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STEAM-GENERATOR CHEMICAL-CLEANING PROJECT

STEAM-GENERATOR DILUTE CHEMICAL-CLEANING PROGRAM

ANNUAL REPORT
FOR THE PERIOD
PROGRAM START THROUGH 1980

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS USED IN THIS REPORT

AISI	American Iron and Steel Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing Materials
CECO	Commonwealth Edison Company
CRC	Commonwealth Research Corporation
C/S	Carbon Steel
DETU	Diethylthiourea
DOE	Department of Energy
DTPA	Diethylenetriaminepentaacetic Acid
EDTA	Ethylenediaminetetraacetic Acid
EPRI	Electric Power Research Institute
HAZ	Heat Affected Zone
HEEDTA*	Hydroxyethylethylenediaminetriacetic Acid
LPR	Linear Polarization Resistance
NSSS	Nuclear Steam Supply System
PWR	Pressurized Water Reactor
SA	Steel Alloy
SG	Steam Generator

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*Sometimes known as HEDTA.

ABSTRACT

Vertical U-tube steam generators in Pressurized Water Reactors (PWRs) operating an All Volatile Treatment (AVT) secondary chemistry have experienced corrosion problems that must be resolved to keep these generators in service. Concentration of acid chlorides and other impurities in the crevices between the tube support plates and the Inconel 600 tubes during normal operation causes enhanced corrosion of the support plate material. Corrosion products in the crevice are nearly pure magnetite and increase in volume until the crevice is completely filled and the Inconel tube is deformed beyond its yield point. This phenomenon is known as "denting"

A further problem occurring in PWR steam generators is the introduction of loose corrosion products and impurities from the feedwater system, which then deposit on steam generator surfaces. These deposits are generally referred to as "sludge", and the accumulation tends to be the heaviest on the steam generator tubesheet.

The studies reported herein evaluate the feasibility of using a low-concentration (0.5 wt%) chemical cleaning process to remove corrosion product deposits from steam generator surfaces and magnetite from tube-to-support plate crevices of PWR steam generators. The process potentially may be applied at schedule intervals, such as during normal refueling outages, to maintain a steam generator in clean operating condition.

This report describes the results of testing to evaluate the effectiveness of several chelant acids for dissolving steam generator sludges and crevice magnetite. Corrosion of carbon steel by the chelant acids and the effects of varous inhibitors are evaluated. The effectiveness of ion-exchange regeneration of several chelant-based solvents is also addressed.

SECTION 1.0

INTRODUCTION

1.1 BACKGROUND

Accumulation of corrosion products and impurities (sludge) on the secondary side of vertical steam generators continues to be an operational problem for many PWR plants. Steam generator sludges consist primarily of metal oxides and metallic copper deposits distributed non-uniformly throughout the generator. Most of the sludges settle to the tubesheet or support plate surfaces where they can remain as a loose deposit or agglomerate into a rock hard layer. Sludges baked onto the steam generator tube surfaces reduce heat transfer properties. In either case, these deposits can cause rapid localized corrosion of the tubes and support plates. A major concern is the buildup of these impurities and subsequent concentration of dissolved chemicals in the tube-to-support plate crevice areas, causing accelerated local corrosion and eventual tube denting.

Commonwealth Research Corporation (CRC) initiated a DOE-sponsored program in 1980 to evaluate the concept of using dilute chemical cleaning processes to remove the corrosion deposits from PWR steam generators. As a participant in this program, UNC Nuclear Industries (UNC) was contracted to (1) identify a dilute, regenerable cleaning process, (2) conceptually design the equipment, and (3) demonstrate the cleaning process on a model steam generator.

The quantity and composition of sludge requiring removal varies widely from plant to plant because of differences in secondary water treatment, length of operating time between sludge lancing, quality of the returning condensate, and operational history. "Typical" sludge quantities and distribution for a steam generator which could be considered a candidate for chemical cleaning using a dilute process are indicated in the following table:

Location of Deposit	Approximate Quantity (lb)
Tubesheet	100 to 500
Internal Surfaces	250 to 1000
Support Plate Crevices	50 to 200

Even the lowest estimated sludge quantity (400 lb) poses a formidable problem for a dilute cleaning process designed to remove surface deposits and clean the support plate crevices, without extending outage time. Conceptually, the application time of a dilute chemical cleaning process should permit periodic application during normally scheduled plant outages to maintain a steam generator in clean condition.

Large amounts of sludge could be removed using relatively high chemical concentrations (5 to 10%), but the solvents may be too corrosive for repeated applications and the resultant large quantity of liquid waste would pose a significant disposal problem. A dilute chemical cleaning process would be potentially less corrosive, and with in-situ solvent regeneration, would minimize waste as shown below. (The data shown are based on a steam generator liquid volume of 20,000 gal for cleaning, and two solvent applications required for either process to remove iron deposits.)

ESTIMATED WASTE PER SG CLEANING

Process	Chemical Requirements	Type of Chemical Wastes	Volume of Waste
Conventional Cleaning	33,400 lb (at 10% Conc)	Liquid	40,000 gal (Conc) 40,000 gal (Rinse)
Dilute Chemical Cleaning	1,000 lb (at 0.3% Conc)	Solid (IX Resin)	5,980 gal (800 cu ft)

1.2 PROCESS CONCEPT

Conceptually, a dilute solvent at a concentration of about 0.3 wt% would be circulated through the steam generator at some temperature below boiling. The solvent would dissolve the sludge and crevice deposits, forming soluble complexes during its residence in the steam generator. The solvent would exit the steam generator and be passed through an ion-exchange material, where the metal ions would be removed from the complex, and the restored solvent recycled to the steam generator. The ion-exchange process would likely be carried out using a strong acid cation-exchange resin operating at or near the temperature of the solvent in the steam generator.

Dilute chemical processes are being studied in the U.S. and are currently used in Canada for decontaminating portions of commercial nuclear reactor primary systems. The dilute chemical decontamination process provides a basis for establishing the feasibility of using dilute reagents to clean the secondary side of nuclear steam generators. The cleaning would be performed during routine reactor shutdowns without extending the outage. A logic diagram for the conceptual process is shown by Figure 1-1.

When application of the cleaning process is first scheduled, a sludge lance is followed by a one-time application of a bulk sludge cleaning step. The sludge-lance and bulk-sludge cleaning remove surface deposits. Bulk sludge removal prevents excessive depletion of the solvent by fouled surfaces during the dilute chemical cleaning step.

The original concept as shown in Figure 1-1 assumes the dilute process is to be applied to a PWR plant that has operated several years, resulting in "typical" steam generator sludge loadings of 400 to 1700 lb. In this case a sludge-lance operation followed by a one-time application of a high-concentration solvent would be necessary to remove accumulated sludge deposits before the dilute cleaning process could be effective. Thereafter, the dilute process would be applied periodically as a preventive maintenance measure to prevent accumulation of detrimental quantities of loose sludges and to remove corrosion products from the tube-to-support plate annuli, thus preventing tube denting. For newly operational steam generators or steam generators which are not heavily fouled, the dilute process could be used periodically to maintain the generators in a clean condition, without a prior high-concentration cleaning.

1.3 DILUTE CHEMICAL CLEANING PROGRAM

The UNC dilute chemical cleaning program is one phase of the DOE-sponsored Steam Generator Cleaning Program being managed by CRC. The objective of the dilute chemical cleaning program is to evaluate the feasibility of using a regenerative, low-concentration solvent to chemically clean the secondary side of a fouled PWR generator. The selected process should dissolve moderate quantities of surface corrosion deposits and effectively clean the corrosion products from SG tube support plate crevices with minimal corrosion. If successful, the process may be demonstrated by application at the Commonwealth Edison (CECO) Zion station to qualify it for general use.

The program is divided into four major tasks:

Task 1 - Plant Inspections (Section 3.0)

Task 2 - Process Development (Section 4.0)

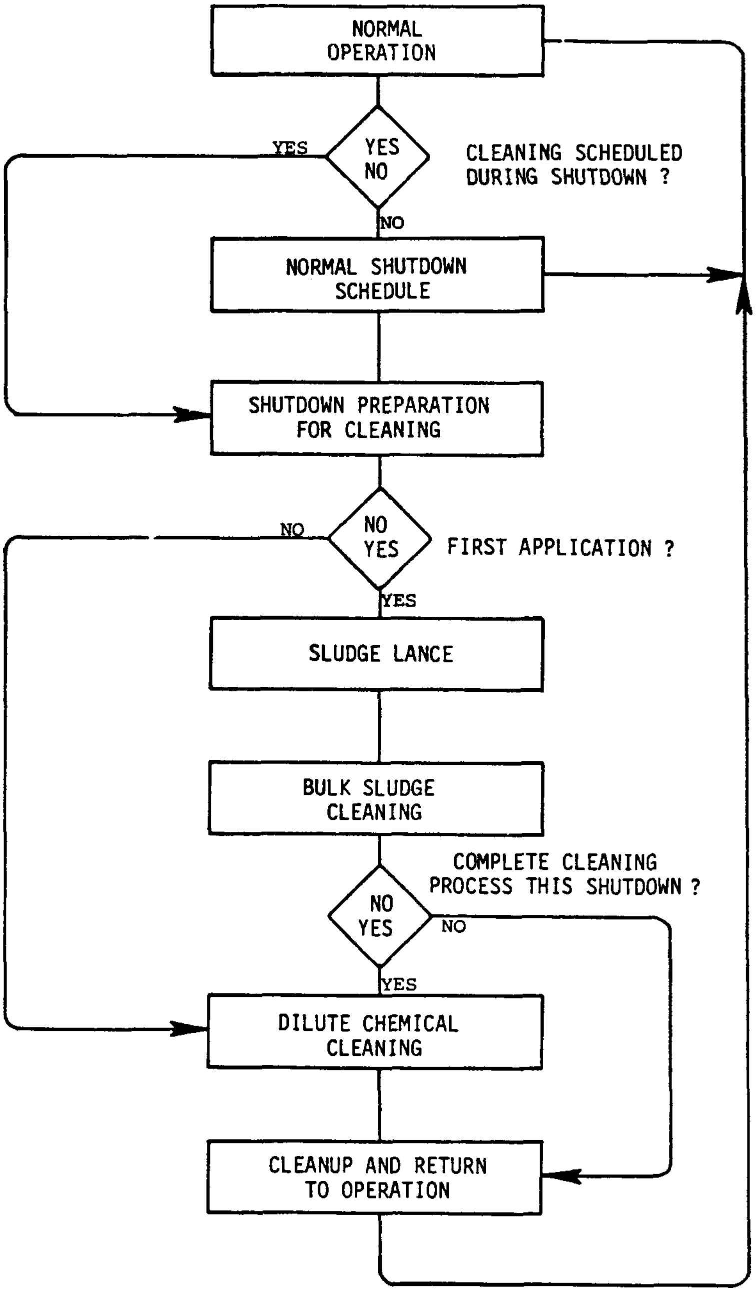

FIGURE 1-1. Logic Diagram for Dilute Steam Generator Chemical Cleaning Process.

Task 3 - Design for Plant Modification and Process Equipment
(To be covered in later report)

Task 4 - Cost Estimation (To be covered in later report)

Each major task is divided into subtasks, and where necessary further divisions have been made to address specific experimental work.

Criteria established to determine the success of this program include:

- The dilute chemical cleaning process can be applied during routine reactor outages, thus avoiding loss of revenue from extended reactor downtime.

- The final dilute solvent and cleaning process can be demonstrated on one or more DOE/CRC model steam generators. This demonstration will include a low-concentration (< 0.5 wt%) crevice cleaning operation.

- The dilute chemical cleaning process will be a repetitive process which generates smaller waste volumes than conventional chemical cleaning via fill and drain. All wastes produced will be in solid form.

- The dilute process to be demonstrated using the model steam generators can be scaled up for use on operating PWR steam generators.

SECTION 2.0

SUMMARY

This report presents a detailed description of studies carried out from the initiation of the program through December 31, 1980. Experimental studies carried out during this report period were essentially screening tests to identify a suitable dilute solvent composition to (1) maximize sludge dissolution and (2) minimize corrosion effects. Several candidate chelants, organic acids and inhibitors were evaluated.

Studies were also carried out with several solvents to determine the feasibility of ion-exchange regeneration of depleted solvents.

The solvent-screening studies were carried out at a temperature of 95°C with periodic analyses made to determine the amount of sludge dissolved as a function of contact time. In addition, the final dissolution was confirmed by weighing the residual sludge at the end of the test. Corrosion effects were determined from calculations based on coupon weight loss. Appendix A describes the actual experimental methods in detail.

The feasibility of solvent regeneration by ion exchange was determined by passing spent dilute solvent downflow through various ion-exchange materials. Analyses of the influent and effluent were made to determine iron removal, copper removal, and degree of restoration of the dilute solvent by ion-exchange regeneration. Appendix A provides a detailed description of the experimental procedure used for the determination of dilute solvent regenerability.

Highlights and conclusions derived from the test data follow.

- Inhibitor screening studies were conducted using a solvent known to be effective for dissolving actual SG sludge (citric acid and HEEDTA at pH 3.5). As a result of this testing, the number of candidate inhibitors was reduced from sixteen candidates to two. These are diethylthiourea and cinnamonitrile (see Section 4.3).

- Surfactants or wetting agents did not provide any significant advantage. They were deleted as constituents from the dilute solvent formulations.

- Inhibitors will be required to reduce the carbon steel (C/S) corrosion by dilute solvents to the target criterion of < 1 mil/day.

- In the presence of hydrazine, steel alloy SA533A (shell alloy for Westinghouse SGs) exhibits an increased corrosion sensitivity that is dependent upon the hydrazine concentration. This selective corrosion is essentially eliminated by reducing the hydrazine concentration to 200 ppm and using ammonium hydroxide for pH control (see Section 4.4.1.4).

- Testing identified commercially available magnetite that exhibits dissolution characteristics equivalent to actual Zion sludge in dilute solvent systems, permitting testing with nonradioactive synthetic sludge formulations (see Section 4.2.3).

- The ion-exchange process using hydrogen-form strong acid cation-exchange resin does not regenerate chelants (DTPA, EDTA, or HEEDTA), and exhibits only marginal removal of chelated iron (see Section 4.4.2).

SECTION 3.0

TASK 1 - PLANT INSPECTIONS

3.1 TASK DESCRIPTION

The objective of Task 1 is to acquire familiarity with operating plants, to scope siting and installation of new equipment for SG cleaning, and to evaluate the condition of typical PWR steam generators that may be cleaned to demonstrate the dilute process concept. CRC has identified the Zion 1 or 2 units as potential candidates for cleaning demonstrations; Task 1 includes work to review appropriate Zion technical information and drawings covering the:

- Steam generators
- Feed and steam systems
- Radwaste handling system
- Blowdown system
- General plant arrangements

This task also provides for site visits and steam generator inspections to determine:

- Condition of crevices
- Nature of sludge and corrosion products
- Radioactivity levels expected

3.2 PLANT FAMILIARIZATION

UNC personnel visited the Zion plant in August, 1980 to obtain an overview of the general plant layout and construction features for those in-plant systems which could potentially be used for chemical cleaning of the steam generators using the dilute process concept.

The plant tour identified several acceptable points to tie-in to the steam generator secondary side with little or no modification of existing systems and with minimum exposure required for installation and removal of temporary equipment.

Photographs were taken of several potential equipment locations, including the Blowdown and Feedwater Systems where existing flanged connections could be removed to install temporary spool pieces for providing solvent recirculation and nitrogen gas sparge. Existing mixed-bed ion exchange units and associated resin handling equipment are already in place at the Zion Station for treatment of SG blowdown wastes. These units could be used for either solvent on line regeneration or final solvent removal, further reducing requirements for installation of temporary equipment. All photographs and detailed notes of observation made during the plant tour are on file for reference in development of design concepts for demonstrating the dilute cleaning process.

3.3 STEAM GENERATOR EVALUATIONS

A large quantity of actual sludge was obtained from the CECO's Zion 1 steam generators during a water lance performed in October, 1979. Chemical analysis results were used to formulate a non-radioactive sludge that could be used for laboratory studies. Composition of the Zion 1 sludge is presented in Table 3-1. Suitability of the synthetic sludge for use as a testing substitute for actual Zion SG sludge was established by work described in Section 4.2.3.

Calculations of steam generator surface areas, and identification of materials of construction were based on general arrangement drawings of the Westinghouse Model 51 SGs installed at the Zion Station. The results of these calculations are given in Table 3-2.

Estimation of total SG sludge quantities and expected solvent sludge loading in g/ℓ is shown in Table 3-3 for the Zion SGs. Surface sludge film thickness was estimated from Commonwealth photographs. The data developed in Tables 3-1 and 3-2 are used to estimate the amount of sludge to be removed, and to establish performance requirements for the dilute cleaning process.

Based on the photographic evidence, the Zion steam generators are not highly fouled.

TABLE 3-1

COMPOSITION OF ZION SG SLUDGE

Radionuclides	μCi/g
^{60}Co	5.0×10^{-4}
^{58}Co	3.4×10^{-4}
^{137}Cs	0.36×10^{-4}

Major Composition	~wt%
Fe_3O_4	60
Fe_2O_3	30
Cu	10

Elements	wt%*	Elements	wt%*
Fe	65.3	Zn	0.17
Cu	4.99	Ca	0.47
Ni	0.74	Na	0.08
P	0.40	Pb	0.05
Mn	0.66	K	0.08
Cr	0.27	Co	0.06
Si	0.16	Mg	0.14
Al	0.13		
Total Metals	73.7 wt%	Insoluble Residue	0.8 wt%

* Average of duplicate analysis by ICP emission spectrometer.

TABLE 3-2

CHARACTERISTICS OF ZION STEAM GENERATORS

Structural Component	Alloy[a]	Area (sq ft)	Ratio (gal/sq ft)
Tubes	IN600	51,500	0.43
Tube Sheet	SA508	77	288
Support Plates (7)	SA285C	1,622	13.7
Wrapper	SA285C	2,572	8.61
Shell	SA533A	1,383	16.0

[a] ASME alloy designations.

TABLE 3-3

ESTIMATED SLUDGE LOADING FOR THE ZION STEAM GENERATORS

Location	Estimated Quantity (lb)	
	Without Lancing	With Lancing
Tubesheet Accumulation	425	212
Tubing Film (0.2 mil)	278	278
C/S Film (2.0 mil)	306	306
Crevice Sludge[a]	98	98
Total	1107	894
Overall Sludge Conc (g/ℓ)[b]	6.07	4.89

[a] All crevices filled Magnetite density 5.2 g/cm.

[b] Internal volume 22,138 gallons.

SECTION 4.0

TASK 2 - PROCESS DEVELOPMENT

4.1 TASK DESCRIPTION

The objective of Task 2 is to identify a suitable solvent and application process for chemically cleaning mildly fouled steam generators, and to demonstrate process feasibility by applying the process to a pilot-scale model generator fouled under representative faulted chemistry conditions. Task 2 includes the development and demonstration work required to establish the validity of the proposed process for application in a separate subsequent project to clean a nuclear steam generator.

All laboratory work is included in this task. The concentration of the dilute cleaning solution for the crevice cleaning step is expected to be < 0.5 wt%.

Candidate dilute solvent formulations will be evaluated for effectiveness of sludge dissolution, crevice cleaning ability, corrosiveness to steam generator materials of construction, and ease of waste processing.

A pilot scale steam generator cleaning is to be demonstrated with the proposed dilute solvent process on one or more DOE model steam generators. The demonstration is to provide data suitable to scale up the design for application to a nuclear steam generator.

4.2 MATERIALS TEST PLAN

This portion of Task 2 is the evaluation of corrosion effects of the dilute cleaning solvents on steam generator materials of construction.

4.2.1 Selection of Test Alloys

The materials used in this work were identified as the major structural materials. The ASME grades with major areas of use are listed below.

ASME ALLOY NO.	SG LOCATION
IN600	Tubes
SA285C	Support Plates & Wrapper
SA533A	Shell
SA508	Tubesheet

The plate materials from which the coupons were prepared are identifiable as to source and heat number. Chemical composition and the mechanical test data for each alloy heat are maintained on file. Several additional alloys, which would be contacted by solvent during a field application of the dilute cleaning process, were purchased during this report period for testing in later phases of the program.

4.2.2 Fabrication of Corrosion Specimens

The materials test program utilized two types of coupons:

1. Uniform corrosion test coupons

2. U-Bend stress corrosion test specimens

Uniform corrosion test coupons and U-bend stress corrosion coupons were prepared from welded material as well as from untreated plate material to evaluate corrosion of weld Heat Affected Zones (HAZ).

4.2.2.1 Uniform Test Coupons

Fabrication of the two sizes (4.75 in. x 0.5 in. x .062 in. and 1.50 in. x 1.0 in. x .062 in.) of uniform corrosion test specimens followed the guide lines of ASTM G4, Standard Recommended Practices for Conducting Plant Corrosion Tests, Section 5, "Preparation of Test Specimens," and ASTM G-31, Standard Recommended Practice for Laboratory Immersion Corrosion Testing of Metals, Section 5, "Test Specimen." The coupons were cut from plate material in a manner to orient the large coupon surfaces parallel to the rolled surface area of the parent plate metal. All specimens cut from a particular heat were oriented in the same manner by use of cut maps to assure that the axes of all coupons were in the same alignments as cut from the parent material.

All coupons, except Inconel specimens, were bandsawed from the parent material, then wet ground to size. Wet grinding produced a finish that was approximately 30 micro-inches. Final surface preparation for testing was produced by finishing with a 120-grit aluminum oxide cloth. Inconel specimens were sheared from 0.050 in.-thick sheet material then edge ground to remove work hardened material. All mounting holes were drilled, rather than punched, to avoid work hardening.

Welded uniform corrosion specimens were cut and finished by the same procedures as unwelded specimens. To test HAZ corrosion, portions of the weldment and the full adjoining HAZ were cut with each specimen. The 4.75 in. x 0.5 in. strips contained a section of weld through the weld bead and the HAZ on each side of the weld section. The 1.5 in. x 1.0 in. rectangular specimens were cut to contain a partial section of weldment along the 1.0 in. edge plus the full width of HAZ from one side of the weld bead.

4.2.2.2 U-Bend Stress Specimens

The U-bend stress corrosion test specimens are duplicates of the 4.75 in. x 0.5 in. x .062 in. uniform specimens with mounting holes drilled at each end. The U-bends are hand bent over a round form of 0.5 in. radius using the two stage method of stressing according to ASTM G-30, Standard Recommended Practice for Making and Using U-Bend Stress Corrosion Test Specimens. Welded specimens were cut with the weld section slightly off center to place the HAZ area directly in the center of the coupon. The HAZ receives the maximum stress when the specimen is bent.

4.2.3 Zion Sludge vs Synthetic Sludge

As shown in Table 3-1, sludge obtained from the Zion SG is radioactive (8.8×10^{-4} μCi/g). As a result, a comparison dissolution test was conducted to determine if a sludge prepared from chemically pure oxides could be substituted for Zion Sludge to eliminate radioactive materials handling problems during the testing. The results of this comparison are given in Table 4-1.

Dissolution characteristics of the two sludges were nearly identical and all subsequent kettle tests to evaluate dilute solvent effectiveness for sludge dissolution were performed with the synthetic mixture.

4.3 INHIBITOR SELECTION

The initial testing for inhibitor selection was carried out with a solvent previously determined by UNC to be effective for dissolving actual deposits obtained from an operating PWR steam generator. The solvent formulation is 5 wt% citric acid, 3 wt% HEEDTA, and was adjusted to pH 3.5 with ammonium hydroxide. This solvent was chosen to increase the contrast of the corrosion results observed.

Eighteen kettle tests (three sets of six tests each) were performed to evaluate fourteen candidate inhibitors. Diethylthiourea (DETU), a known effective inhibitor, was used as a "benchmark" for each of the three sets of inhibitor test runs.

The objective of this study was to determine the relative effectiveness of selected inhibitors as compared to DETU for maximum sludge dissolution and minimum corrosion, and to identify, if possible, an effective sulfur-free inhibitor.

TABLE 4-1

COMPARISON OF LOOSE ZION SLUDGE AND SYNTHETIC SLUDGE IN DILUTE SOLVENT

Synthetic Sludge Composition	- 95 wt% Fe_3O_4	(Cerac lot 3278)
	- 5 wt% CuO	(Cerac lot 3561)

Solvent Composition	- EDTA	0.1 wt%
	- Citric Acid	0.1 wt%
	- Initial pH	3.52 ± 0.04
	- Hydrazine	200 ± 30 mg/ℓ

	Synthetic Sludge		Zion Sludge	
Time (hr)	Iron (mg/ℓ)	Copper (mg/ℓ)	Iron (mg/ℓ)	Copper (mg/ℓ)
0.5	47	67	110	55
1	96	81	162	65
2	172	70	185	41
3	210	33	186	16
4	214	--	196	--
5	223	--	222	--
6	222	24	223	16
Sludge Dissolution	68 wt%		69 wt%	

The tests were carried out in 4-liter glass kettles, each containing 3 liters of solvent with the candidate inhibitor. Temperature was maintained at 93 ± 2°C for 8 hours. Three materials of construction (SA285C, SA533A, and IN600) and 5.6 g of Zion sludge (3 pellets) were included in each test. Pelletized Zion sludge was used to approximate the worst case condition of densely packed corrosion product scales known to exist in some steam generators. The solid pellets also assured some undissolved sludge would remain to enable quantitative determination of any inhibitor effects on sludge dissolution efficiency.

Dissolved oxygen was controlled by continuously sparging the solvents with nitrogen at 200 cm^3/min. Corrosion readings were taken at frequent intervals during the 8-hour test period using a Corrator* probe fitted with AISI 1010 carbon steel electrodes. The Corrator is used to monitor and record corrosion rates by measuring the minute "corrosion currents" generated at the immersed electrodes. The electrochemical measurement technique is known as Linear Polarization Resistance (LPR). Total corrosion was also measured for three major SG alloys from weight loss calculations for coupon specimens. The percent sludge dissolution was determined by weighing the dry pellets before and after exposure. (Appendix A provides additional details of the test technique.)

The observed degree of sludge dissolution and corrosion rates are given in Table 4-2, together with a calculated value for inhibitor efficiency. Table 4-2 data show that results for the reference inhibitor (DETU) were consistent between each of the three test sets, establishing the validity of using the test results for comparison purposes.

All four of the sulfur bearing inhibitors (DETU, Chronox 272, Tretolite M-153, and CCI-80/1) controlled corrosion of SA285C and SA533A to less than 1 mil for the 8-hour test period, while allowing dissolution of from 5.7% to 9.5% of the available sludge. However, since sulfur has been frequently linked with intergranular attack on Inconel 600 steam generator tubes**, the low sulfur bearing inhibitors were considered less desirable than

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*Registered trademark of Rohrback Corporation.

**Unpublished EPRI and NSSS vendor data.

TABLE 4-2

RELATIVE EFFECTIVENESS OF SELECTED INHIBITORS

Inhibitor	Conc (wt%)	Surfactant wt%		Sludge Dissolution wt%	Corrosion (mil/day)			Inhibitor Eff (%)	
		Triton X-100(b)	Chevron NI-W(b)		285C	533A	IN600	285C	533A
None	None	0.05	0.1	16.4	9.9	22.2	0.004	--	--
Diethylthiourea	0.5	0.05	0.1	7.2	0.36	0.20	0.004	98.4	99.1
Dodecylamine	0.5	0.05	0.1	4.2	11.5	10.7	(a)	0	51.9
Octadecylamine	0.5	0.05	0.1	11.2	5.0	9.1	(a)	49.5	59.0
Tretolite CCI 80/1(b)	0.5	0.05	0.1	7.7	0.33	0.36	(a)	96.7	98.4
Tretolite M-153(b)	0.5	0.05	0.1	7.5	0.57	0.35	(a)	95.3	98.4
Diethylthiourea	0.31	None	0.1	9.9	0.28	0.30	0.007	97.2	98.6
Chronox - 272(b)	0.29	None	0.1	5.7	0.26	0.30	0.019	97.4	98.6
Cinnamonitrile	0.28	None	0.1	15.5	2.40	3.22	0.001	75.8	85.5
N-Methylmorpholine	0.30	None	0.1	19.4	12.3	24.3	0.004	0	0
Hexamethylenetetramine	0.31	None	0.1	14.8	12.0	20.0	0.004	0	9.9
Hexamethylenediamine	0.31	None	0.1	17.9	10.7	23.1	0.001	0	0
Diethylthiourea	0.31	None	None	9.5	0.28	0.27	0.007	97.2	98.8
Succinonitrile	0.31	None	None	15.4	2.16	13.2	0.006	79.2	40.5(c)
Cyclohexanone-Oxime	0.31	None	None	14.6	14.6	24.1	0.004	0	0
Adenine	0.31	None	None	16.2	6.7	12.8	0.005	32.3	42.3
1-Cyanonaphthalene	0.31	None	None	22.0	13.5	21.5	0.002	0	3.2
2-Cyanopyridine	0.31	None	None	30.8	11.2	23.3	0.026	0	0

(a) Not measured because of adherent copper plate.

(b) Trade names: exact composition or formulation is proprietary.

(c) Pinhole penetrations were observed in this coupon.

cinnamonitrile, which provided the highest inhibition of the non-sulfur inhibitors. Cinnamonitrile also allowed comparatively high dissolution (15.5%) of the available sludge. On this basis cinnamonitrile was selected for further study in evaluating candidate dilute solvents.

Figures 4-1 through 4-6 show corrosion rates as measured by the Corrator during the inhibitor screening tests. The average corrosion rate for the three diethylthiourea tests (Figure 4-1) is plotted as a dotted line on Figures 4-2 through 4-6 for reference. Corrator readings are not intended to provide accurate corrosion measurements, but are primarily used to monitor for changes in corrosion rate. Although the Corrator responses shown in the figures are for AISI 1010 C/S, which corroded at a lower rate than the two corrosion coupon alloys (SA533A and SA285C) shown in Table 4-2, they do illustrate the same degree of inhibitor effectiveness measured using actual corrosion coupon specimens.

Within the context of these experimental results it is evident that:

1. DETU is the most effective inhibitor for corrosion, but reduces sludge dissolution.

2. Cinnamonitrile provides acceptable inhibition of corrosion compared to DETU, without decreasing the rate of sludge dissolution.

3. A comparison of the performance of DETU with and without surfactants indicates that no significant benefit is realized with surfactants. Since sufactants have been known to affect ion-exchange processes, they will be deleted from future dilute solvent formulations.

The screening tests using the concentrated citric acid/HEEDTA reference solvent identified cinnamonitrile as the most effective sulfur-free inhibitor. It will be necessary in the development of a dilute chemical cleaning solvent to determine the concentration of cinnamonitrile required to keep corrosion levels below 1 mil/day. Although sulfur-bearing inhibitors are not expected to be suitable for the final process, diethylthiourea was retained in the program as an alternate nonproprietary inhibitor in the event that its sulfur content can be shown to be acceptable for steam generator use.

Future dilute solvent testing will establish if a threshold inhibitor concentration is required in dilute solvents or if the inhibitor concentration can be reduced proportionately with solvent concentration.

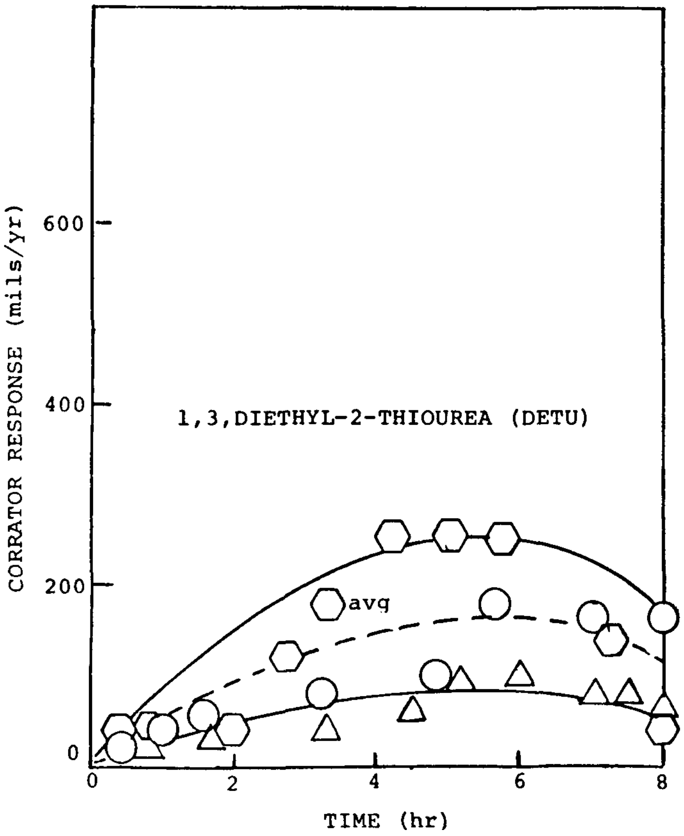


FIGURE 4-1. Effect of Inhibitor on Corrator Response - 1,3, Diethyl-2-Thiourea (DETU).

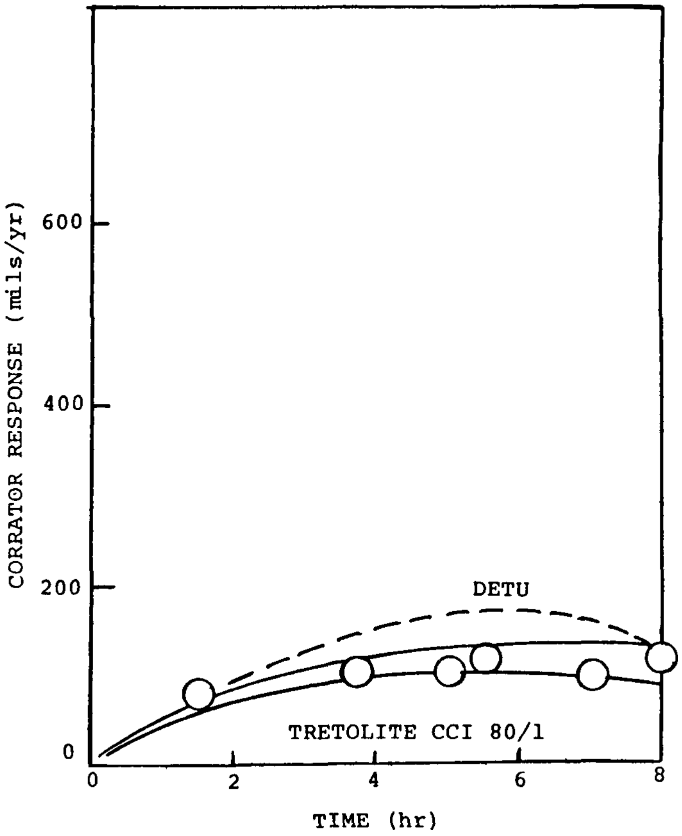


FIGURE 4-2. Effect of Inhibitor on Corrator Response (Tretolite 80/1).

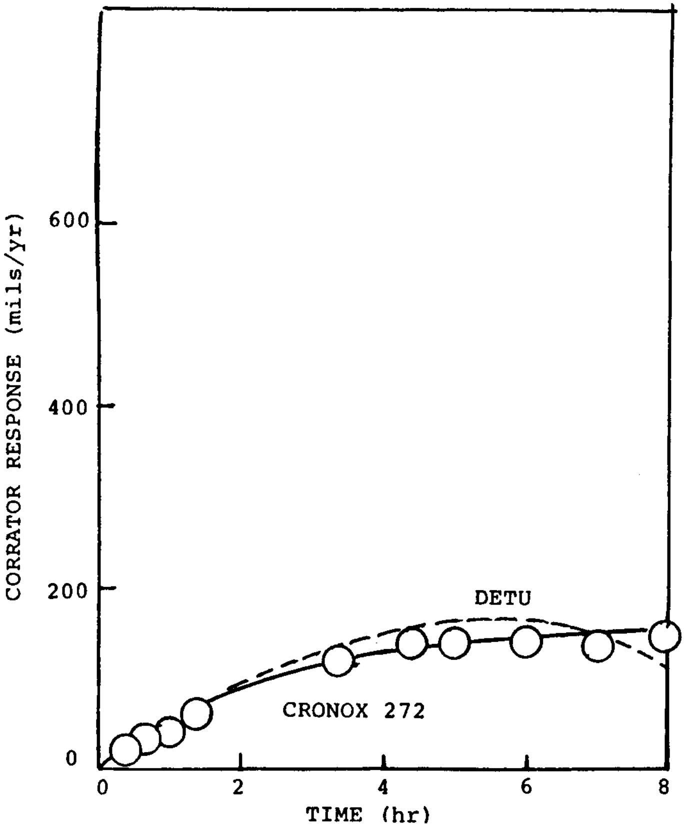


FIGURE 4-3. Effect of Inhibitor on Corrator Response (Cronox 272).

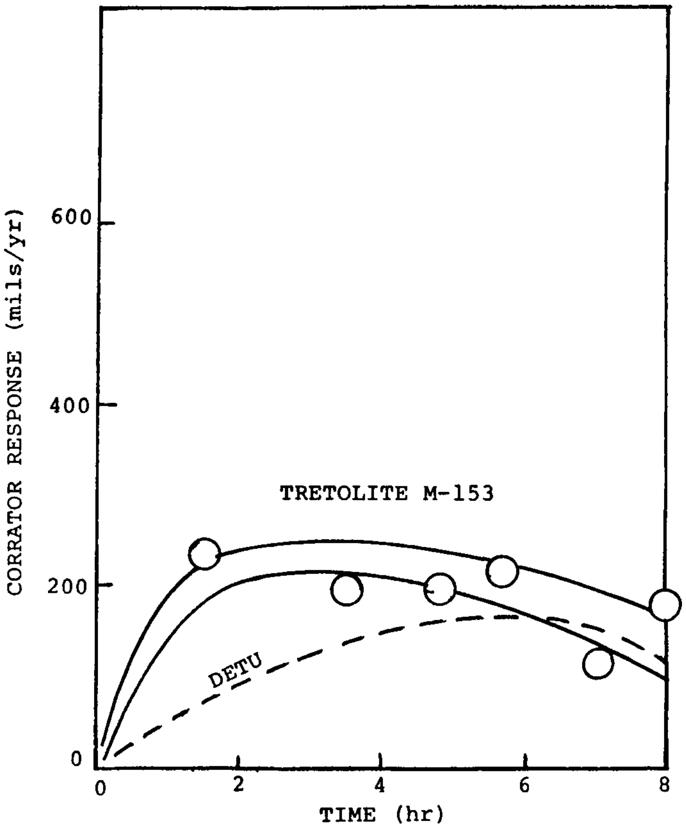


FIGURE 4-4. Effect of Inhibitor on Corrator Response (Tretolite M-153).

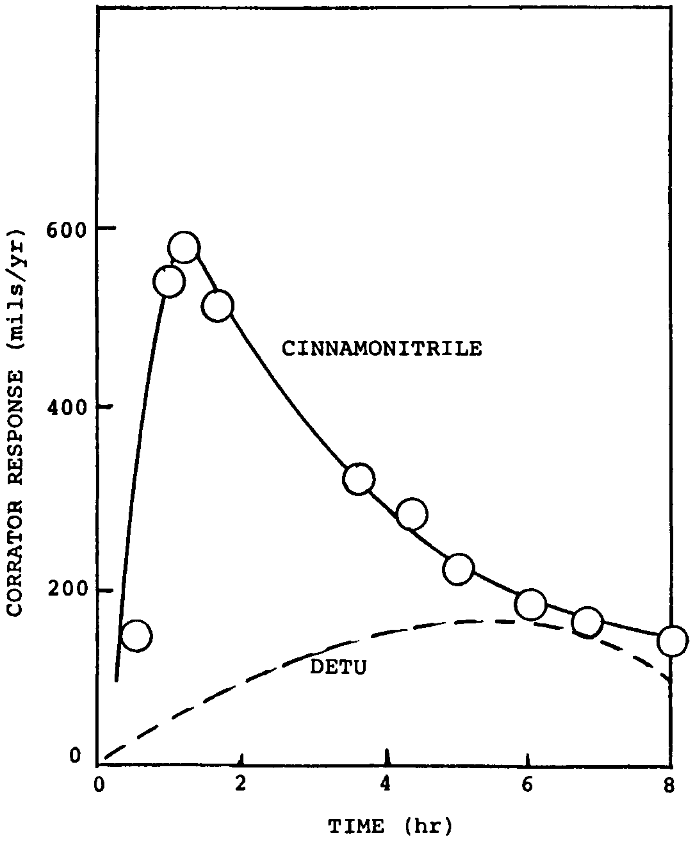


FIGURE 4-5. Effect of Inhibitor on Corrator Response (Cinnamonitrile).

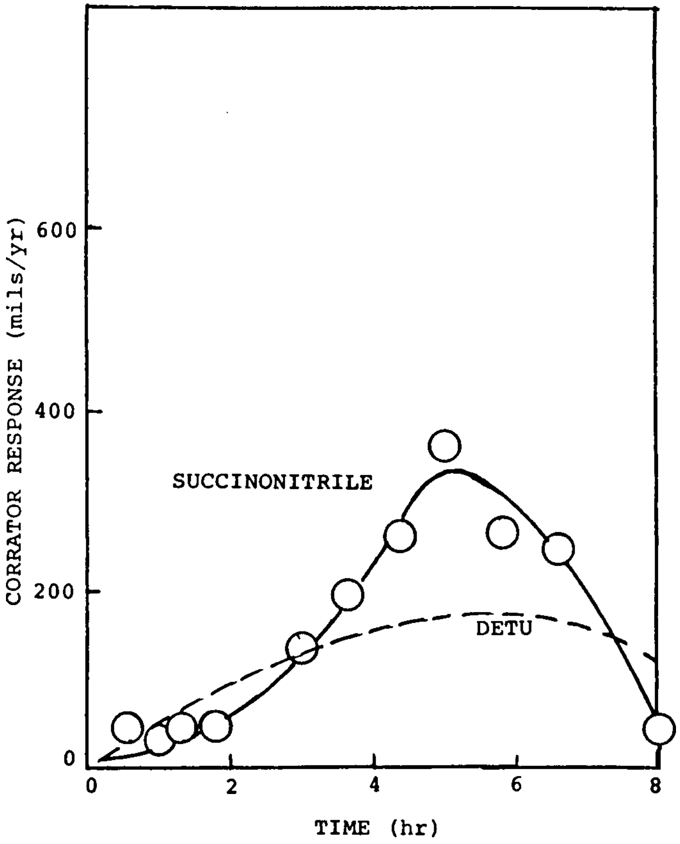


FIGURE 4-6. Effect of Inhibitor on Corrator Response (Succinonitrile).

4.4 SOLVENT DEVELOPMENT

4.4.1 Sludge Dissolution

This work was carried out to develop a dilute solvent formulation for maximum sludge dissolution and crevice cleaning effectiveness while maintaining minimum corrosion to steam generator materials of construction. The experimental method used was primarily a screening study in which a large number of tests could be completed in a relatively short time.

The dilute solvent screening studies were carried out using six 4-liter glass kettles. The kettles were maintained at a temperature of 93°C in an insulated and thermostatically controlled water bath. Each kettle was equipped with a condenser, nitrogen gas sparger tube, chemical addition tube, and sampling tube. A total of 48 kettle tests were completed. The detailed test procedure and equipment arrangement common to these tests are described in Appendix A.

4.4.1.1 Oxidizing vs Reducing Conditions

Six kettle tests with uninhibited solvents were carried out to evaluate the effect of oxidizing and reducing environments on the performance of dilute solvents.

The relative effects of oxidizing and reducing systems were determined by comparing dilute solvents containing hydrogen peroxide at ~0.1 wt% with dilute solvents containing hydrazine at ~0.05 wt%. In addition, oxalic acid at 0.05 wt% to 0.10 wt% was included in several of the kettle tests to determine its effect on sludge dissolution and corrosion. The solvent compositions and test results are shown in Table 4-3.

The overall corrosion under oxidizing conditions was about a factor of two lower than that found for reducing conditions, probably because the solvent pH became basic as a result of peroxide degraduation of the chelants. However, the amount of sludge dissolution observed for the oxidizing solvents was close to zero. The ineffective sludge dissolution is believed to be due to the presence of oxalic acid.

The effect of oxalic acid in dilute solvent formulations was further evaluated; the data are given in Table 4-4. The data confirm that sludge dissolution in the presence of oxalic acid is very low. This effect is consistent and is probably due to the formation of a ferrous oxalate precipitate $[Fe(HCOO)]_2$, which was visually evident as a yellow-tan deposit on the specimen surfaces at the end of the test. Actual determination that the insoluble species was ferrous oxalate was not confirmed analytically.

TABLE 4-3

COMPARISON OF OXIDIZING AND REDUCING SYSTEMS

(Temperature 95°C for 12.5 h)

Solvent Constituent	Oxidizing Solvents (wt%)			Reducing Solvents (wt%)		
EDTA	--	0.10	--	--	0.10	--
DTPA	--	--	0.10	--	--	0.10
Citric Acid	0.10	0.05	0.05	0.10	0.10	0.10
Oxalic Acid	0.10	0.05	0.05	0.10	--	--
H_2O_2	0.08	0.08	0.09	--	--	--
NH_2-H_2N	--	--	--	0.05	0.04	0.04
Initial pH	3.5	3.5	3.5	3.5	3.5	3.5
Test Results						
Final pH	8.8	9.2	9.1	4.1	4.5	4.7
Sludge Dissolution (wt%)	*	*	*	*	33.0	43.0
Corrosion Rates (mils/day)						
SA285C	0.400	1.900	1.400	0.400	3.000	4.100
SA533A	1.100	2.000	1.600	0.600	4.000	4.400
SA508	0.900	2.000	1.500	0.500	3.400	4.300
IN600	0.014	0.008	0.013	0.006	0.011	0.009

*In presence of oxalic acid, recovered sludge weight was greater than the original weight used for this test.

TABLE 4-4

EFFECT OF OXALIC ACID IN DILUTE SOLVENTS

Solvent Constituents					Test Results			
						Corrosion (mils/day)		
EDTA (wt%)	Citric Acid (wt%)	H_2O_2 (wt%)	Oxalic Acid (wt%)	Run No.	Sludge Dissolution (wt%)	SA285C	SA533	SA508
--	0.10	0.08	0.10(a)	1	(c)	0.4	0.6	0.5
				2	(c)	0.4	1.1	0.9
0.1	0.10	None	None(a)	1	43.0	2.6	2.8	2.6
				2	22.0	2.2	2.4	2.3
0.1	0.05	0.08	0.05(a)	1	12.0	1.4	1.5	1.4
				2	(c)	1.3	1.8	1.5
0.1	0.05	None	0.05(b)	1	9.8	1.8	2.1	2.2
				2	9.8	1.7	1.8	1.8

(a) Initial pH = 3.5
(adjusted with ammonium hydroxide)

(b) Initial pH = 5.1
(adjusted with ammonium hydroxide to 3.5
and finally with ethylene diamine to 5.1)

(c) Final weight of recovered sludge was greater
than the initial weight used in this test

The observations made from this series of tests provided the following conclusions:

1. A reducing environment is more effective than an oxidizing environment for dissolution of bulk sludge.

2. Oxalic acid provides low corrosion rates, but the formation of insoluble ferrous oxalate precludes its use in dilute solvent systems. Review of previous UNC concentrated solvent studies confirmed that the oxalate precipitation drastically reduces penetration of solvent into crevice areas.

3. The corrosion rates observed confirm that an inhibitor will be needed to reduce carbon steel corrosion rate to the target criterion of less than 1 mil/day.

4.4.1.2 Effects of Inhibitor Concentration

During the investigation of dilute solvent formulations, a number of experiments were carried out at different inhibitor concentrations. The two inhibitors used were DETU (reference inhibitor) and cinnamonitrile (inhibitor of choice). These inhibitors were selected based on earlier tests discussed in Section 4.3.

The objective of these experiments was to evaluate the relative effectiveness of diethylthiourea and cinnamonitrile at concentrations up to 0.3 wt% for reducing corrosion without compromising the sludge dissolution effectiveness of the solvent.

The data relating the effects of inhibitor and inhibitor concentration to percent sludge dissolution and corrosion of materials of construction are given in Table 4-5.

It is apparent that for all of the solvent formulations in this test series DETU is a more effective inhibitor than cinnamonitrile when tested at equal concentrations. The data also show that for a given dilute solvent composition the use of DETU yields higher percent sludge dissolution. This is probably because lower corrosion in a static kettle test results in less solvent depletion, leaving more active solvent to react with the sludge. On this basis, the effectiveness of the cinnamonitrile inhibited solvents was expected to improve when the solvent is regenerated on line. The fact that cinnamonitrile is a sulfur-free compound makes it more attractive than DETU considering current concerns about the role of sulfur and sulfur compounds in causing intergranular corrosion of Inconel.

The test data given in Table 4-5 and the considerations discussed above indicate that:

TABLE 4-5

EFFECT OF INHIBITOR AND INHIBITOR CONCENTRATION

Solvent Composition (wt%)					Inhibitor		Sludge Diss (wt%)	Corrosion (mils/day)		
EDTA	DTPA	HEEDTA	Gluconic Acid	Citric Acid	Type	(wt%)		SA285C	SA533A	SA508
0.1					None	--	36	1.9	2.2	2.1
0.1				0.1	None	--	52	2.4	3.6	2.7
					DETU	0.05	63	2.0	--	1.6
					DETU	0.30	72	1.5	--	1.0
					CINN	0.10	58	2.8	--	3.0
	0.1			0.1	None	--	46	4.7	--	5.8
					DETU	0.01	62	1.4	1.9	1.9
					DETU	0.05	60	1.6	1.8	1.2
					DETU	0.10	60	1.6	1.5	1.3
					CINN	0.01	48	3.0	3.2	2.3
					CINN	0.05	47	2.9	2.8	3.6
		0.1		0.1	None	--	42	4.6	7.0	6.1
			0.1	0.1	None	--	22	2.1	2.4	2.3
					DETU	0.01	44	1.1	1.8	0.4
					CINN	0.01	37	2.7	2.5	3.2

EDTA - Ethylene diamine tetra acetic acid
DTPA - Diethylene triamine penta acetic acid
HEEDTA - N(2-hydroxyethyl)ethylene diamine tri acetic acid
DETU - Diethyl thiourea
CINN - Cinnamonitrile

1. DETU is a more effective inhibitor than cinnamonitrile.

2. Concentrations of cinnamonitrile at 0.3 wt% or more will be necessary to reduce the corrosion rate to 1.0 mil/day level, unless less agressive dilute solvents can be identified later in the program.

4.4.1.3 Effect of Chelant Concentration

A series of screening tests was conducted using several chelants at concentrations ranging from 0.1 wt% to 0.3 wt% in combination with 0.1 wt% citric acid.

The objective of this study was to evaluate the relative effectiveness of four candidate solvent formations for sludge dissolution. The dependence of sludge dissolution on chelant concentration was determined for one chelant (DTPA).

The data summarized in Table 4-6 were obtained by following the detailed test method outline in Appendix A. Without inhibitor, the EDTA, HEEDTA and DTPA solvents were essentially equivalent in their capacity to dissolve sludge. Effectiveness of the gluconic acid solvent, however, was lower by a factor of two. As expected, the degree of sludge dissolution was improved by increasing the chelant concentration. Additional improvement was achieved by using an inhibitor, which reduced solvent depletion resulting from corrosion.

In the absence of an inhibitor, the corrosion rates of all materials of construction used in these tests are significantly higher than the 1 mil/day target criterion.

The experimental results presented in Table 4-6 lead to the following conclusions:

1. The highest degree of sludge dissolution is achieved with EDTA and DTPA.

2. HEEDTA yields the lowest degree of sludge dissolution and was deleted from future dilute solvent formulations.

3. The high corrosion rates observed confirm that an effective, regenerable inhibitor will be required to control corrosion even when using a very dilute solvent.

4.4.1.4 Effect of Hydrazine Concentration

Evaluation of the effect of hydrazine concentration on the corrosion of materials of construction was not initially considered to be a necessary part of this program. However, corrosion results for several of the early dilute solvent

TABLE 4-6

EFFECT OF CHELATE AND CHELATE CONCENTRATION

Solvent Composition (wt%)						Sludge Dissolution (wt%)	Corrosion (mils/day)		
EDTA	HEEDTA	DTPA	Gluconic Acid	Citric Acid	DETU		SA285C	SA533A	SA508
0.1				0.1	None	48	3.1	3.5	3.5
		0.1		0.1	None	45	4.9	--	5.3
		0.2		0.1	None	65	6.9	--	7.8
					0.1	77	2.0	--	1.5
		0.3		0.1	None	78	6.3	--	10.0
					0.1	93	2.6	--	2.1
					0.1	83	2.2	--	1.8
	0.1			0.1	None	42	4.6	7.0	6.1
			0.1	0.1	None	22	2.2	2.4	2.3
					0.1	44	1.1	1.8	0.4

EDTA - Ethylene diamine tetra acetic acid
HEEDTA - N(2-hydroxyethyl) ethylene diamine tri acetic acid
DTPA - Diethylene triamine penta acetic acid
DETU - Diethyl thiourea

screening tests showed a trend toward higher corrosion (especially for SA533A) when hydrazine was used in the solvent formulation. Review of past UNC laboratory test results developed for a previous DOE sponsored solvent development program showed the same trend. Therefore, a study was undertaken to explain the unusually high corrosion rates observed for those tests where the hydrazine was analyzed and found to be at a higher concentration than usual.

The objective of this test series was to determine if there was any direct relationship between the observed corrosion rates and the average hydrazine concentration of the solvent. Using a dilute solvent formulation of equal concentrations of EDTA and citric acid, the average hydrazine concentration was varied from 100 mg/ℓ to 600 mg/ℓ by adjusting solvent pH with hydrazine. The dilute solvent concentration was also varied, from 0.1 wt% to 0.4 wt%, to enable use of the higher hydrazine concentrations.

The correlation between C/S corrosion and hydrazine concentration is shown in Table 4-7 and illustrated more clearly in Figure 4-7. The observed effect is particularly evident for uninhibited formulations, showing generally increased corrosion of all C/S alloys at high hydrazine concentration. It is apparent from Figure 4-7 that corrosion to C/S alloy SA533A is particularly sensitive to hydrazine concentrations above 200 ppm. All subsequent kettle tests will be conducted with hydrazine concentrations less than 200 ppm.

4.4.2 Solvent Regeneration

A series of screening tests was conducted to determine the feasibility for regeneration of spent dilute solvents by cation-exchange resins when the solvent contains iron-chelant complexes.

With the dilute chemical cleaning solvent formulated as

0.50 wt% EDTA,
0.25 wt% Citric Acid,
adjusted to pH 3.5 with ammonium hydroxide

a series of once through ion-exchange tests was performed using partially spent solvent. The spent solvent was passed downflow through small ion-exchange columns, and selected effluent samples were analyzed for dissolved iron, copper, and acidity. A detailed description of the method and apparatus used for the ion exchange tests is given in Appendix A.

For this ion exchange study, the partially depleted solvent was prepared by dissolving Fe_3O_4 and CuO_2 at 90°C for 6 hours. After filtration the solution pH was 3.7 and the residual EDTA was found to be 0.44 wt%. Chemical analysis showed the solution

TABLE 4-7

EFFECT OF HYDRAZINE CONCENTRATION ON CORROSION RATES

(Temperature 94 ± 2°C)

H_2N-NH_2 Conc Range (mg/ℓ)	Average Corrosion Rate (mils/day)					
	SA285C		SA533A		SA508	
	No Inhibitor	Diethylthiourea	No Inhibitor	Diethylthiourea	No Inhibitor	Diethylthiourea
100-199	2.8	1.6	3.4	2.0	3.1	1.1
200-299	4.8	1.6	6.2	2.8	5.8	1.5
300-399	--	1.8	--	3.4	--	1.2
400-459	6.9	2.0	--	4.8	7.8	1.5
460-575	6.3	2.6	--	5.5	10.0	2.1

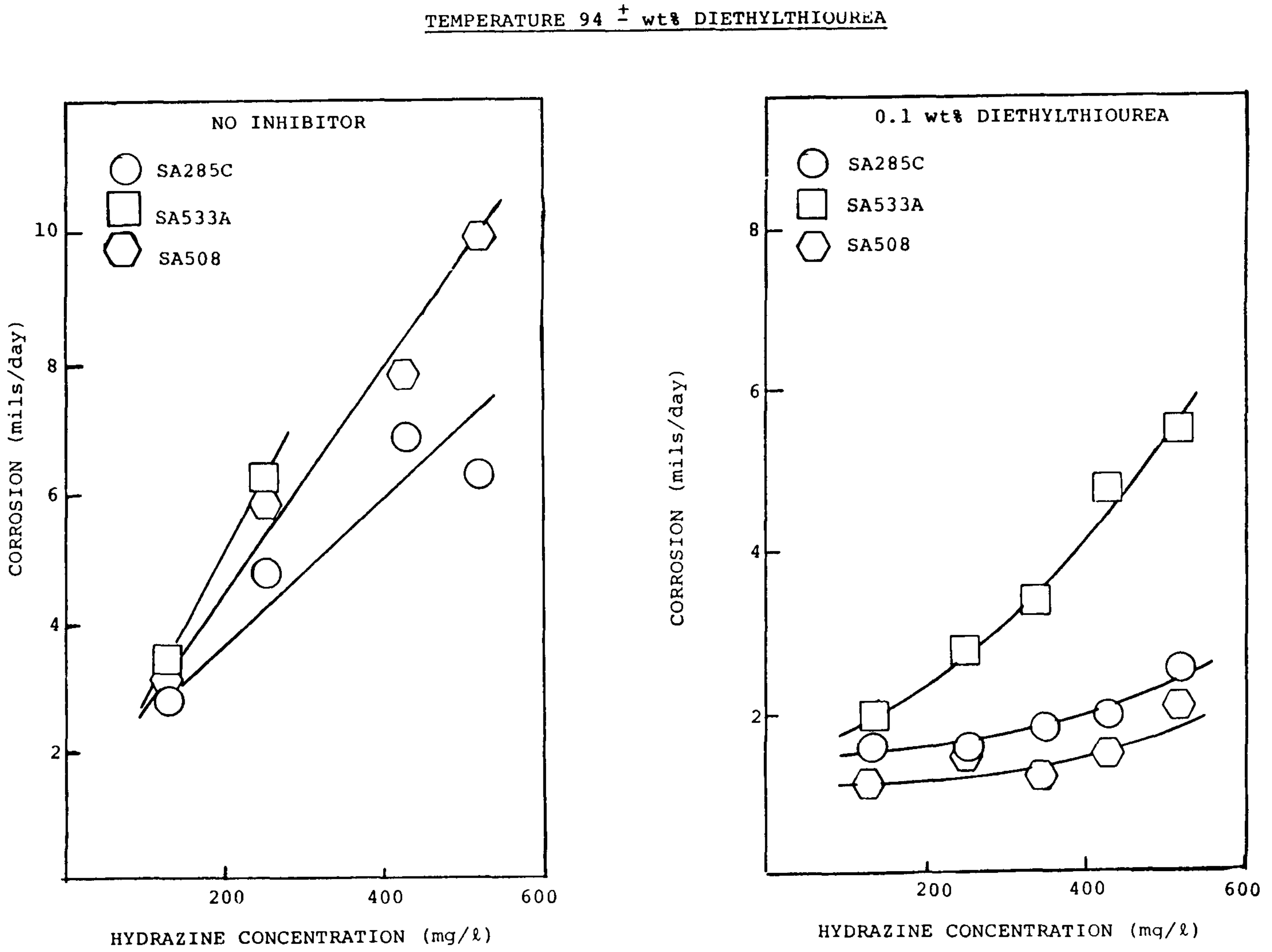


FIGURE 4-7. Effect of Hydrazine Concentration on Observed Corrosion Rates.

contained complexed Fe and Cu at 800 mg/ℓ and 132 mg/ℓ respectively.

The partially spent solvent was diluted and separated into two equal volumes. One portion was passed downflow through a 110-cm^3 strong acid cation exchanger in the hydrogen form. The second portion was similarly treated by passing it through a strong acid cation exchanger which had been converted to the hydrazine form. In both runs, 100-mℓ portions of the column effluent were collected and analyzed for pH, conductivity, iron, copper and hydrazine where appropriate. These data are given in Table 4-8.

The choice of strong acid-form cation-exchange resin for regeneration was based on the assumption that the partially spent dilute solvent would contain mostly Fe (III), Cu (II), and trace amounts of radioisotopes. In addition, it was assumed that a strong acid-cation exchanger would not remove the free chelant anion from the solvent. The Table 4-8 results indicate that a portion of the iron and copper can be removed from the spent solvent by ion exchange. It also appears that the amount of iron removed from solution on a single pass is not dependent on the ionic form of the cation exchanger. However, analysis of selected samples from both runs for chelant concentration (by titration with standardized $CaCl_2$) indicated that no regeneration of the chelant was accomplished. The relatively low pH values observed with the H+-form cation exchanger were evidently due to the chelant complex exchanging with H+ on the resin without splitting the very stable Fe-EDTA complex. This behavior indicates that the cation exchanger is an irreversible sink for the Fe-EDTA iron complex.

The irreversible absorption of chelant complexes was confirmed by performing additional ion-exchange tests. Two dilute chelant solvents containing 0.1 wt% EDTA and DTPA respectively, were passed downflow through H+-strong acid-cation exchangers and the wt% chelant concentration determined in effluent samples. The results are given in Table 4-9. In both cases, the chelant was absorbed onto the resin displacing H+ until the resin was depleted.

The once through ion-exchange regeneration studies conducted during this report period indicate that:

1. Iron and copper removal by ion exchange of partially depleted solvents is only marginal (40% to 70%) because the Fe-chelant complex is not broken by the ion-exchange process.

2. Strong acid-cation exchangers in the H+ form do not regenerate chelant complexes of iron or copper in spent dilute cleaning solvents.

TABLE 4-8

THE ION EXCHANGE BEHAVIOR OF SPENT DILUTE SOLVENT CONTAINING THE EDTA-$(Fe)_x$ COMPLEX

Influent	
pH	3.65
Iron (mg/l)	141
Copper (mg/l)	35
Cond (μmho/cm)	5250

Ionic Form	$Rc-H^+$				$R_c-H_2N-NH_3^+$				
Bed Volume (cm^3)	110				96				
Flowrate (ml/min)	32				28				
Effluent Vol. (ml)	**Cond (μmhos/cm)**	**pH**	**Iron (mg/l)**	**Copper (mg/l)**	**Cond (μmhos/cm)**	**pH**	**Hydrazine (mg/l)**	**Iron (mg/l)**	**Copper (mg/l)**
0-100	8500	1.82	80	0.05	5400	4.25	3720	67	17
100-200	8850	1.76	83	--	5100	3.83	2250	69	--
200-300	9000	1.80	88	0.04	4500	3.70	2130	72	17
300-400	9200	1.77	77	--	4600	3.65	2180	--	--
400-500	9400	1.74	72	0.06	4450	3.62	2130	73	18
500-600	9100	1.77	--	0.12	4300	3.59	2050	74	--
600-700	9400	1.75	69	0.51	4200	3.58	1950	--	18
700-800	9400	1.74	--	2.6	4200	3.62	2130	72	--
800-900	9300	1.72	67	12.7	4300	3.63	13	69	18
900-1000	9200	1.74	64	27.0	4500	3.64	0	60	17
Removal	Fe 41% Cu 70%				Fe 50% Cu 50%				

TABLE 4-9

IRREVERSIBLE ABSORPTION OF CHELATES ON STRONG ACID (H^+ FORM) CATION EXCHANGE

	Influent		Influent	
Chelate	EDTA (0.1 wt%)		DTPA (0.1 wt%)	
pH	2.4		2.4	
Cond (μmhos/cm)	1160		1060	
Bed Volume (cm^3)	125		125	
Flowrate (ml/min)	25		25	
Eff Vol (liters)	Effluent		Effluent	
	pH	EDTA (wt%)	pH	DTPA (wt%)
0-1	3.2	0.02		
1-2	2.9	0.03		
2-3	2.8	0.04		
3-4	2.7	0.06		
4-5	2.6	0.07	3.5	0.006
6-7	2.6	0.07		
9-10	2.5	--	3.4	0.01
11-12	2.6	0.09		
12-13	2.6	0.09	3.3	0.02
13-14	2.6	0.09		
16-17	2.4	0.09	3.2	0.03
20-21			2.8	0.05
23-24			2.5	0.07
27-28			2.6	0.09
29-30			2.6	0.09

EDTA - Ethylene diamine tetra acetic acid

DTPA - Diethylene triamine penta acetic acid

Additional ion-exchange studies will be performed during the next report period to evaluate complexing organic acids which are known to be effective for dissolving iron-oxide deposits. The complexes formed by iron with organic acids are expected to be less stable than those formed with chelants and, therefore, more likely to be regenerated by ion exchange.

4.4.3 Crevice Cleaning

As a part of this program, the crevice cleaning capability of dilute solvents will also be demonstrated. However, no crevice cleaning tests were run during this report period, as the preparation of packed and partially packed reverse dents was only partially completed. Since reproducible dent specimens are needed to evaluate the dilute solvents' effectiveness for crevice cleaning, preparation of reverse dents will continue during the next report period.

4.5 PILOT SCALE DEMONSTRATION

The development of a suitable dilute chemical cleaning solvent had not progressed sufficiently by the end of this report period to allow for the design for a recirculating system. This subject will be addressed in the next semi-annual report.

SECTION 5.0

CONCLUSIONS AND FUTURE WORK

5.1 CONCLUSIONS

Within the frame work of the data included in this report, the following conclusions are apparent:

- Zion sludge and a UNC prepared synthetic sludge consisting of Fe_3O_4 and CuO_2 exhibit equivalent dissolution characteristics in a dilute solvent containing EDTA and citric acid.

- DETU and cinnamonitrile are inhibitors of choice for dilute solvent cleaning formulations containing combinations of chelants and citric acid. (Note: Several instances of intergranular attack on Inconel alloys have been attributed to sulfur and may limit the inhibitor choice to cinnamonitrile.)

- A reducing environment is necessary for effective dissolution of bulk sludge.

- Hydrazine has been found to cause generally increased corrosion with enhanced selective corrosion of SA533A. This effect can be reduced by limiting the hydrazine concentration to < 200 ppm and using NH_4OH for final adjustment to pH 3.5.

- Spent dilute solvents containing EDTA or DTPA cannot be effectively regenerated by strong acid-cation-exchange resins in either the hydrogen or hydrazine form.

5.2 FUTURE WORK

The conclusions reached in this report period indicate the direction that additional studies should take in the next report period. These are:

- Evaluate the sludge dissolution properties and corrosiveness of dilute solvent formulations prepared with organic complexing acids (i.e., citric acid, gluconic acid, ascorbic acid, and combinations thereof).

- Determine the ion-exchange regenerability of spent dilute solvents containing organic complexing acids.

- Continue the preparation of partially packed, packed, and dented reverse dent specimens for crevice cleaning tests.

- Initiate the design of a bench-scale recirculating system to simulate the model generator cleaning system that will be required for the planned demonstration test at CECO's Stateline facility.

- Demonstrate the ability of mixed-bed ion exchange for clean up of spent recirculating solvents to reduce liquid waste disposal requirements.

- Identify appropriate processes for removal of copper deposits and passivation of steel surfaces after the cleaning.

APPENDIX A

TEST APPARATUS AND METHODS

APPENDIX A

Apparatus and Method for Static Pot Tests

Figure A-1 shows a typical test assembly. A typical experiment was carried out in the following way.

1. A 3500-mℓ batch of the selected solvent was prepared by dissolving the chemicals in deionized water to yield the appropriate wt% composition. This solution was adjusted to pH 3.5 by small additions of hydrazine and/or ammonia hydroxide.

2. A 250-mℓ sample of the final solvent was set aside as a reference sample.

3. A 3000-mℓ batch of the final solvent was transferred to a 4-ℓ glass kettle in a temperature controlled water bath.

4. The temperatures in the water bath and test kettle were monitored and recorded throughout each test.

5. The corrosion coupons were degreased with acetone, polished, and washed with acetone a second time, air dried, and weighed.

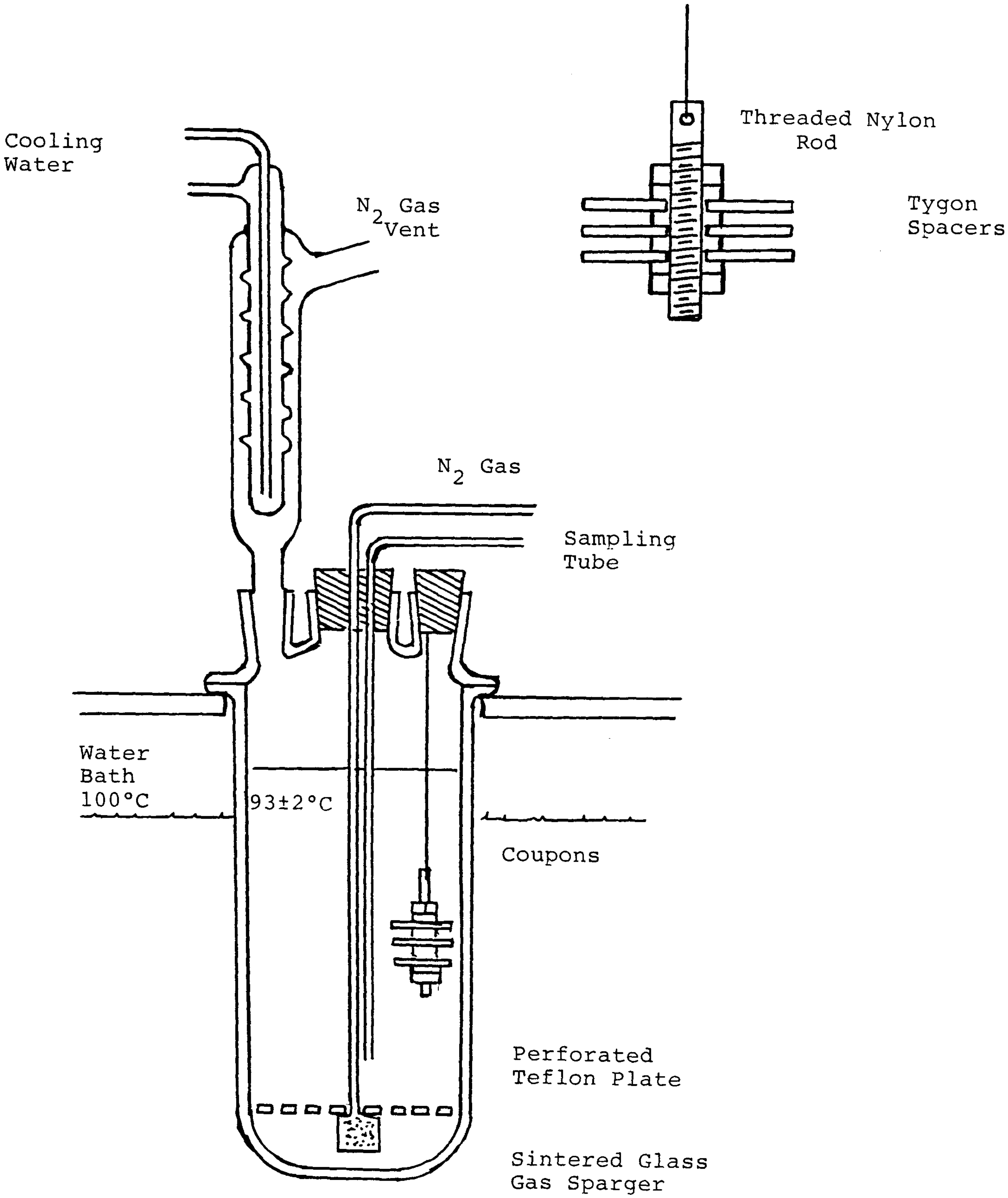
6. The mounted coupons were suspended in the vapor space and the cover of the resin pot was clamped in place. Nitrogen gas flow was started at 200 cm^3/min, and continued at this rate throughout the test period.

7. When the temperature of the solvent in the test pot stabilized at 93 ± 1°C, previously weighed amounts of sludge were added and the coupons were lowered into the solvent. This operation was used to define T=0 for the test. These additions were made without removing the top of the test kettle, so introduction of air to the test system was eliminated.

8. During the course of each test, 60-mℓ to 70-mℓ samples of the solvent were taken at 0.5-hour and 1-hour intervals. These samples were evaluated for pH, hydrazine, iron, and copper. Other analyses were performed as necessary.

Figure A-1

Typical Test Assembly



9. At the conclusion of the test, the corrosion coupons were removed while the N_2 gas was still flowing. These were immediately transferred to 1:1 NH_4OH solutions to arrest any further reaction, and the water bath heaters were turned off.

10. The flow of N_2 gas was stopped and the kettles were removed from the water bath. Any suspended residual sludge was allowed to settle.

11. While the solvents were still hot , the clear solutions were carefully decanted and their individual volumes were measured and recorded. After cooling to ambient temperature, approximately 250 mℓ of the spent solvent was taken as a reference sample for the completed test.

12. While the solvents were still hot, the residual sludge was separated from the small amount of remaining solvent by filtration through a 0.8-micron Gelman filter. Any undissolved sludge pellets were recovered intact.

13. After drying at 105°C overnight, the weight of residual sludge was determined.

14. The corrosion coupons were inspected visually, washed with acetone, air dried, and weighed. The difference between the initial and final coupon weights is used to calculate the uniform corrosion rate, expressed as mils penetration per day, as follows:

$$\text{mils/day} = \frac{(A-B)\times 1000}{S \times T \times F}$$

Where: A is the initial coupon wt, g
B is the final coupon wt, g
S is the expose coupon area, sq. in.
T is the solvent contact time, days
F is a conversion factor of 128 mg/sq. in./mil based on the density of carbon steel

Appartus and Method for Ion Exchange Tests

Figure A-2 shows a typical ion exchange column assembly used for once-through tests with spent dilute solvents. In general, these experiments are carried out in the following way:

1. The appropriate quantity of ion exchange material is tranferred to a beaker and soaked overnight in deioniozed water to ensure that it is in a fully swollen, wet state.
2. The swollen ion exchange material is transferred to the ion exchange test column with deionized water and backwashed for 10 minutes with deionized water to classify and settle the ion exchange bed.
3. The excess deionized water is drained to just cover the top of the ion exchange bed.
4. The influent test solution is introduced to the column, and the flowrate adjusted to the desired value.
5. The effluent solution flows through the sample line and is collected in appropriate sampling bottles. An in-line conductivity cell can be installed in the sample line if desirable.
6. The effluent samples are analyzed for pH, conductivity, dissolved metal concentrations and chemical concentration as required.

Figure A-2

Ion Exchange Test Column