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DILUTE CHEMICAL DECONTAMINATION PROGRAM QUARTERLY REPORT 3

APRIL 1 TO JUNE 30, 1978

Report

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FOREWORD

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The technical activities of this program are being conducted by the General Electric Company.

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DILUTE CHEMICAL DECONTAMINATION PROGRAM

QUARTERLY REPORT 3

APRIL 1 TO JUNE 30, 1978

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ABSTRACT

The progress of the Dilute Chemical Decontamination Program for the period from April 1, 1978, through June 30, 1978, is discussed.

1. INTRODUCTION

This third quarterly report for the Dilute Chemical Decontamination Program covers the General Electric work during the second quarter (April through June) of 1978. Previous work performed from program inception through March 1978 was described in the previous quarterly reports.[1,2]

2. SUMMARY

The major experimental and engineering highlights of the Dilute Chemical Decontamination Program during the second quarter of 1978 are as follows:

1. The by-products generated by the radiolytic decomposition of oxalic acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, and ascorbic acid were determined by exposing 0.01 M solutions of the metal-ion-free acids to a dose of 4×10^7 rad at 90°C with an inert gas atmosphere. The decomposition by-products of oxalic acid are essentially all volatile, while the decomposition by-products of the other 4 reagents are primarily non-volatile, degraded forms of the reagents. Oxalic acid decomposes to H_2 and CO_2. The volatile decomposition by-products of the other four reagents are H_2, CO_2, CO, CH_4, C_2H_6, N_2, and other unidentified hydrocarbons.

2. The radiolytic decomposition rates of oxalic acid, NTA, and EDTA were investigated. At a dose of 1 X 10^7 rad, the residual concentrations of 0.01 M solutions of oxalic acid, NTA, and EDTA were 0.002, 0.005, and 0.0003 M, respectively. Based on present estimates of BWR core dose rates, exposures of 1 X 10^7 rad during a dilute chemical decontamination seem reasonable. Thus, significant quantities of the reagents will decompose. However, the desired reagent concentrations probably can be maintained by periodic or continuous injections of the reagents.

3. The dissolution rates of unirradiated UO_2 pellets in 0.01 M solutions of oxalic acid, EDTA, and NTA at 90°C were acceptably low.

4. The general corrosion rates of unirradiated production-line Zircaloy-2 fuel cladding in 0.01 M solutions of oxalic acid and EDTA at 90°C were acceptably low.

5. The reagent regeneration and water purification processes were investigated under mini-loop conditions. The Co-60 activity in solution was controlled successfully by periodic regeneration during mini-loop dissolution tests conducted with oxalic acid and NTA. Cation-exchange resins were used in both tests. The water purification process was demonstrated by removing EDTA and Co-60 activity from solution at the conclusion of a mini-loop dissolution test. A mixed bed of ion-exchange resins was used. These loop tests support the previous ion-exchange process results obtained in beaker tests.

6. The radionuclides absorbed on the regeneration and purification ion-exchange resins during a dilute chemical decontamination of a 5-year-old BWR will not cause significant radiation damage to the resins.

7. At filter loadings below 10% of the filter matrix weight and flow rates below 40 ℓ/sec/m^2, the removal efficiency for Fe_2O_3 of the SALA-HGMS magnetic filter (Model 10-15-5) with SALA medium-grade Type-430 stainless steel wool was greater than 80%. However, the removal efficiency decreases as the filter

loadings increase; i.e., the efficiency is approximately 50% at loadings equal to 30% of the filter matrix weight. The filter system tested in this program could be effectively backwashed.

8. Preoperational testing of the VNC test loop was successfully completed. All instrumentation was calibrated.

9. General corrosion tests were conducted under static conditions to provide data on the general corrosiveness of the potential reagents. The low alloy steel corrosion rate in 0.01 M solutions of oxalic acid was acceptably low, while the corrosion rates in 0.01 M solutions of EDTA, NTA, and citric acid were excessive.

10. Additional general corrosion tests were conducted to evaluate the effects of several additives and corrosion inhibitors on the corrosion rate of a low alloy steel in 0.01 M NTA. Only phenylthiourea, a sulfur compound, was effective in reducing the corrosion rate to an acceptable level. However, because certain sulfur compounds (such as, polythionic acid) initiate stress corrosion cracking in austenitic stainless steels, phenylthiourea will not be used in the dilute chemical decontamination solvent formulation.

3. TASK 1 – SOLVENT EVALUATION AND SELECTION

3.1 SOLVENT DEVELOPMENT – J. P. Peterson and R. E. Gest

During the previous report periods,[1,2] ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and oxalic acid, were selected for further study. Dilute solutions of these reagents are capable of dissolving 80% or more of the Co-60 in BWR out-of-core deposits in less than 72 h. In addition, the previous efforts included: (a) evaluating the effects of pH, temperature, and reducing agents on the dissolution rate of BWR out-of-core oxide films; (b) evaluating the response of the reagents under mini-loop conditions; and (c) measuring the dissolution rate of fuel deposit scrapings.

Solvent development efforts during this report period were: (a) initial evaluation of the radiolytic stability of the various reagents, (b) evaluation of the effect of selected reagents on unirradiated UO_2 pellets and on fuel cladding, and (c) evaluation of the properties of the various solvent systems under mini-loop conditions.

3.1.1 Experimental Apparatus and Facilities

The out-of-core deposit dissolution and process studies were conducted in reaction kettles and glass mini-loops whereas the UO_2 dissolution and cladding tests were conducted only in reaction kettles.

The solvent radiation stability measurements were performed in the VNC Co-60 facility. This facility consists of 12 stainless steel pins which contain approximately 15 kCi of Co-60. These pins were placed in a circular array around a 10-cm-diameter pipe, whose length extended from the pins through a 6-m water shield to the surface, providing a drywell. With this configuration, a dose rate of 1.6×10^6 R/h was obtained.

Two types of radiation stability tests were conducted. The initial tests were run for 24 h in a stainless steel cylindrical vessel which contained approximately 50 ml of solution. The vessel (Figure 1.) was equipped with three ports which were used for gas sparging, for a thermocouple, and for collecting the gas generated during the irradiation. The vessel was wrapped with a Nichrome wire and insulated for elevated temperature operation. A subsequent test was performed to measure the decomposition of the reagents as a function of cumulative dose. In this case, small vials were used and no attempt was made to contain or to analyze the gas produced.

3.1.2 Reagent Radiation Stability

3.1.2.1 Radiolytic Decomposition By-Products

Tests were conducted to obtain information on the radiation stability of the three primary reagents. In addition, tests were conducted with citric and ascorbic acids because citric acid may be required in an oxalic acid system and ascorbic acid will be required in NTA and EDTA systems. These tests, performed with the metal-ion-free organic acids, were designed to determine the extent of degradation at a radiation exposure equivalent to that expected during a plant decontamination. A 24-h exposure was used. To distinguish between thermal and radiolytic decomposition, comparison tests were made in an identical vessel under identical conditions without the radiation field. All tests were conducted at 90°C, with 0.01 $\underline{M}$ solutions of the metal-ion-free organic acids at pH 3.5. The solutions were de-oxygenated in the test vessel before the tests by sparging with helium gas. The vessel was sealed at the end of the sparging to provide an inert atmosphere during the test.

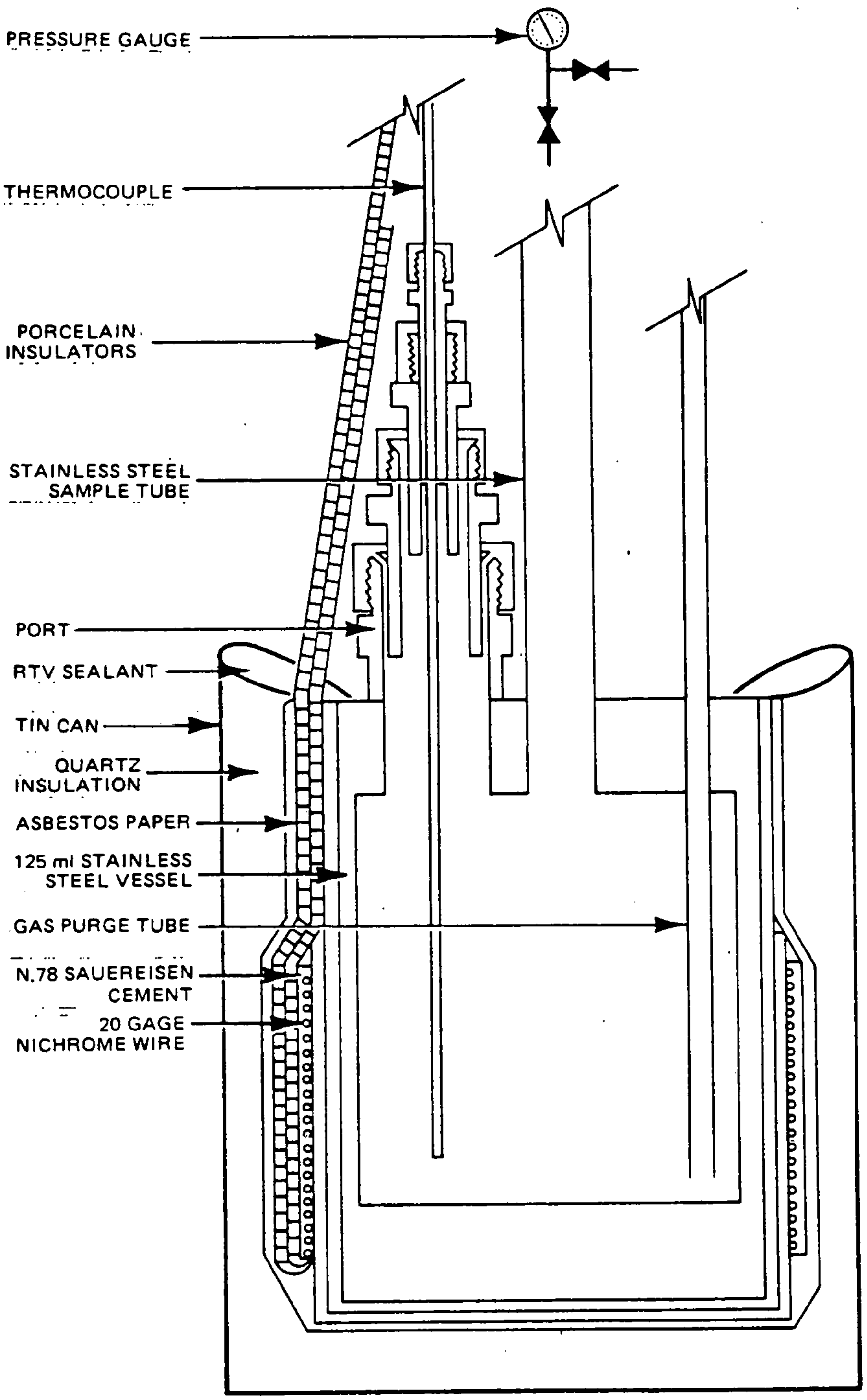

FIGURE 1. REAGENT IRRADIATION TEST VESSEL

The results of the first experiment with EDTA showed extensive degradation; therefore, a method was added to obtain quantitative data on the volatile species produced. This method involved introducing a known quantity of krypton gas into the vessel after the vessel was sparged with helium and sealed. After irradiation, the quantities of volatile species were measurd by gas chromatography. In addition, the solutions were analyzed for residual oxalic acid, NTA, and EDTA concentrations. The oxalic acid was determined by titration with $KMnO_4$.[3] The NTA was determined by titration with magnesium using a buffer, masking agent, and oxidyl blue as an indicator[4] and the EDTA by titration with zinc using Erichrome Black T indicator.[5]

The various species observed in the gas phase above the irradiated solutions and their relative abundances are presented in Table 1. Hydrogen was a major constituent in all five tests. The hydrogen could have resulted from several sources; such as, the H_2O, the ammonia, or the reagent. Since the concentrations of nitrogen and oxygen were low relative to hydrogen, it can be concluded that the reagents were the major source of hydrogen.

The relative abundances of the carbon-bearing gas species are given in Table 2. The predominant gas species were CO and CO_2. In three tests, however, other hydrocarbons (such as, methane and ethane) were also observed. The abundances of the species which were not readily identifiable are reported (Tables 1 and 2) as the sum of the species observed. Ammonia was observed only in the EDTA test.

The quantity of each organic species generated in each test was determined by comparing the concentration of the organic species to the krypton spike concentration. The total quantity of carbon atoms collected in the gaseous phase was calculated by summing the quantity of carbon atoms in each organic species. For the unidentified species, it was assumed each molecule contained an average of two carbon atoms. The total quantity of carbon atoms collected was compared with the number of carbon atoms initially present in solution, which was determined from the measured concentration of the reagent. This comparison provided an estimate of the extent of decomposition to volatile species.

The results obtained by this interpretation of the gas phase data and by the titre of the solutions are given in Table 3. At a cumulative dose of 4×10^7 rad, oxalic acid has nearly completely decomposed to CO_2 and H_2. In the nonirradiated oxalic acid test, appreciable decomposition was also observed, but intermediate nonvolatile products were formed. The residual oxalic acid solutions were utilized in dissolution tests with contaminated pipe

TABLE 1. Volatile Species Resulting from Radiolytic Decomposition

(4×10^7 rad; 90°C, 24 h)

Reagent	Relative Abundances (%)									Number of Unidentified Species
	H_2	N_2	NH_3	O_2	CO	CO_2	CH_4	C_2H_6	Unidentified Hydrocarbons	
Oxalic Acid	50.1	0.4	-	-	0.3	49.2	-	-	-	0
NTA	83.8	0.5	-	-	7.0	4.7	2.1	1.2	0.6	3
EDTA	76.0	5.8	1.1	0.4	7.0	7.7	0.7	-	1.3	6
Citric Acid	65.3	0.1	-	-	0.8	31.8	0.2	-	0.5	1
Ascorbic Acid	40.9	0.3	-	-	3.3	55.5	-	-	-	0

TABLE 2. Carbon-Bearing Gas Species Resulting from Radiolytic Decomposition

(4×10^7 rad; 90°C, 24 h)

Reagent	Relative Abundances (%)					Number of Unidentified Species
	CO	CO_2	CH_4	C_2H_6	Unidentified Hydrocarbons	
Oxalic Acid	0.6	99.4	-	-	-	0
NTA	44.6	30.1	13.4	7.3	4.3	3
EDTA	41.8	46.3	4.1	-	7.8	6
Citric Acid	2.3	95.8	0.4	-	1.5	1
Ascorbic Acid	5.4	94.6	-	-	-	0

TABLE 3. Radiolytic and Thermal Decomposition
(4×10^7 rad; 90°C, 24 h)

	Radiolytic + Thermal Decomposition (% Decomposed)		Thermal Decomposition (% Decomposed)	
Reagent	Solution Phase	Gas Phase (Volatile Carbon Species)	Solution Phase	Gas Phase (Volatile Carbon Species)
Oxalic Acid	97	95	91[a]	1
NTA	99	17	b	1
EDTA	99	c	b	b
Citric Acid	b	60	b	0
Ascorbic Acid	b	22	b	3

[a] A residual of 57% was measured at a titration rate significantly slower than that for oxalic acid.

[b] Not performed or analyzed.

[c] Not spiked with krypton.

coupons. No dissolution was observed to occur in either test. This indicates the nonvolatile species which titrated in the nonirradiated oxalic acid solutions probably were not oxalic acid. Further investigation is required on the thermal stability of oxalic acid.

The results with NTA and EDTA show no complexing agent remains after the 24 h exposure. Since the gas analysis for the NTA experiment indicates only 17% of the NTA decomposed to volatile species, the remainder of the NTA must have decomposed to degraded forms of NTA. Most likely EDTA also decomposes to degraded nonvolatile species. Thermal decomposition of the nonirradiated solutions of EDTA and NTA would not be expected at the temperatures used.[6]

A visual observation was made of the inside surface of the stainless steel container after each irradiation experiment for possible film formation. Only in the ascorbic acid test was a film observed and this film was high in iron and contained no organic material.

The radiolytic decomposition results are in general agreement with the findings of others,[7-9] which indicated that for an EDTA-citric acid solution (Trilon B) only "traces" of the reagents remain at an absorbed dose of 1.3×10^7 rad and that for an oxalic acid solution the concentration is depleted from 0.01 to .001 M after an exposure of approximately 3×10^7 rads.

3.1.2.2 Reagent Radiolytic Decomposition Rate

Based on the results presented in Section 3.1.2.1, it was apparent that extensive depletion of the reagents would occur and that this depletion could have important process implications. It was necessary to establish the rates of radiolytic decomposition for the reagents. Solutions of the three reagents at 0.01 M and pH 3.5 were placed in glass vials, deoxygenated with helium gas, and irradiated for 1.5, 3.5, 6, 7.5, 17, and 24 h with the same Co-60 pin configuration as used in the previous tests. The irradiations were conducted at approximately 30°C. The vials were lowered into the gamma field in a container in which one vial of each reagent was irradiated at the same elevation. At the end of an exposure period, vials at a single elevation were removed and the container re-inserted into the field. In this way, the vials containing the three different reagents removed at a given time received the same exposure. The initial and irradiated solutions were analyzed for reagent concentrations.[3,4,5]

The results of the analyses are shown in Figure 2. The EDTA is totally depleted by approximately 1 x 10^7 rad, which is consistent with the rate observed for Trilon B.[7] The oxalic acid result is in reasonably good agreement with the decomposition rate reported by Motojima[8] (Figure 2). Based on present estimates of BWR core dose rates, the radiolytic decomposition rate of oxalic acid will be significant in a decontamination performed within a few days after a reactor shutdown. However, this problem probably can be overcome by continuous or periodic injections of the reagents.

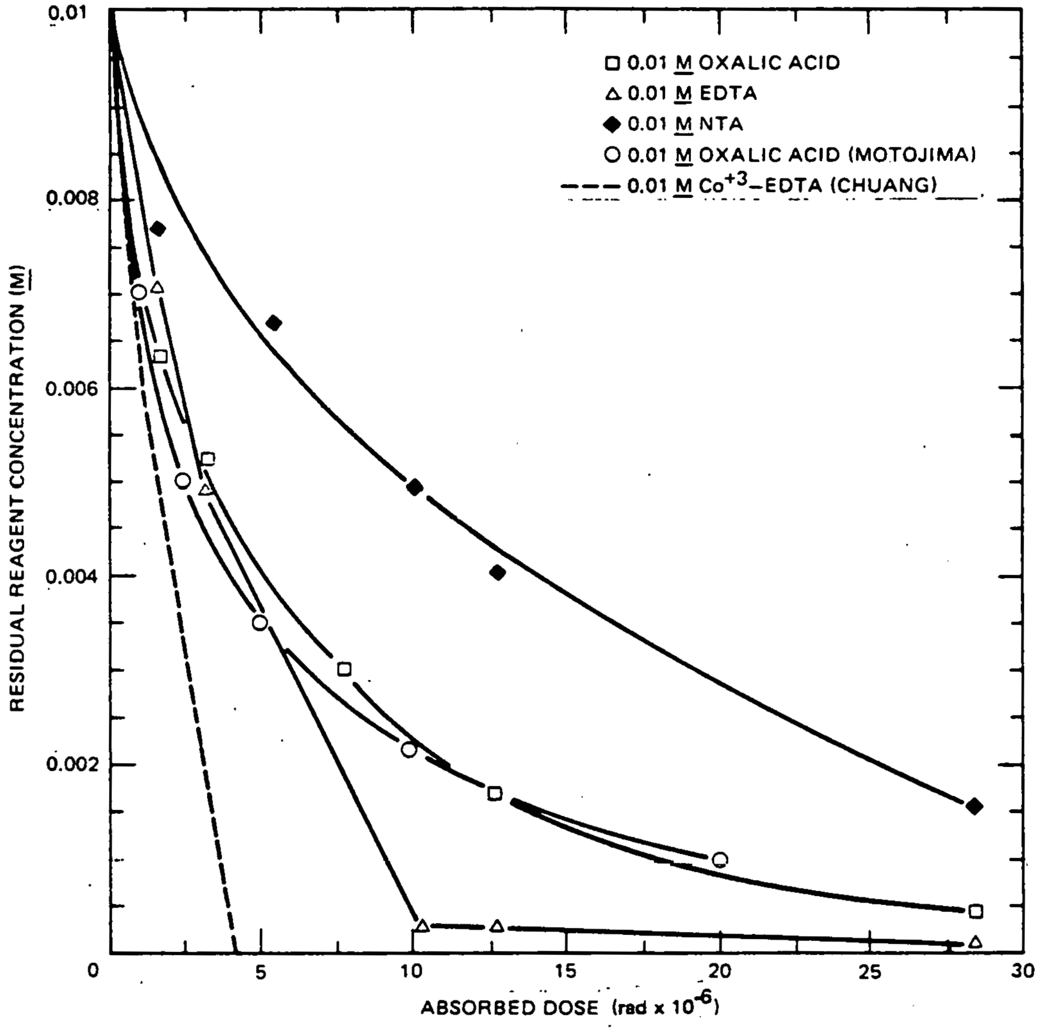

FIGURE 2. REAGENT RADIOLYTIC DECOMPOSITION RATES

Chuang[10] determined the radiolytic decomposition rate of the Co^{+3}-EDTA complex to be considerably more rapid (Figure 2). This may have resulted because the radiolytic decomposition rate of metal-ion complexes may be more rapid than the radiolytic decomposition rate of metal-ion-free complex. Additional experiments will be performed to evaluate the decomposition rate of the Fe^{+3} complexes.

3.1.3 Dissolution of Unirradiated UO_2 Fuel Pellets

Since the dilute chemical decontamination process potentially may be applied when defective fuel is in the core, the effects of the process on exposed fuel must be evaluated. The major concern in this area is the dissolution of the UO_2 fuel or leaching of the fission products or actinides. Dissolution tests were conducted to evaluate the dissolution rate of unirradiated UO_2 fuel pellets in 0.01 M solutions of the three reagents under low O_2 conditions at 90°C. Periodic samples were taken and analyzed for uranium concentration by fluorometry. The final solutions were analyzed by isotope dilution mass spectrometry, using U-233 as the isotopic diluent. In addition, the weight loss for each of the UO_2 pellets was determined.

The dissolution curves for the three experiments are shown in Figure 3. In the oxalic acid and NTA tests, the inital samples taken after approximately 1 h contained 70 to 80% of the total uranium dissolved in the experiments which lasted 75 h. The dissolution rate between 1 and 75 h was extremely small. This behavior probably resulted from the dissolution of fine UO_2 particles which were created in preparing the samples. The dissolution curve in the EDTA experiment did not exhibit the rapid initial dissolution. In all three experiments the dissolution rate was acceptably low.

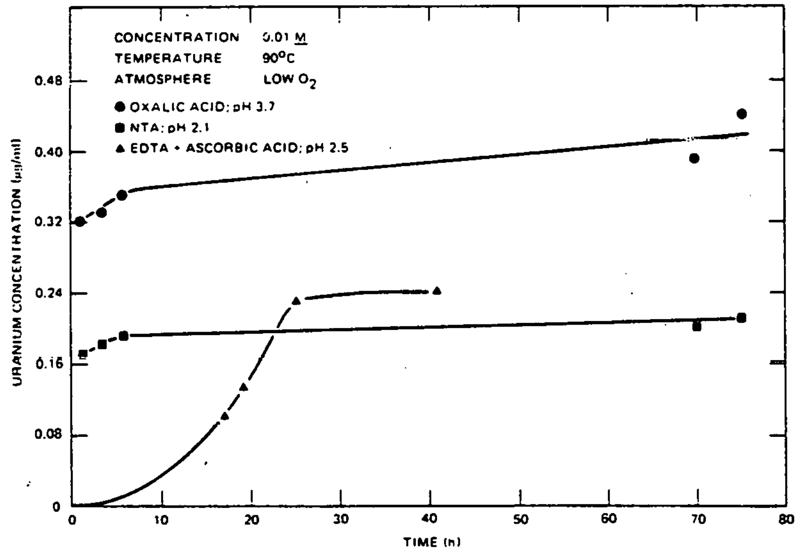

FIGURE 3. UNIRRADIATED UO_2 PELLET DISSOLUTION

Additional experiments will be performed to determine the dissolution rate of irradiated UO_2 and the leaching rate of plutonium, transplutonium elements, and fission products.

3.1.4 Effect of Solvent on Fuel Cladding

Several experiments were conducted to determine the general corrosion rate of unirradiated production-line Zircaloy-2 fuel cladding in 0.01 M solutions of EDTA and oxalic acid. Stainless steel and carbon steel corrosion coupons also were subjected to the solutions to simulate a decontamination solution environment. The tests were conducted at 90°C. The experimental conditions and results are given in Table 4. The corrosion rates of the Zircaloy coupons were extremely low in all four tests. In addition, an optical microscopic inspection (at 100 x) of the coupons indicated no penetrations or breaks in the ZrO_2 film.

TABLE 4. Zircaloy-2 General Corrosion Results

Solution	pH	Low[a] O_2	Time (h)	Total Corrosion (mg/cm^2)
EDTA	3.5	No	88	0.024
EDTA	3.6	No	18	0.031
EDTA	6.0	Yes	43	0.029
Oxalic	3.7	No	45	0.021

[a] Low O_2 condition established by sparging with nitrogen for $\geq$ 2h before the test.

3.1.5 Mini-Loop Tests

A side loop with an ion-exchange column was added to one of the mini-loops. Several experiments were conducted to evaluate the ability of the reagent regeneration and water purification systems to process solutions generated by dissolving BWR corrosion products and activity. All previous tests have been conducted with solutions containing simulated corrosion products.

The experimental conditions for three mini-loop tests are given in Table 5. In the oxalic acid and NTA experiments the reagents were regenerated during portions of the tests by passing the solutions through a cation-exchange resin bed. The cation-resin regeneration process probably removed only the divalent ions (such as, Co^{+2}, Fe^{+2}, and Ni^{+2}) and did not remove Fe^{+3}. However, removal of Fe^{+3} was not important in these experiments because there was an excess solvent capacity relative to the quantity of iron available for dissolution. Therefore, the dissolved Fe^{+3} should not have had an adverse effect on the chemistry. The dissolution curves (percentage Co-60 dissolved as a function of time) and the Co-60 activities in the solutions (shown as percentage of the total cobalt initially on the coupon as a function of time) are given in Figures 4 through 6.

TABLE 5. Mini-Loop Tests with Ion-Exchange Processes.

				Ion Exchange Process		
Test	Reagent	Concentration (M)	pH	Process	Resin	Rate (% Solution vol/min)
1	Oxalic Acid Citric Acid	0.006 0.0016	2.6-3.2	Regeneration	Cation NH_4^+	2.4
2	NTA Citric Acid Ascorbic Acid	0.0086 0.0015 0.0019	3.5	Regeneration	Cation 50% H^+ 50% NH_4^+	2.4
3	EDTA Ascorbic Acid	0.0065 0.0007	4.4	Water Purification	Mixed-Bed OH^-, H^+	2.4

In both experiments, the cation-exchange resin was effective in removing the Co-60 from the solution. The rates of removal of the Co-60 from solution agree reasonably well with the rates predicted from the regeneration equation.[2] These experiments demonstrate cation-exchange resin can be effective in controlling the Co-60 in solution during a dilute chemical decontamination with either an oxalate or NTA-based solvent system.

Since EDTA solutions cannot be regenerated,[2] the EDTA mini-loop test was conducted without regeneration. After approximately 20 h of dissolution, the solution was passed through a mixed-bed ion-exchange resin column to evaluate the water purification process. When the Co-60 activity in solution reached essentially zero, the mixed-bed column was valved out and a second injection of EDTA and ascorbic acid was made. After an additional 20 h of disolution, the mixed-bed column was valved in and the Co-60 activity in solution again dropped rapidly to essentially zero. The removal rates were in reasonable agreement with values predicted from the regeneration equation[2] using a zero addition rate. This experiment demonstrated the Co-60 activity can be removed at the end of a decontamination with mixed-bed ion-exchange resin.

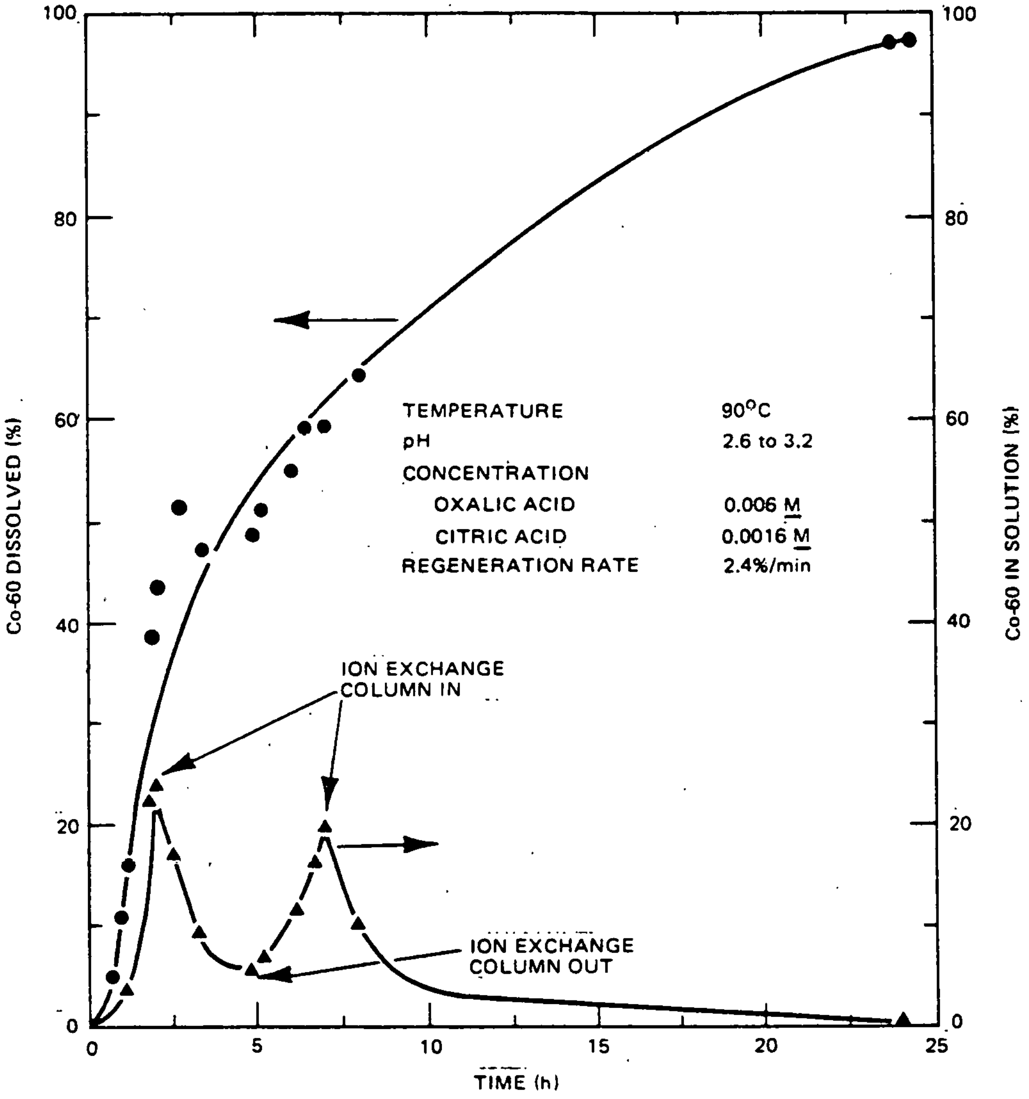

FIGURE 4. OXALIC ACID MINI-LOOP TEST WITH REGENERATION

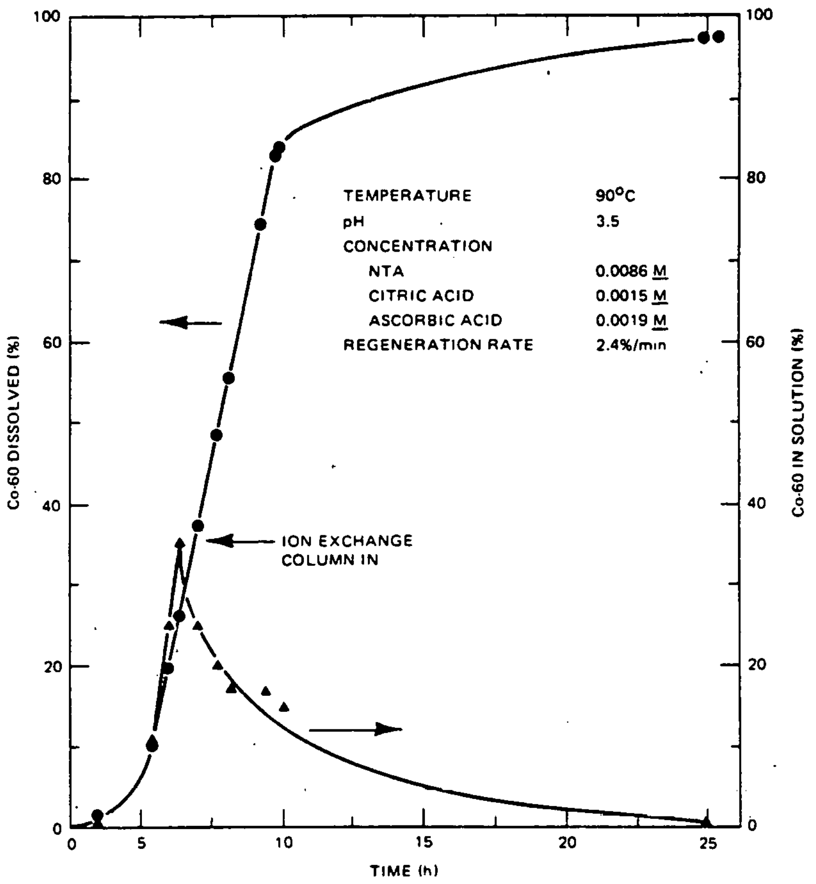

FIGURE 5. NTA MINI-LOOP TEST WITH REGENERATION

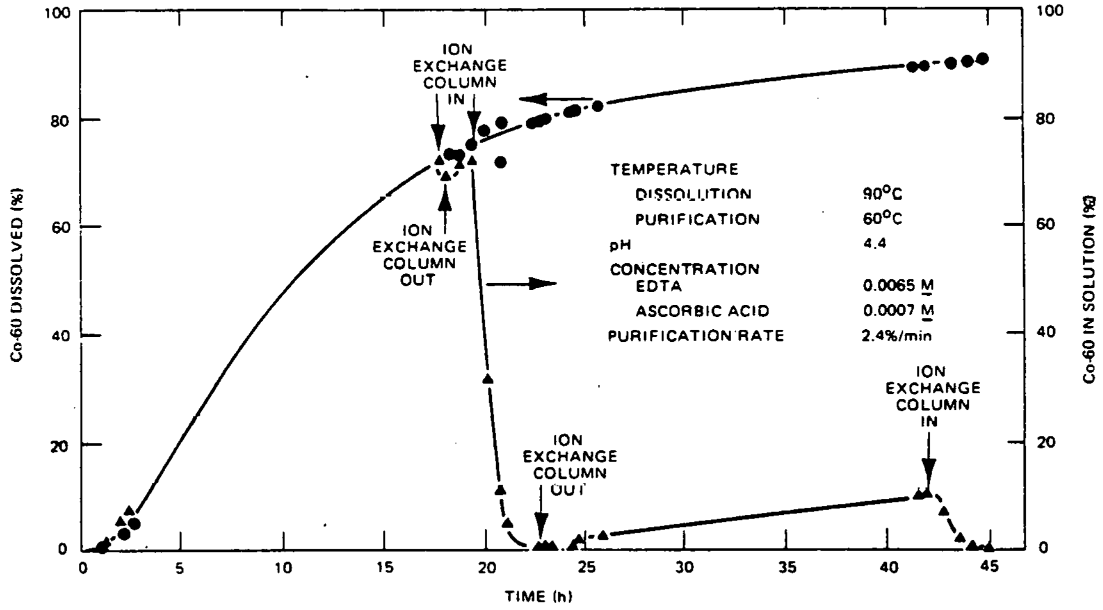

FIGURE 6. EDTA MINI-LOOP TEST WITH WATER PURIFICATION

3.2 WATER PURIFICATION (SOLUBLE SPECIES)

3.2.1 Effect of Radiation on Ion-Exchange Resins – R. L. Hobart

Since it is anticipated that most of the radionuclides removed from the out-of-core and fuel surfaces during a dilute chemical decontamination will be collected on ion-exchange resins, the potential degradation or loss of capacity of the resin because of radiation is of concern. Consequently, the maximum anticipated dose rate to the resin during a BWR decontamination was estimated and compared with literature data on the effect of radiation on ion-exchange resins.

The dose rate, ϕ, at the center of a cylinder can be estimated by[11]

$$\phi = \frac{S_v B}{\mu_s} \qquad (1)$$

where

S_v = specific strength of the volume source

B = buildup factor, and

μ_s = linear absorption coefficient

An estimated resin volume[2] of 15,000 liters was assumed to be contained in a single cylindrical column. A maximum inventory of 50,000 Ci of Co-60 was determined by multiplying the highest Co-60 concentration (~9.5 Ci/m^2)[12] measured to date on a BWR fuel bundle by the approximate fuel cladding surface area in Nine Mile Point[1] (4.3×10^3 m^2) and assuming Co-60 represented 80% of the total dose to the resin.

Thus, the volume source term is

$$S_v = 50{,}000 \text{ Ci} \div 15{,}000 \text{ liters} = 3.33 \text{ Ci/liter}$$

or

$$3.1 \times 10^8 \text{ MeV sec}^{-1} \text{ cm}^{-3}.$$

The linear absorption coefficient was assumed to be 0.06 cm^{-1}. The buildup factor was estimated by[11]

$$B = \frac{A_1}{1+\alpha_1} + \frac{1-A_1}{1+\alpha_2}$$

where A_1, α_1, and α_2 are the buildup parameters.

With water as the attenuating media and 1.0 MeV gamma rays, the values for A_1, α_1, and α_2 are 19.601, 0.0904, and -0.0252, respectively. Thus, B is equal to 2.5. A maximum dose rate, ϕ, of 1.3×10^{10} MeV/cm^2 sec or 2.3×10^4 R/h, was determined by multiplying the values determined for S_v, μ_s, and B.

Baumann[13] concluded that, "When the dose exceeds 10^7 rad, perceptible damage to the resin is to be expected." However, Baumann's data[13] indicate that below a cumulative dose of 10^7 rad, neither cation-exchange nor anion-exchange resins have significant degradation or loss of capacity. Thus, degradation of the ion-exchange resins should not be a problem during the decontamination of a BWR nor for approximately 20 days after the decontamination.

In addition, even if perceptible degradation does begin to occur after 20 days, this should not create a major problem since the resins will probably be discarded, then loss of capacity will not be so important.

3.3 FILTRATION – E.A. Melaika

During a dilute chemical decontamination process, crud particles will be released to the circulating solvent from low-flow areas, crud traps, and the fuel and non-fuel surfaces. The primary species is anticipated to be αFe_2O_3, which typically dissolves at a lower rate than the other major species present in BWRs ($NiFe_2O_4$). To prevent the released particles from settling into low-flow areas and potentially creating "hot spots," a filtration system will be needed to remove the 0.1 to 5.0 m particles from the solution. The actual filtration system selected will depend on several factors; e.g., the quantity of crud released, available space in the reactor, and operational considerations.

In the first quarterly report, the results of an engineering study to evaluate filter systems for use in a dilute chemical decontamination process were presented. Two commercially available filter units which appeared to be promising systems were identified for testing. These were: (1) a high gradient magnetic separator (HGMS), and (2) the Votator-Schenk filter which utilizes filter aid with automatic cake discharge. In addition, cartridge filtration which is widely used in the nuclear industry may be a acceptable alternative. However, cartridge filters can be used only in situations where relatively small quantities of crud are expected to be released.

A SALA-HGMF magnetic filter (Model 10-15-5) was purchased. The experimental program conducted with this system consisted of evaluating: (1) the filtration efficiency with a constant feed concentration at low and high filter loadings, (2) the filtration efficiency in a recirculating system, and (3) the efficiency of backwashing techniques. The tests intended to evaluate the Votator-Schenk filter technique were deleted from the program because sufficient experience exists within the filtration industry to show that iron corrosion products in the 0.1 to 5.0 μm range can be filtered efficiently with available pressure filtration systems and techniques. Also, no tests were performed with cartridge-type filters because suitable laboratory scale equipment was not available.

3.3.1 Experimental Techniques

The Dresden-2 reactor contains approximately 3,800,00 liters of coolant and approximately 280 kg of corrosion product oxides.[1] It is anticipated that up to 25% (70 Kg) might be sloughed during a decontamination. If all of the sloughed corrosion product were in suspension at one time, the particle concentration would be approximately 180 ppm. Consequently, 180 ppm was selected as the reference concentration for the initial tests.

All filtration tests were performed using 0.1 to 1.0 μm Fe_2O_3 to simulate the sloughed corrosion products. This selection was made because the loosely-adherent oxides which probably will be sloughed from the fuel and non-fuel surfaces are essentially 100% αFe_2O_3. In addition, the reagents being considered in this program dissolve αFe_2O_3 at a considerably lower rate than they dissolve $NiFe_2O_4$.

The filter test apparatus is shown in Figure 7. The feed reservoir was a 12 liter, 3-neck flask equipped with electric heating mantles. A gear pump was used to recirculate the feed slurry in the reservoir and to pump the slurry through the test loop. A motor-driven stirrer

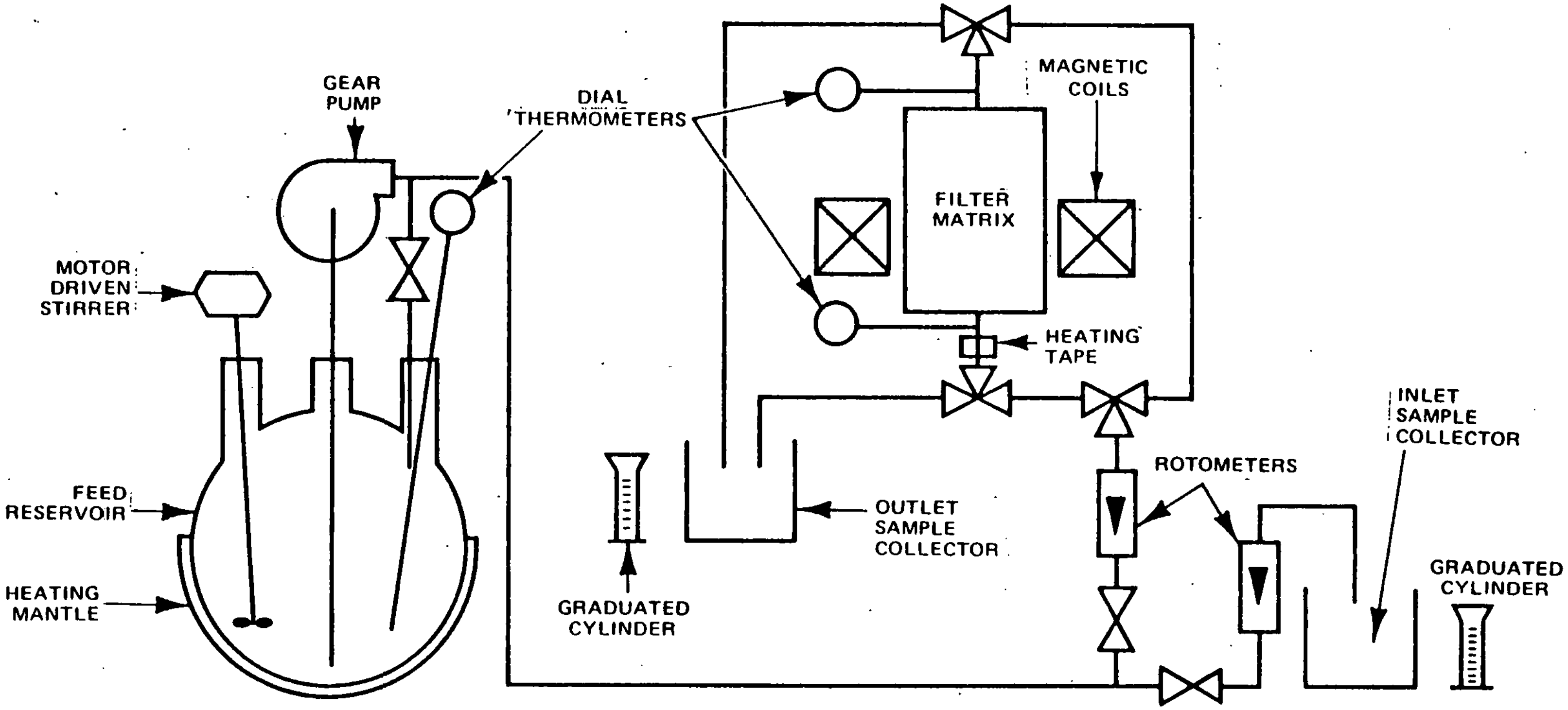

FIGURE 7. MAGNETIC FILTER TEST LOOP

was used to agitate the feed slurry. Three-way valves were used to route the slurry to the magnetic filter and the sampling containers. The temperature of the slurry was measured with dial thermometers at the inlet and outlet of the filter. Rotometers were used to establish flow rates; however, the actual flow rates were determined by measuring the volume of liquid collected in a given time.

The 1.15-cm-diameter filter tube was packed with 15.2 cm of SALA medium grade Type 430 stainless steel wool. The filter matrix weighed 4.9 gm and occupied a volume of 16 ml. All tests were run at 5000 gauss, the maximum available field of the instrument.

In each test, 11 liters of solution were added to the feed reservoir and adjusted to the test temperature. The desired amount of $Fe_2 0_3$ was mixed with 300 ml of water in a blender and added to the solution in the feed reservoir. The process flow paths for the three types of tests are shown in Figures 8, 9, and 10. The flow rate was controlled by adjusting the throttle valve on the recirculation line. Sample lines were flushed with the test slurry for a minimum of 2 minutes before sampling to ensure the samples were representative.

The concentrations of $Fe_2 0_3$ in the inlet and outlet samples were determined by measuring the volume of collected slurry with a graduated cylinder; by filtering the $Fe_2 0_3$ with preweighed 0.45 μm, 47 mm, Type HA Millipore^R filters; by washing with water to remove NTA; by air-drying overnight; and by reweighing the loaded Millipore filter. Loadings on the magnetic filter were calculated by multiplying the difference between the inlet and the outlet $Fe_2 0_3$ concentrations by the quantity of slurry passed through the magnetic filter.

3.3.2 Constant Feed Concentration Tests

Four tests were conducted to evaluate the efficiency of the magnetic filter for removing $Fe_2 0_3$ at low filter loadings; i.e., less than 10% of the matrix weight. Tests 1 and 2 were conducted under the same conditions, while Test 3 evaluated the difference between using water or NTA as the liquid media and Test 4 studied the effect of feed temperaure. In each experiment, the flow rate was reduced sequentially from an initial high rate. The experimental conditions and results are given in Figure 11.

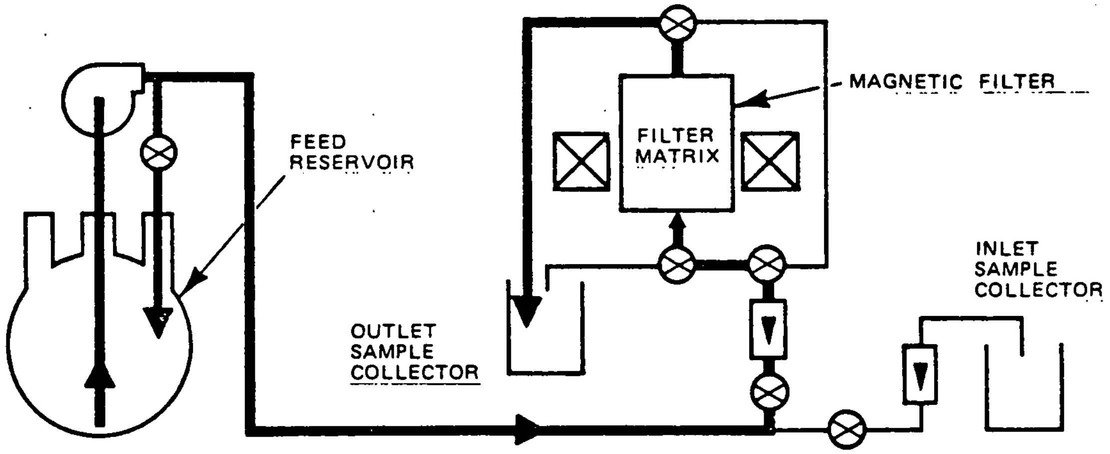

FIGURE 8. CONSTANT FEED FLOW PATH

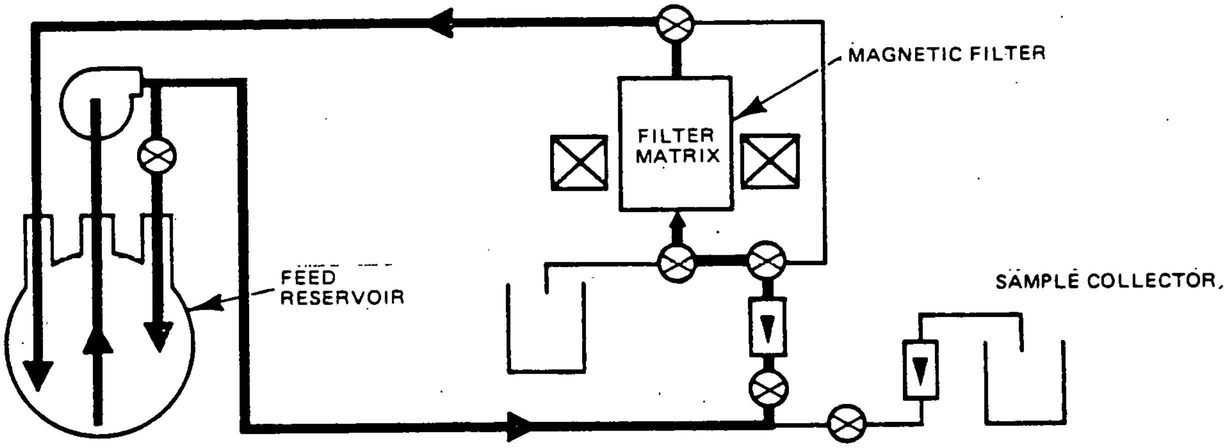

FIGURE 9. RECIRCULATION FLOW PATH

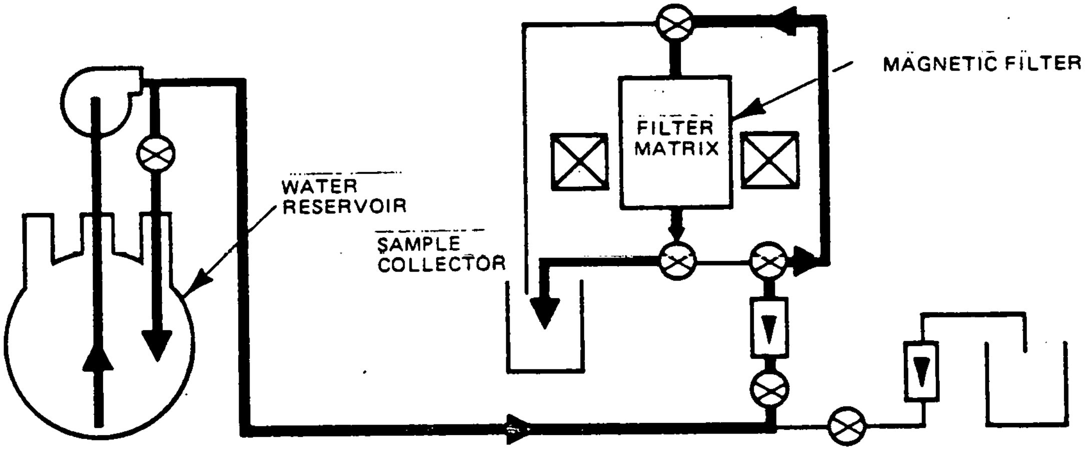

FIGURE 10. BACKWASH FLOW PATH

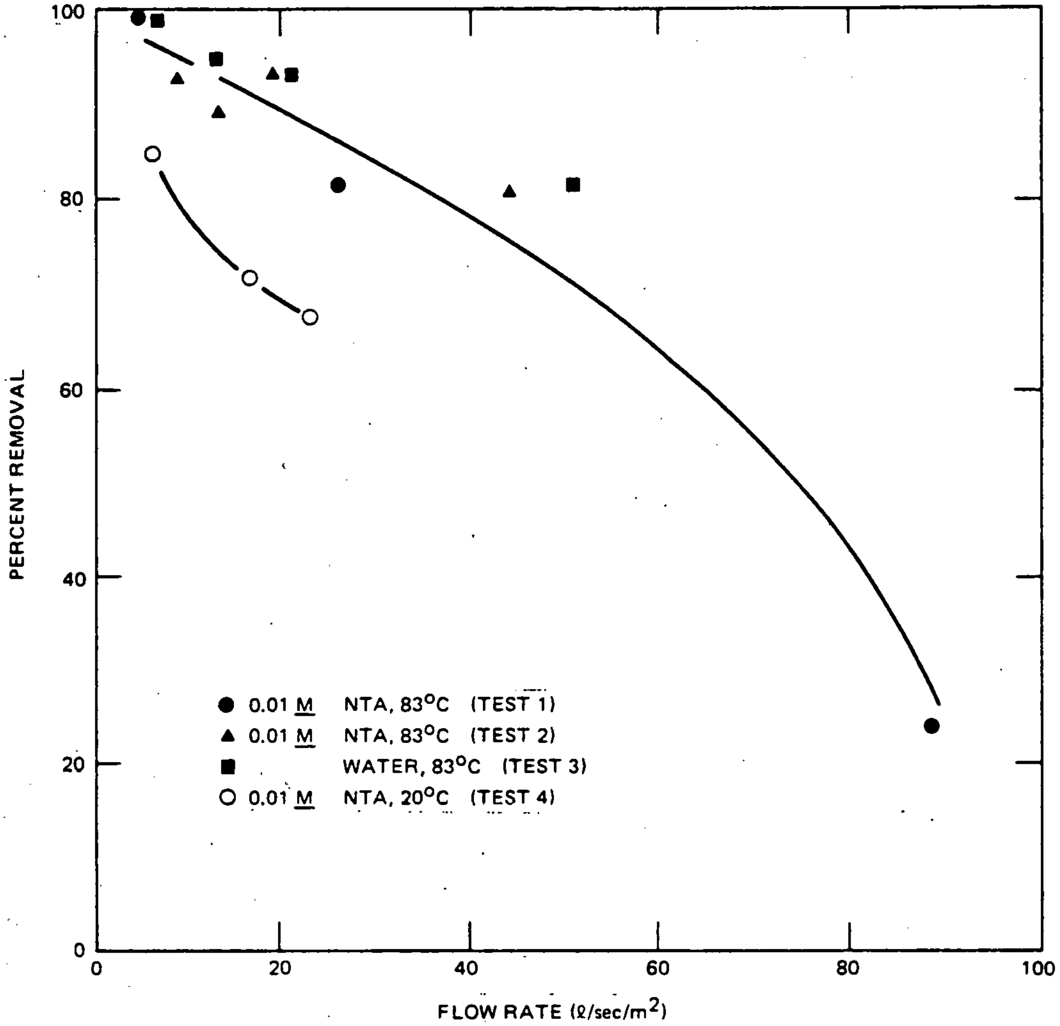

FIGURE 11. FILTRATION EFFICIENCY AT LOW LOADINGS

The data for the three tests conducted at 83°C are in reasonable agreement. There were no significant differences between the results obtained with 0.01 M NTA and water. The lower efficiencies obtained at 20°C relative to those obtained at 83°C were the result of the increased viscosity at the lower temperature, causing an increased drag force on the particles.

Three additional tests were conducted to determine the efficiency of the magnetic filter as a function of loading. The experimental conditions are given in Table 6. In these tests, a Fe_2O_3 slurry was pumped through the filter until the iron loading was approximately 25 to 60% of the filter matrix weight. The experimental results are given in Figure 12.

TABLE 6. Filter Loading Tests (pH 3, 85°C)

Test	Average Flow Rate (ℓ/sec/m^2)	Feed Concentration (ppm)	NTA Concentration (M)
1	26	155	0.01
2	8	575	0.01
3	14	1250	0.003

In the first test the average feed concentration was 155 ppm and the removal efficiency of the filter was still relatively high (~70%) when the first 11-liter batch was completed. Consequently, two additional 11-liter batches were prepared and processed through the filter. When the flow was restarted for the second and third batches, Fe_2O_3 was sloughed from the filter. In addition, smaller amounts of Fe_2O_3 were sloughed twice during the third batch when power to the magnet was interrupted. Corrections were made to the data plotted in Figure 12 to account for the loss of material from the filter matrix. The data for the time interval during which material was sloughed from the filter were deleted from Figure 12.

To eliminate the need for multiple batches, the second and third loading tests were conducted at higher average feed concentrations of 575 and 1250 ppm, respectively. Also, the NTA concentration was reduced in the third test to 0.003 M to reduce the dissolution of Fe_2O_3. At the beginning of the 8ℓ/sec/m^2 test, the flow was started to the filter before turning on the magnetic field. The removal efficiency during this period was approximately 80%, but increased during the next two test intervals to 96 and 98% before decreasing to 70% during the fourth interval. In analyzing the data, the assumption was made that the majority of the Fe_2O_3 removed during the first interval was removed by mechanical separation and did not consume a significant quantity of the magnetic capacity of the filter.

The results plotted in Figure 12 indicate that the removal efficiency drops off significantly as the filter loading increases. To obtain filtration efficiencies above 80%, the filter loading must be maintained below approximately 10% of the filter matrix weight. Also, it appears that the removal efficiency is independent of fluid velocity once the filter is loaded to 5 to 10% of the matrix weight.

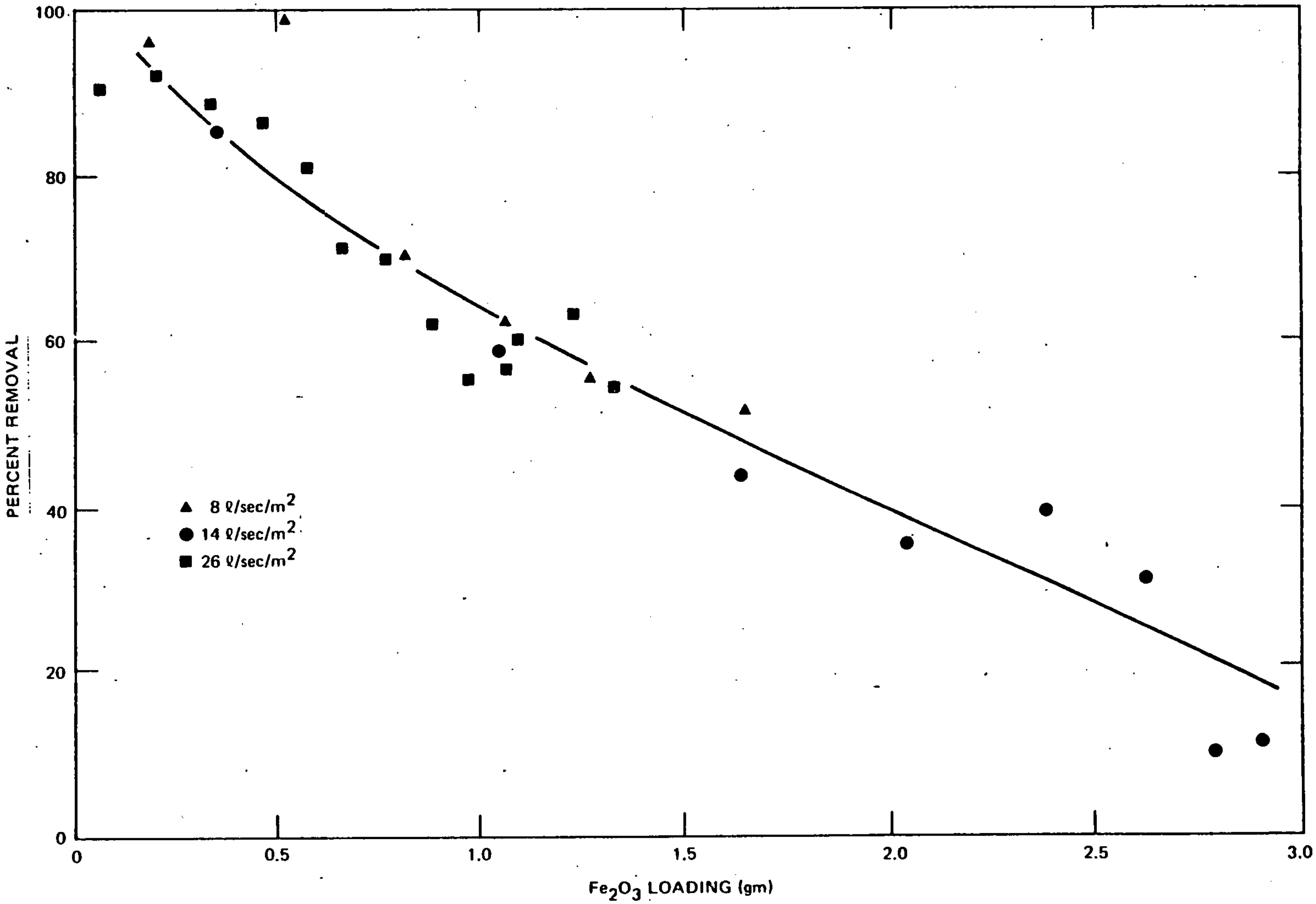

FIGURE 12. FILTRATION EFFICIENCY AS A FUNCTION FILTER LOADING

There probably were two filtration mechanisms responsible for removing the iron oxide particles: magnetic and mechanical entrapment. At low filter loadings (< 10% of the matrix weight) magnetic separation dominated and relatively high removal efficiencies were obtained. However, as particle buildup occurred on the portions of the fibers with the high-gradient magnetic field, the "magnetic capacity" of the filter for the paramagnetic Fe_2O_3 decreased and the primary mechanism for removal became mechanical separation. Mechanical separation probably occurred in the regions where several fibers intersected to create a web-like lattice structure. As entrapment in the web-like areas increased, the mechanical separation efficiency also decreased as shown in Figure 12. It can be hypothesized that the mechanical separation was not highly flow dependent. Thus, in the latter portions of the loading experiments where mechanical separation dominated, the removal efficiency would be independent of flow rate.

It should be noted that the feed concentrations of the loading tests (180 to 1250 ppm) greatly exceeded the maximum concentrations (20 to 90 ppm) anticipated in an actual decontamination. It is entirely possible that different removal results might be obtained at lower particle concentrations. However, completion of similar loading tests with lower particle concentrations was not experimentally feasible with the existing apparatus and fabrication of an acceptable system was not warranted.

3.3.3 Recirculating Feed Tests

An experiment was conducted to evaluate the performance of the filter with a decreasing feed concentration. An 11-liter batch with an initial Fe_2O_3 concentration of 270 ppm was recirculated through the filter at a flow rate between 7 and 14 $\ell/sec/m^2$. Instead of NTA, water was used as the feed solution to eliminate the dissolution of Fe_2O_3. The experiment was terminated after 29 hours at which time the Fe_2O_3 concentration was 7 ppm. The results are plotted in Figure 13.

3.3.4 Backwashing Tests

At the conclusion of each of the filter loading tests (Section 3.3.2), the power to the magnet was turned off and a backwashing test conducted. The first step was to flush the filter matrix at 200 $\ell/sec/m^2$ in the reverse direction as shown in Figure 10. Typically, approximately 20 bed volumes of water at 90°C were flushed through the filter. The flow was then switched to the forward direction as shown in Figure 8 and again flushed at 200 ℓ/sec/m^2 with approximately 20 bed volumes. Then, the filter matrix was flushed at 600 ℓ/sec/m^2 in both directions with approximately 15 bed volumes of water at 20°C. The filter tube was then removed and cleaned ultrasonically. Essentially no additional Fe_2O_3 was removed by the ultrasonic cleaning. The results (Table 8) indicate the filter can be effectively backwashed. The quantity of liquid required for backwashing probably could be reduced considerably from the approximately 55 bed volumes used in the laboratory tests.

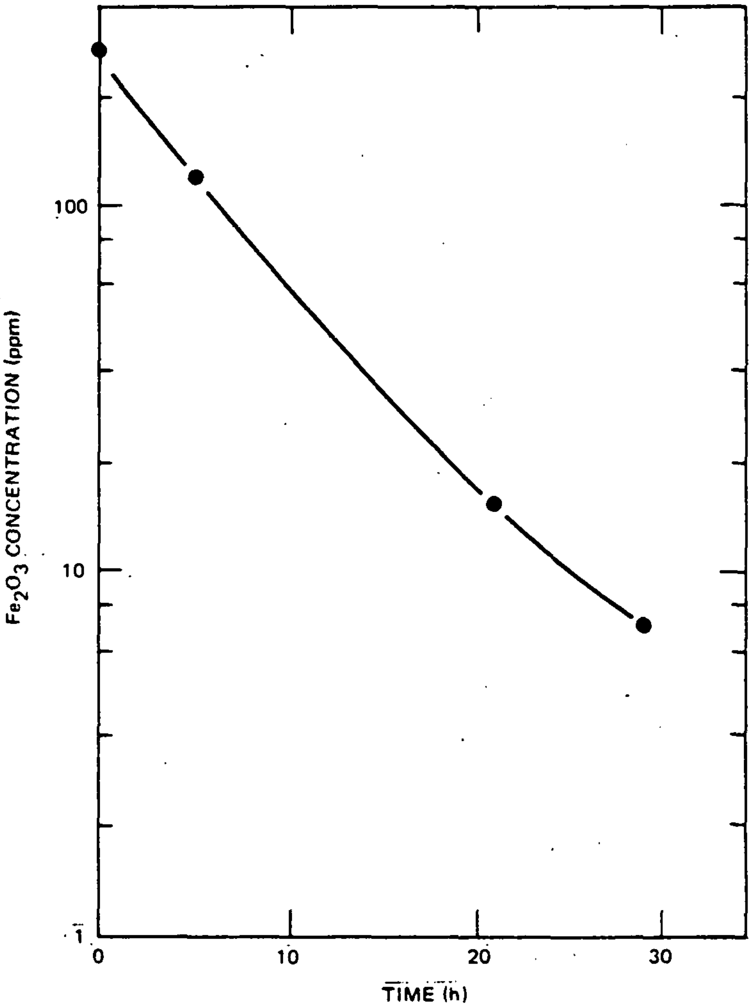

FIGURE 13. Fe_2O_3 REMOVAL IN A RECIRCULATING SYSTEM

TABLE 7. Backwashing Tests

Flow Rate (ℓ/sec/m^2)	Flow Direction	Temperature (^{o}C)	Fe_2O_3 Removed (%) Test 1	Test 2	Test 3
200	reverse	90	87	83	91
200	forward	90	6	8	8
600	both	20	7	9	1
Ultrasonic Cleaning	-	20	0	0	0

3.4 VNC DECONTAMINATION TEST LOOP – R.L. Hobart, J.P. Peterson, R.E. Gest

The pre-operational testing of the VNC test loop was successfully completed using a section of uncontaminated pipe. All instrumentation has been calibrated.

A 0.76-m section of 15.2-cm diameter piping was prepared from the inventory of Nine Mile Point pipe. The first test will be conducted using 0.01M NTA and 0.01M ascorbic acid. The nominal temperature will be 90^{o}C. The pH will be adjusted initially to 3.5 and maintained by injection of NH_4OH or by passing the solution through hydrogen-formcation-exchange resin. The dissolved oxygen concentration will be maintained at a low level by using nitrogen as the cover gas.

4. TASK 2 – CORROSION PRODUCT CHARACTERIZATION

There were no major activities during this report period.

5. TASK 3 – CORROSION TEST PROGRAM – D. E. Wax

Several potential major corrosion concerns (such as, general corrosion, intergranular attack, and stress corrosion cracking) associated with the application of a dilute chemical decontamination process to an operating BWR have been identified.[1] During the process development stage, it was not practical to evaluate all of these concerns for each potential reagent. However, general corrosion was evaluated as an integral part of the process development to ensure that the potential reagents and conditions did not dissolve excessive amounts of base metal.

During this report period, static general corrosion tests were completed in support of the process development activities. The primary emphasis was placed on low alloy steel experiments.

5.1 LOW ALLOY STEEL CORROSION ALLOWANCE

The acceptance criterion for the corrosion rate of low alloy steels in a dilute chemical decontamination process was established by assuming that 50% of the total corrosion allowance (1mm or 800mg/cm^2) provided for low alloy steels in BWR systems could be utilized in repetitive decontaminations. Dividing the 50% value by an estimated 20 decontaminations during the 40-year life of a BWR gave a corrosion allowance of 20 mg/cm^2 per decontamination. By assuming the corrosion rate was linear for a 12-hour decontamination, a 6-hour corrosion rate goal of 10 mg/cm^2 was obtained. The assumption of a linear corrosion rate for 12 hours is conservative, since the corrosion rate of low alloy steels decreases significantly after approximately 6 hours in dilute solutions of the reagents investigated .

5.2 EXPERIMENTAL TECHNIQUES

The general corrosion tests were conducted in 1-liter, 3-neck, round-bottom flasks. Each flask was equipped with a thermometer, gas purge line, and reflux condenser. The flasks were heated with heating mantles which were controlled by variable transformers.

In each corrosion test, 700 ml of test solution was introduced into the round-bottom flasks. The solution was sparged with the selected cover gas for a minimum of sixteen hours before heating was initiated. Nitrogen was used as the sparge gas when low dissolved oxygen concentrations were desired, while oxygen or air were used when oxygenated solutions were desired. Sparging was continued throughout the test to provide gentle mixing and to maintain the desired dissolved oxygen concentration. No mechanical agitation was used. The nominal temperature for all tests was 90°C.

The systems were susceptable to major chemical changes because of the dilute concentrations (0.01 M) of reagents used in the tests. As the corrosion process proceeded and the iron concentration in solution increased, hydrogen ions and complexing capacity were consumed. Consequently, the ratio of solution volume to coupon surface area was selected both to provide experimental convenience and minor changes in the system chemistry for solutions which produced acceptable corrosion rates. However, in tests where the corrosion rates of the low alloy steel were excessive, the pH changes were significant; for example, the pH in a corrosion test with uninhibited 0.01 M NTA increased from 3.5 to 8.0 during the test. However, the corrosion rate (16 $mg/cm^2/6h$) during this test was excessive, and this system was considered unacceptable from a corrosion standpoint. Thus, while the changing pH and residual complexing capacity may have had an effect on the actual corrosion rate measured, they had no effect on the conclusion drawn from the experiment.

The corrosion coupons were prepared by cutting a standard bent-beam specimen[1] (7.6 X 0.9 X 0.2 cm) through the weld region to form two approximately equal sections. Prior to the corrosion tests the coupons were:

1. ultrasonically cleaned in hot detergent water for 10 minutes,
2. rinsed in tap water,
3. rinsed in distilled water,
4. ultrasonically cleaned in acetone for 10 minutes,
5. dried in air, and
6. weighed.

After the test, the coupons were:

1. rinsed in distilled water,
2. ultrasonically cleaned in acetone for 10 minutes,
3. dried in air, and
4. weighed.

5.3 SCOPING TESTS

Six-hour static corrosion tests were conducted to evaluate the general corrosion rates of a low alloy steel (A508) in 0.01 M solutions of oxalic acid, EDTA, NTA, and citric acid. Three tests, each with a different initial pH, were conducted with each reagent. The EDTA, NTA, and citric acid tests were conducted using N_2 as the sparge gas, while the oxalic acid tests were conducted using 0_2 as the sparge gas. In addition, an experiment with oxalic acid at pH 3.5 was conducted with N_2 as the sparge gas. The results are given in Table 9.

The corrosion rates in oxalic acid with both sparge gases were aceptably low. The dissolved oxygen concentration did not have a significant effect on the low alloy steel corrosion rate. However, in the experiment with N_2, the coupon had a tenacious ferrous oxalate film which had to be removed with a stainless steel brush to obtain an accurate corrosion rate.

TABLE 8. Scoping Tests

(0.01 M, A 508, 6h, 90°C)

Reagent	Sparge Gas	pH Initial	pH Final	Weight Loss (mg/cm^2)
Oxalic Acid	0_2	3.0	3.9	2.4
Oxalic Acid	0_2	3.5	5.5	3.5
Oxalic Acid	0_2	4.0	5.5	2.5
Oxalic Acid	N_2	3.5	4.0	2.2
EDTA	N_2	3.0	—	33
EDTA	N_2	3.5	—	25
EDTA	N_2	4.0	—	19
NTA	N_2	3.0	7.7	17
NTA	N_2	3.5	8.2	16
NTA	N_2	4.0	8.3	16
Citric Acid	N_2	3.0	3.9	18
Citric Acid	N_2	3.5	4.1	15
Citric Acid	N_2	4.0	4.3	14

The corrosion rates in EDTA, NTA, and critic acid were excessive. Utilization of these reagents in a dilute chemical decontamination process will probably require the inclusion of a corrosion inhibitor. Consequently, the remaining tests with these reagents were focused on identifying an acceptable corrosion inhibitor.

Additional static corrosion tests were conducted with 0.01 M oxalic acid to evaluate the effect of contact time on the corrosion rate of A508 and to evaluate the corrosion rate of Type-304 stainless steel. The results of these tests are given in Table 10. The data indicate the corrosion rate of A508 decreases significantly between 6 and 40 hours of contact time. Also, the corrosion rate of Type-304 stainless steel in 0.01 M oxalic acid is acceptably low.

TABLE 9. Additional Oxalic Acid Tests

(0.01 M, 90°C, 0_2)

Material	Time (h)	pH Initial	pH Final	Weight Loss (mg/cm^2)
Type-304 Stainless Steel	24	3.0	3.4	0.2
Type-304 Stainless Steel	24	3.3	3.8	0.2
Type-304 Stainless Steel	24	4.0	4.2	0.4
A508	40	3.0	4.8	6
A508	40	3.5	4.9	4
A508	40	4.0	5.2	3

5.4 INHIBITOR AND ADDITIVE TESTS

The excessive corrosion rates of A508 in dilute solutions of NTA, EDTA and citric acid indicated that an acceptable corrosion inhibitor needed to be identified if these reagents were to be used in a dilute chemical decontamination process. Screening tests using 0.01 M NTA were conducted with several additives and corrosion inhibitors. NTA was selected as the test reagent because a regeneration scheme had been identified for NTA but not for EDTA.[2] The experimental conditions and results are given in Table 11.

Phenylthiourea was the only chemical additive that reduced the corrosion rate of A508 in solutions of 0.01 M NTA to an acceptable level. However, because certain sulfur compounds (such as, polythionic acid) initiate stress corrosion cracking in austenitic stainless steel and nickel-base alloys,[14] no sulfur-bearing compounds will be used in the dilute chemical decontamination solvent formulation.

TABLE 10. Inhibitor and Additive Tests
(0.01 M NTA, A508, 6h, 90°C, N_2, pH 3.5)

Inhibitor/ Additive	Concentration (M)	Weight Loss (mg/cm^2)
Ascorbic Acid	0.005	16
Hydrazine	0.005	12
Dimethylamine	0.005	17
Maleic Acid Hydrazide	0.02	11[a]
Quinaldine	0.025	9[a]
Triethanolamine	0.02	13[a]
Phenylthiourea	0.01	0.14
Phenylthiourea	0.001	2

a - Test duration 5h

6. TASK 4 – PILOT LOOP DEMONSTRATION

There were no major activities during this report period.

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