparation of Solutions. Solutions were prepared in deionized or triply distilled water that had been previously bubbled with helium to remove dissolved gases. Stock solutions of 0.01M nitric acid were prepared from reagent-grade nitric acid. Stock solutions containing mixtures of HNO_2 and HNO_3 were prepared as needed by dissolving the NO_2 evolved from thermal decomposition of uranyl nitrate. The NO_2 disproportionates in solution to form HNO_2 and HNO_3 [Equation (1)]; only a negligible fraction remains as NO_2 at these low concentrations. The respective concentrations of HNO_2 and HNO_3 were determined colorimetrically after final dilution to a total concentration of about 20μM.

Preparation of Aluminum. The aluminum test pieces were fabricated from 7/8-inch-diameter rods of type 1100 aluminum, as shown in Figure 4. Surface characteristics were established by a cleaning treatment or by the cleaning treatment plus a silicate treatment. These treatments are the same as procedures used to prepare fuel elements for reactor irradiation.[5]

- Cleaning Treatment

  1. Immerse tube 3 minutes at 60-70°C in caustic bath (23 g "Oakite"* per liter), raising and lowering at least once.
  2. Immerse in cold water, raise and lower twice; rinse in stream of water.
  3. Immerse 3 minutes in 64% HNO_3 at 80-90°C, raising and lowering at least twice, after the first 1-1/2 minutes.
  4. Dip twice in cold water.
  5. Immerse one minute in 90-100°C water; raise and lower twice.
  6. Air dry and store in air.

* Registered tradename of Oakite Prod., Inc.

- Silicate Treatment

  1. Immerse tube in "Ludox"* AS (ammonia stabilized; 95 cc "Ludox" per liter) for 5 minutes at room temperature.

  2. Drain 30 seconds.

  3. Dip twice in cold water.

  4. Drain 30 seconds.

  5. Immerse in "Lithsil"* (4.4 ml "Lithsil"-4 per liter); leave for 1 hour at 95 ±5°C.

  6. Rinse, drain, and air dry the tube; store in air.

Results

The tests described by Figure 5 were combinations of the following conditions:

- Aluminum surface freshly cleaned or used in one or more tests.
- Solution of HNO_2 or NO_2 (a mixture of HNO_2 and HNO_3).
- Helium blanket only or helium blanket with hydrogen bubbled through the solution.

The freshly cleaned aluminum surfaces were notably more reactive, and, except for Figure 5e, information obtained with used surfaces is not included. Greater loss of H^+ than anions indicates that acidity was lost by neutralization. Reaction rate decreased after 30 minutes, probably because a protective film of aluminum oxide was formed.

Loss of nitrogen anions with fresh aluminum increased when the system was purged with hydrogen (Figures 5c and 5d). This may have been caused by removal of the gaseous NO_2 reduction product by the purge, rather than by chemical action of the hydrogen purge gas. The experiment was not repeated with helium to verify this explanation. The presence of HNO_2 in the system also enhanced nitrogen anion losses (Figures 5b and 5d). Only traces of NO_2^- were detected in the HNO_3 systems by spot checks during the experiments.

* Registered tradename of Du Pont.

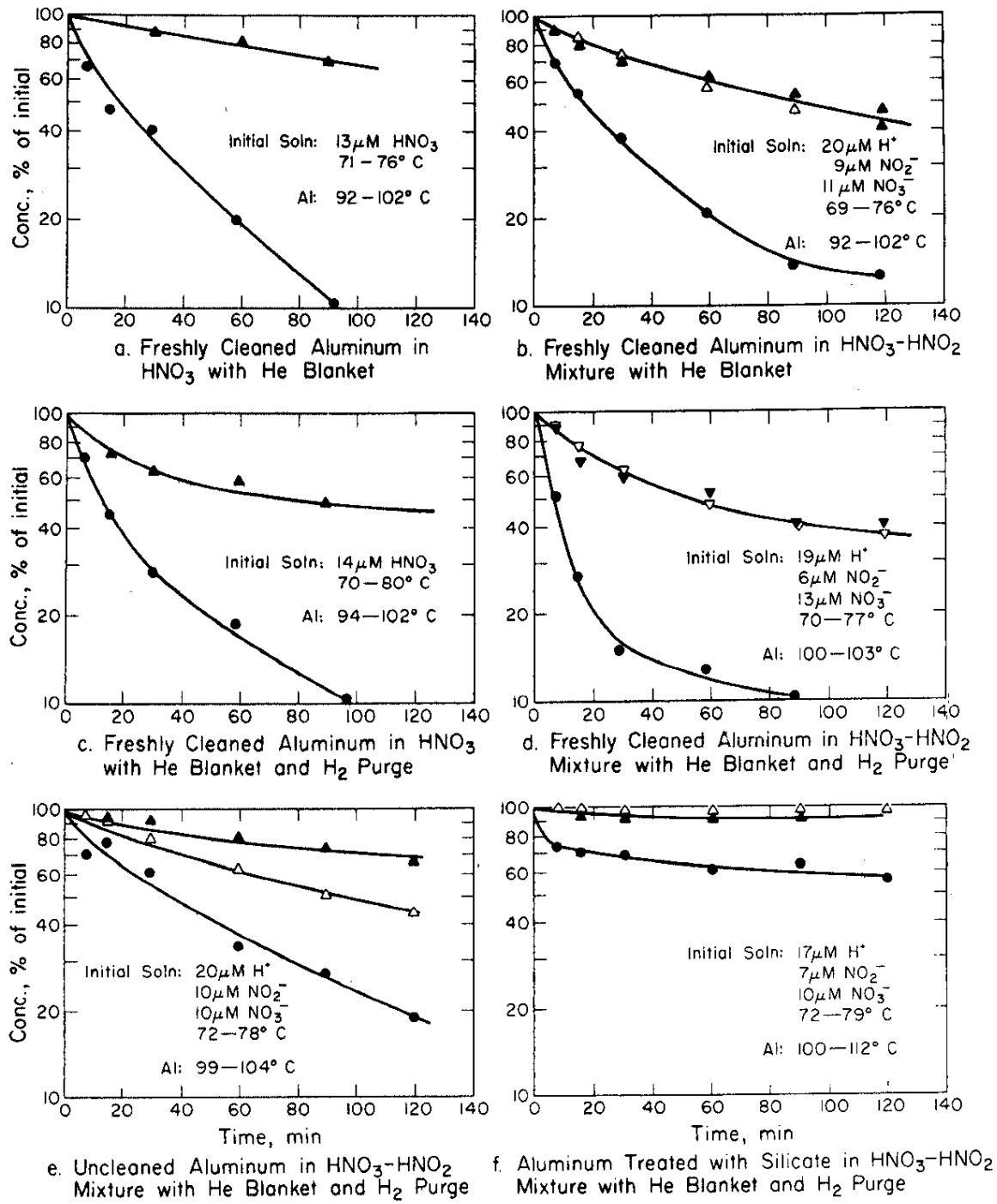

FIG. 5 EFFECT OF HEATED ALUMINUM ON DILUTE NITRIC ACID SOLUTIONS

●, H^+; ▲, $NO_3^- + NO_2^-$; △, NO_2^-

Loss of nitrogen anions and hydrogen ion was substantially reduced when aluminum was used that had undergone the additional treatment with silicate (Figure 5f). The conditions for this experiment are the same as those that caused maximum loss of acidity and nitrate in the experiments with freshly cleaned aluminum: namely, the NO_2 solution and the hydrogen purge. During the first 15-30 minutes of the test, the acid was partially neutralized, perhaps by alkalinity from residual "Lithsil" on the aluminum surface, which was not rinsed after the final treatment. The amount of neutralization was reduced from 60% to the 30% shown in Figure 5f by soaking the "Lithsil"-treated aluminum in water and in 10μM nitric acid (without heating) prior to the test. This is analogous to conditions in the reactor before nuclear startup when "Lithsil"-treated fuel elements are used.

The possibility that nitrates were lost from solution by absorption on the aluminum surface was investigated by determining the NO_3^- content of 0.1% NaOH solution in which the aluminum pieces were soaked after the test. Freshly cleaned aluminum used in only one test showed the same amount of nitrate as the control (<1% of the total NO_3^- in solution). Aluminum used in a second heating test without recleaning absorbed an additional 2% of the nitrate from the fresh solutions.

DISCUSSION OF RESULTS

The radiolysis experiments with helium-saturated (oxygen-free), triply distilled water as solvent demonstrate that steady-state stability of nitric acid can be attained with no oxidizing additives. However, the presence of hydrogen, analogous to excess deuterium in the reactor during periods of accelerated aluminum corrosion, causes abrupt loss of nitric acid. Likewise, oxidizable organics in the water, e.g., from a new deionizer resin, cause loss of nitric acid.

The aluminum heating experiments confirm that acidity may be lost through neutralization even before radiolysis becomes significant, thus setting the stage for radiolytic destruction of nitrate. As radiolysis begins to take place after criticality, the back-reaction [Equation (4)] will not readily occur, and loss of acidity and nitrate will be enhanced by the combined effects of aluminum corrosion and radiolysis.

These results are compatible with observations in Savannah River reactors. Losses during startup periods can be caused by radiolysis combined with neutralization from aluminum corrosion and/or dissolution of alumina, to produce:

- a reducing environment of hydrogen from corroding aluminum
- a neutral solution that slows the back reaction that oxidizes nitrite.

Losses during full-power operation can be attributed to a system upset (e.g., introduction of oxidizable impurities) that disrupts the redox balance of the system, which results in lowered acidity and enhanced aluminum corrosion and culminates in a self-accelerating process in which nitric acid is continuously destroyed.

APPENDIX

ANALYTICAL METHODS

Nitrate

Ultraviolet Absorption.[6] Nitrate and nitrite ions absorb in the ultraviolet region with large extinction coefficients. Absorbance was determined at 210 mμ in a 5-cm cell. Sensitivity: 1μM NO_3^-.

Colorimetric.[7] Controlled reduction of nitrate to nitrite, followed by diazotization and coupling with alphanaphthol, produces a colored compound. A 5-ml sample in 25 ml total volume was used; the absorbance was measured in a 5-cm cell at 525 mμ. This determined nitrite plus nitrate; nitrite alone can be determined by omitting the reduction step. Sensitivity: 1μM NO_3^-.

Hydrogen Ion[8]

An indicator method developed for SRP reactor moderator was used for the test solutions which are also dilute unbuffered solutions. The fraction of bromocresol green indicator (about 10^{-6} M final concentration) converted to the base form by the test solution determines hydrogen ion concentration. Range: 1.5 to 20μM H^+.

Peroxide[9]

H_2O_2 reacts with KI to free I_2. A 2.5-ml sample was added to 2.5 ml of reagent in a 5-ml volumetric flask as soon as feasible after irradiation. Absorbance was determined in a 1-cm cell at 350 mμ. Sensitivity: 3μM H_2O_2.

Dissolved Oxygen[10]

The Winkler method, adapted by Case for spectrophotometric detection, was used for semiquantitative estimation of dissolved oxygen in the helium-purged solutions. The alkaline KI and $MnSO_4$ reagents were deoxygenated with He or N_2. The reagents KI, $MnSO_4$, and (after 5 minutes) H_2SO_4 were added under the surface of the solution from a syringe whose needle pierced the rubber syringe cap of the closed vessel. This avoided introducing O_2 from the environment. The absorbance in a 5-cm cell at 350 mμ indicated the amount of I_2 released by the dissolved oxygen. Sensitivity: 2μM dissolved oxygen.

WATER QUALITY

The progress of the radiolytic reaction is strongly affected by traces of impurities that can compete in the reaction and distort the results. Therefore, particular attention was paid to the quality of the solvent water.

The most plausible and consistent results were obtained with triply distilled (TD) water, a product of three distillations of normal distilled water: with alkaline permanganate added, with acid dichromate added and the distillate vapor heated in a stream of oxygen, and finally without additives from quartz equipment.

Water deionized by a bed of "Amberlite" MB-1 was also used for some radiolysis experiments. The behavior of irradiations with deionized water depended on the service of the resin bed. That is, water from a new resin bed (D-1) caused prompt and complete disappearance of nitric acid, presumably because dissolved oxidizable organics acted as scavengers and prevented the back-reaction to form nitrate. Irradiations in water from a well-flushed deionizer that had been in use for several weeks (D-2) resembled those in TD water.

An additional test of water quality was made by preparing ferrous sulfate solutions (Fricke dosimeter) with TD and D-2 water and measuring the oxidation of Fe^{2+} in these samples when irradiated in a calibrated ^{60}Co radiation source. This ferrous sulfate system is sensitive to the presence of trace organic materials, which carry a chain reaction that increases the rate of Fe^{2+} oxidation. However, the rates of oxidation in the two samples were similar and agreed well with the anticipated value.

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