COMMONWEALTH RESEARCH CORPORATION

72 WEST ADAMS STREET ★ CHICAGO, ILLINOIS

Address Reply to:

POST OFFICE BOX 428 ★ CHICAGO, ILLINOIS 60690

October 9, 1984

DOE/ET/34015--8

DE85 001443

To: Distribution

Subject: Evaluation of On-Line Chelant Addition and Dilute Chemical Cleaning of PWR Steam Generators, DOE Final Report DOE/ET/34015-8

Attached is a copy of the subject DOE report written by Commonwealth Research Corporation.

J. C. Blomgren
Project Manager
Technical Services -- Nuclear

JCB/cak
Attachment

cc: R. L. Bolg
S. T. Naum

DOE REPORT NO. DOE/ET/34015-8
DISTRIBUTION CATEGORY: U-78
DECEMBER, 1983

STEAM GENERATOR CHEMICAL CLEANING PROJECT

ON-LINE CHELANT ADDITION DILUTE CHEMICAL CLEANING

FINAL REPORT

Edited By: J. C. Blomgren (Commonwealth Edison Company)

Authors:

F. E. Swan, Jr. (Commonwealth Edison Company)
D. Schneidmiller (UNC Nuclear Industries)
T. J. Tvedt (Dow Chemical Company)

Commonwealth Research Corporation
72 West Adams Street
Chicago, Illinois 60603

Managed By
Commonwealth Research Corporation
CRC Project Manager: J. C. Blomgren
DOE Project Manager: D. L. Harrison

Prepared For The
U.S. Department of Energy
Under Contract DE/AC02-79ET 34015

ABSTRACT

Corrosion problems in Pressurized Water Reactor (PWR) steam generators are often associated with the accumulation of corrosion products in various locations in the steam generators. Based upon fossil plant experience and new decontamination processes, two potential chemical cleaning processes were evaluated.

The on-line addition of chelants (EDTA, HEDTA) was evaluated based on thermostability of the metal chelate at steam generator operating conditions and based upon material compatability. Both EDTA and HEDTA are promising additives. Testing under prototypical operating conditions in a model steam generator demonstrated the feasibility of this process under various fouling conditions (seawater and freshwater).

The application of dilute chemical cleaning to steam generators was also evaluated. This process was evaluated based upon effectiveness of cleaning a packed crevice and materials compatability. Feasibility of this process was demonstrated by its ability to clean packed crevices. However, application times are long and corrosion rates, while acceptable, require additional development of non-sulfur containing inhibitors.

TABLE OF CONTENTS

TABLE OF CONTENTS - CONTINUED

TABLE OF TABLES

TABLE OF TABLES - CONTINUED

TABLE OF FIGURES

TABLE OF FIGURES (CONTINUED)

1.0 INTRODUCTION

Corrosion problems in the steam generators of Pressurized Water Reactors (PWR) are often related to the accumulation of magnetite (Fe_3O_4) and hematite (Fe_2O_3). These corrosion products are the result of erosion and corrosion of the large surface areas of carbon steel, present in the secondary system. Accumulation of these corrosion products in low flow areas of the steam generator, such as areas of the tube sheet and in the tube - tube support plate crevices, provides a site for the concentration of contaminants that are aggressive to the steam generator tubing or it's support structure.

1.1 BACKGROUND

The steam generator tubing is the boundary between the high pressure, reactor coolant system and the lower pressure, secondary side of the plant. Because the reactor coolant system is radioactive it is important to maintain the integrity of this boundary, the Inconel 600 steam generator tube.

Accumulation of corrosion products and impurities (sludge) on the secondary side of the vertical steam generators continues to be an operational problem for many pressurized water reactor (PWR) plants. A major concern in the build-up of these impurities is the subsequent concentration of dissolved chemicals in the tube-to-support plant crevice areas, causing accelerated local corrosion and eventual tube denting. As a result of denting, two U.S. utilities have replaced steam generators after less than ten years of operation.

Corrosion products also collect in low flow areas on the tube sheet. Concentration of corrodents in this tubesheet sludge has caused stress corrosion cracking and intergranular attack of the Inconel 600 steam generator tubing. These types of tube degradation have resulted in sleeving of the original tubes and are likely to cause replacement of steam generators in the future.

One approach to assuring tube integrity is to eliminate the site for concentration of aggressive species by removal of the accumulated

corrosion product deposits. In the fossil fired power industry, this is accomplished by periodically applying a chemical cleaning agent to the water side of the boiler. This program was developed to evaluate two substantially different chemical cleaning processes as they might be applied to the more complicated geometry and materials of a nuclear steam generator.

Commonwealth Research Corporation (CRC) initiated a U.S. Department of Energy (DOE) sponsored program to evaluate two concepts for the chemical cleaning of PWR steam generators. Primarily intended as preventive maintenance chemical cleaning processes, that could be applied repeatedly to minimize the build-up of corrosion products, these concepts are: 1) an additive to be used during unit operation and 2) a dilute chemical cleaning process in which the cleaning solvent could be regenerated.

Dow Chemical Company was selected by CRC to evaluate the feasibility of using an on-line chelant additive. UNC Nuclear Industries (UNC) was contracted by CRC to develop a suitable dilute chemical cleaning process and demonstrate the feasibility of applying such a process to clean steam generators.

1.2 CHEMICAL CLEANING PROGRAM DESCRIPTION

1.2.1 ON-LINE CHELANT ADDITION

The first process evaluated was Chelant Addition. This process is based upon earlier work by Dow Chemical Company on the use of an on-line chelant additive, EDTA, for the prevention of corrosion product deposition.

The Dow Chemical Company operates numerous boilers which generate steam at approximately 1250 psi. Since 1962, the internal water treatment of a number of these boilers has included Na_4.EDTA (1). The results of these programs have been quite encouraging; no tube failures, due to waterside conditions, have occurred; no evidence of waterside corrosion has been detected; and no chemical or mechanical "out of service" cleaning has been required. Frequent inspections have shown these boilers to be essentially free from deposits.

Several design features should be pointed out. A portion of the superheated steam is passed through the mud drum to control the super-heat temperature. These, so call "submerged atemperators," are constructed from horizontal tubes which are supported by steel plates. They closely resemble PWR steam generators which are lying on their sides. A crevice is also found between the atemperator tube and its support plate. No evidence of either deposit accumulation or "denting" has been noted after twenty years of operation on chelate chemistry. The operating temperatures and heat fluxs on these boilers are somewhat higher than are encountered in PWR steam generators, while the residence times of water treatment chemicals are approximately the same.

Numerous references have appeared in the literature of the Soviet Union, which report the successful use of EDTA as a continuous "on-line" treatment in secondary water systems in nuclear power plants (2,3,4). Claims have been made that both prevention of deposits and corrosion protection have been achieved. It was further stated that "When water is treated with Trilon B(EDTA) and no hydrazine is present in the water, magnetite crystals of much smaller dimensions and irregular form, similar to one another in size, form on the surface of the steel. All this results in a densely packed arrangement. As a result, there is a considerable increase in the strength of the film in relation to the temperature fluctuations and its protective properties are improved" (5).

For these reasons, the use of chelating agents as a continuous treatment for PWR steam generators was encouraged. However, several important differences between fossil-fired boilers and PWR steam generators exist. Included are:

1. The water chemistry for most PWR steam generators consists of ammonia and hydrazine. This is known as "all volatile treatment" (AVT). The fossil boilers, which the Dow Chemical Company operates, use sodium phosphate and sodium sulfite as an internal treatment.

2. The tubes in the PWR steam generators are fabricated from Inconel 600. All tubes in the fossil boilers are steel alloys.

3. The sodium salts of the chelating agents are used in industrial boiler treatment. It will be desirable to use the ammonium salts of the chelating agents for the treating of steam generators. No data has been found on either the application or the high temperature chemistry of the ammonium salts of chelating agents.

This study is only one part of a broader study to investigate the use of chelating agents to clean secondary loops in PWR steam generators. This particular study covers the use of chelating agents in a continuous, on-line treatment program and consists of 5 tasks, a description of each task follows.

TASK 1 - HIGH TEMPERATURE CHEMISTRY OF METAL CHELATES

The high temperature chemistry of metal chelates was studied, including the determination of the kinetics of thermal decomposition, determination of the major decomposition products and derivation of reaction pathways. These data were used to predict survivability of metal chelates in PWR secondary systems.

TASK 2 - MATERIALS COMPATIBILITY

At conditions which are encountered in PWR steam generators, the corrosivity of chelate solutions upon materials of construction was studied. All metals which contact secondary solution and several which only contact steam were evaluated.

TASK 3 - MODEL BOILER OPERATION

Commonwealth Research Corporation operated four model steam generators to demonstrate the feasibility of applying chelate chemistry to PWR's.

TASK 4 - PLANT DEMONSTRATION

If the on-line use of chelating agents in PWR steam generators was proved to be feasible and not detrimental during the first three tasks, then the Commonwealth Edison Company would conduct a plant demonstration. This task was not completed in this program.

TASK 5 - REMOVAL OF METAL CHELATES

Laboratory studies were conducted to evaluate methods of removal or destruction of metal chelates in steam generator blowdown.

1.2.2 DILUTE CHEMICAL CLEANING PROCESS

The second process evaluated was a dilute chemical cleaning process which is based upon earlier work done in the U.S. and Canada on dilute reactor coolant system decontamination processes. The objective of the Steam Generator Dilute Chemical Cleaning program was to evaluate the feasibility of using dilute solvents to maintain the secondary side of PWR Steam Generators in a clean condition. The process was designed to prevent tube "denting" by periodic application of chemical cleaning to remove accumulated corrosion products from steam generator tube-to-support plate crevices, with acceptable corrosion of steam generator materials of construction and minimum generation of wastes requiring treatment for disposal.

The objective of this program was to first develop an effective dilute solvent (0.5 wt%) and application process, and then to determine the feasibility of using the process to clean PWR steam generators by cleaning one or more DOE/CRC model steam generators fouled under typical PWR operating conditions. A logic diagram diagram for the conceptual process proposed by UNC is shown in Figure 1-1. Included in the diagram is a step for the physical removal of loose bulk sludge before the application of the dilute chemical cleaning process. Removal of bulk sludge prior to dilute chemical application was considered to be a necessary first step to increase the efficiency of the process. The dilute chemical cleaning step is a low-concentration process featuring in-situ solvent regeneration by ion exchange. Use of a low-concentration solvent results in reduced waste volume as compared to conventional processes and is potentially less corrosive. With minor plant modifications, the process could be routinely implemented during short outages to reduce sludge build-up and prevent tube denting by keeping the crevices clean.

The dilute chemical cleaning process development and evaluation was divided into the following tasks:

TASK 1 - PLANT INSPECTION

Task 1 is to acquire familiarity with operating plants, to scope siting and installation of new equipment for steam generator cleaning, and to evaluate the condition of typical PWR steam generators that may be cleaned to demonstrate the dilute process concept.

TASK 2 - PROCESS DEVELOPMENT

Task 2 was 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. All laboratory work was included in this task.

Candidate dilute solvent formulations were 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 was conducted to demonstrate the proposed dilute solvent process on one or more model steam generators.

TASK 3 - PROCESS SCALE-UP FOR STEAM GENERATOR CLEANING

Task 3 presents a preliminary engineering evaluation of the application of the dilute chemical cleaning process to full size steam generators. The data developed in this task can serve as a basis for a detailed design for the application of a dilute cleaning process.

1.2.3 MODEL STEAM GENERATOR TESTING

The model steam generator operation and materials evaluation conducted by Commonwealth Edison Company had two primary objectives.

1. Operate the model steam generators to qualify the design as a model of full size steam.

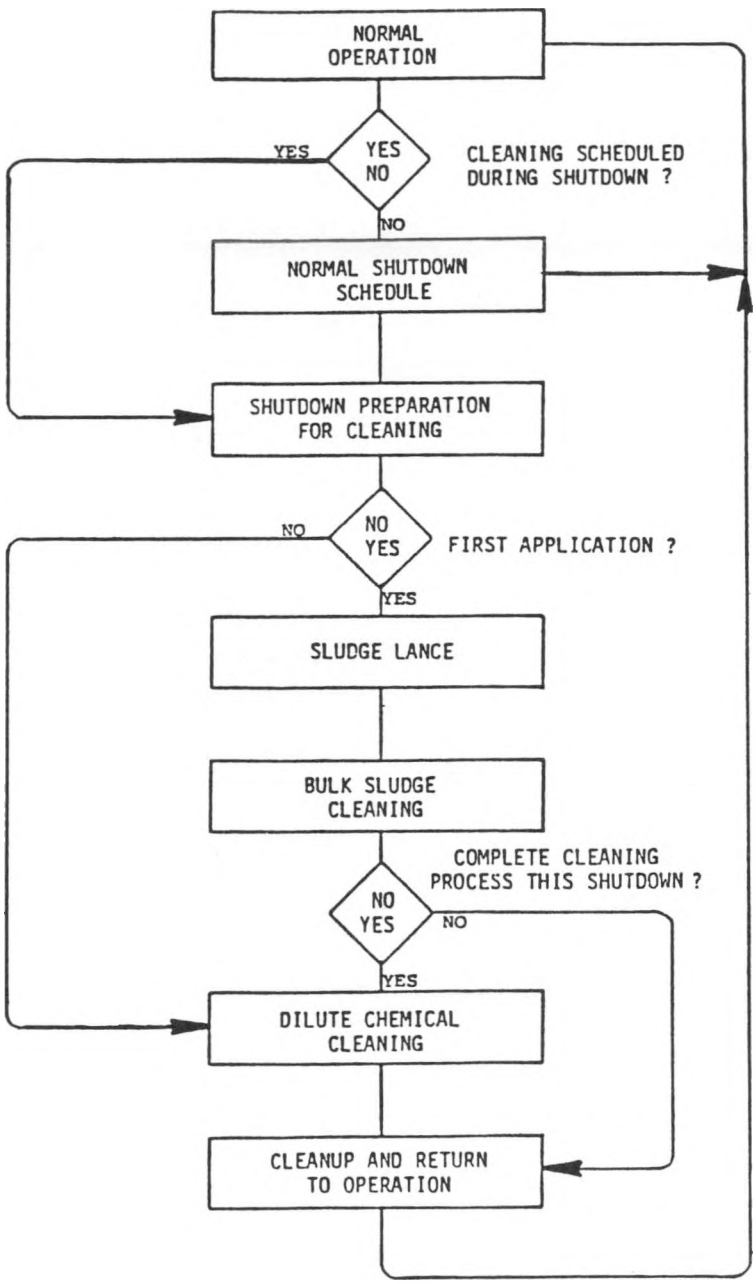


FIGURE 1-1. Logic Diagram for Dilute Steam Generator Chemical Cleaning Process.

2. Prepare the model steam generators for the cleaning demonstrations by operating them with the appropriate chemistries.

These objectives were met through completion of a test matrix having eight tasks (Table 1-1).

The validity of the test vehicle and the success of the cleaning processes will be determined by the following tasks:

Task 1) Demonstrate that the model steam generator (MSG) design will produce denting using a standard sea water dent solution.

Task 2) Evaluate tube support plate corrosion and crevice deposits using fresh water as the fouling agent.

Task 3) Demonstrate the effectiveness of a chelant in maintaining a steam generator clean with sea water as a fouling agent.

Task 4) Demonstrate the effectiveness of a chelant in maintaining a steam generator clean with fresh water as a fouling agent.

Task 5) Evaluate the chelants ability to clean a sea water produced dent.

Task 6) Evaluate the chelant's ability to clean a fresh water-packed crevice.

Task 7) Demonstrate the effectiveness of the dilute chemical cleaning process on sea water and high copper sludge-fouled MSG.

Task 8) Demonstrate the effectiveness of the dilute chemical cleaning process on a fresh water and low copper sludge-fouled MSG.

2.0 SUMMARY

2.1 ON-LINE CHELANT ADDITION

Task 1 (High Temperature Metal Chelate Chemistry) was a study of the thermal stability of metal chelates formed using the following chelants:

Nitrilotriacetic acid (NTA)

Ethylenediaminetetraacetic acid (EDTA)

Hydroxyethylethylenediaminetetraacetic acid (HEDTA)

Diethylenetriaminepentaacetric acid (DTPA)

TABLE 1-1

MODEL STEAM GENERATOR

TEST MATRIX

TEST CONDITIONS	MSG TEST TASK		
	Qualifying	On-Line Chelant	Off-Line Cleaning
Sea Water Fouling	1	3	
Lake Water Fouling	2	4	
Sea Water Prefouled		5	7
Lake Water Prefouled		6	8

It was shown that neither NTA nor DTPA metal chelates had sufficient thermal stability to be useful in PWR steam generators. Both EDTA and HEDTA metal chelates were found to have thermal stabilities sufficient to carry metal ions through a PWR steam generator. HEDTA metal chelates exhibited the highest thermal stability.

Task 2 (Materials Compatability) was a corrosion study to determine the effects of EDTA on PWR steam generator materials of construction. The following types of corrosion specimens were exposed to 1000 ppm EDTA at typical PWR steam generator operating conditions:

General weight loss - Flat coupons
U-Bend Weldments
Pre-cracked Stressed Specimens
Galvanic Couples
Copper plated coupons

General weight loss flat coupons were also exposed to 1000 ppm of HEDTA at PWR conditions. The general weight loss tests showed that EDTA and HEDTA caused a well-formed film of magnetite (Fe_3O_4) to deposit on the coupon surfaces. The rate of weight loss was found to decrease with time. All metals tested showed essentially no further weight loss after 80 days of exposure to 1000 ppm EDTA. Small amounts of Iron were found to decrease the time needed to passivate the coupon surfaces and halt general weight loss.

The U-bend weldments, galvanic couples, and copper plated coupons showed no signs of pitting or stress corrosion cracking. The pre-cracked stressed specimens showed no signs of environmentally-induced-stress-corrosion. EDTA did successfully remove the copper from the copper plated coupons.

Task 3 (Model Boiler Operations) was designed as a pilot test of EDTA addition to PWR steam generators. Two model steam generators (MSG) were operated with high concentrations of synthetic seawater as the fouling agent, in the make-up water. Two other MSG's were operated with high

concentrations of Lake Michigan water as the fouling agent. One MSG from each pair was fouled prior to the start of the EDTA addition.

The clean MSG operating with Lake Michigan water fouling was operated for 169 days with no signs of fouling. Without EDTA, the crevices on a similar unit became packed within the first 80 days of operation. Both MSG's operating with seawater fouling and EDTA, experienced pitting corrosion immediately prior to or during a wet lay-up using water of low pH, and high chloride concentrations. Also, no packed crevices were cleaned during the pilot test. Thus it appears that EDTA could be employed to maintain clean crevices in new or retubed PWR's, where no salt water incursion would occur. However, the effect of EDTA on the pitting potential of Inconel 600 should be studied prior to the addition of EDTA to operating steam generators.

Task 4 (Plant Demonstration) was deferred as a result of testing completed in Task 3. The following concerns were identified:

1. Unknown steam purity and its effect on steam turbines.
2. Unknown effect of EDTA on pitting of Inconel 600.
3. Inconclusive corrosion testing of SA533.

Task 5 (Chelate Removal) was a laboratory scale study to determine if metal chelates could be removed from the secondary loops of PWR steam generators. This study showed that the strong anion exchange resins currently available had the ability to remove the metal chelates.

Future studies should be conducted in the following areas:

1. Determination of the effect of EDTA addition on steam turbine integrity.
2. EDTA's effect on the pitting corrosion of Inconel 600.
3. The collection of data necessary to properly design an ion-exchange bed for the removal of metal chelates from the secondary loop of PWR steam generators.

2.2 DILUTE CHEMICAL CLEANING FINDINGS

Experiments performed during earlier report periods (References 6 and 7) established the solvent formulation, identified a sulfur-free inhibitor, confirmed workable process steps and optimized operating parameters for the steam generator dilute chemical cleaning process. A 10-day continuous bench-top loop operation simulated the full sequence of the process. A pilot-scale chemical cleaning system was constructed and shipped to the Commonwealth Edison Company (CECo) State Line Facility, where two intentionally fouled model steam generators were cleaned as a demonstration of process feasibility.

A summary of major results described in References 6 and 7 which led to the model steam generator cleaning demonstration tests is provided below.

Solvent. The preferred dilute solvent formulation is 0.1 wt% citric acid, 0.1 wt% ascorbic acid, and 0.1 wt% gluconic acid. The solvent pH is adjusted to pH 3.4-3.8 with NH_4OH and inhibited with 0.3 wt% cinnamonitrile.

Inhibitor. The sulfur-free inhibitor, cinnamonitrile, is most effective at 0.3 wt% and is compatible with the cation exchange resins that are used for solvent regeneration. The inhibitor is removed from the system at the end of the process by mixed bed ion exchange.

Corrosion. Corrosion rates of steam generator materials were 0.4 to 1.4 mil/day, except for SA 533A (shell material), which corroded at 1.7 to 2.4 mil/day. The corrosion rates indicate a need for a better inhibitor. Because the scope of the program was primarily a proof of process feasibility, the use of cinnamonitrile was continued for the process demonstration. Further inhibitor development is warranted for full-scale process applications.

Operating Conditions. Solvent pH of 3.4 to 3.8, temperature of $80^{o}C$, and flow of 125 to 250 mL/min were established as the most effective operating conditions. Work completed to define the optimum pH and temperature is described in Reference 7.

Several tests of the dilute solvent process were performed in a recirculating bench-top loop to define process operating parameters. Based upon these results, a flow in the range 125 to 250 ml/min was found to be most effective. Successful pH control was demonstrated by using chemical additions to the recirculating loop and control of the solvent regeneration demineralizers.

Regeneration of partially depleted solvent was successfully demonstrated using H^{+} form strong acid cation exchangers. The inhibitor was not removed by the cation resin. The use of mixed-bed ion exchangers for post-cleaning chemical removal was successfully demonstrated in bench-scale recirculation tests.

2.2.1 RECOMMENDATIONS FOR FUTURE WORK

The dilute chemical cleaning of the DOE model steam generators at CECo's State Line Facility demonstrated feasibility of the process. Qualification of the process for field use will require additional work. The following items are recommended for further evaluation and refinement.

Inhibitors: Cinnamonitrile was fully compatible with the process, but was not effective enough to permit repeated use of the process for preventive maintenance cleanings. Additional inhibitor development is necessary.

Materials: Corrosion of additional site-specific materials of construction in the dilute chemical solvent should be evaluated. Stressed, welded and galvanic couples should be tested using coupon geometries and metal surface-to-volume ratios typical of these existing in the steam generator to be cleaned.

Solvent Application: The model steam generator cleaning studies should be extended to verify process effectiveness for varying degrees of fouling and to define critical operating parameters. Improved inhibitors should also be tested in the model steam generators.

Flow Conditions: Solvent inlet and outlet flow configurations should be mocked up to be representative of full-scale steam generator configurations. Dead spots and low flow areas should be identified and minimized during design of the cleaning system. Minimum fluid velocity and agitation requirements for solvent replenishment should be determined.

Ion Exchange: The upper flowrate limit for solvent regeneration by ion exchange should be determined. Experience with condensate polishers shows that properly designed ion-exchange columns can be operated with good efficiencies up to 50 gpm/ft^2 throughput. Also, determination of the optimum ratio of cation to anion resins could improve mixed bed ion exchange efficiency and reduce cleanup time.

3.0 ON-LINE CLEANING PROCESS EVALUATION

The on-line cleaning process was developed by Dow Chemical U.S.A. The development of the on-line process is detailed in this section according to the task description detailed in Section 1.2.1.

3.1 TASK 1 - CHELANT THERMODYNAMICS

At conditions of temperature, pressure, and water treatment chemical concentration which are encountered in secondary loops of PWR's, the chemistry of metal complexes of commercially available chelating agents were studied. The test solutions included ammonia, hydrazine and metal complexes. The first two materials are normally used in a boiler water treatment scheme referred to as All Volatile Treatment (AVT).

It is well known that uncomplexed chelating agents rapidly decompose at PWR temperatures. However, the thermostability of the metal complexes at typical steam generator operating conditions were not known. Specifically, the decomposition kinetics of the calcium, magnesium, iron (II), and copper (II) complexes were studied. The principal decomposition products were identified and reaction pathways suggested. Chelating agents which were studied, include ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), hydroxyethylenediaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA).

The results of these studies were compared to similar studies on the chemistry of Na_4.EDTA and to predicted residence times in steam generators. The relative merits of different chelating agents were evaluated, and an attempt was made to predict the performance of various chelating agents in steam generators by comparing their stability to that of materials which are known to perform successfully in fossil-fired boilers.

A brief description of the test equipment used for the thermostability studies can be found in Appendix A.1.

3.1.1 IRON (II) CHELATE THERMOSTABILITY

The thermal decomposition of iron (II) chelates of nitrilotriacetric acid (NTA), ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylene-diaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA) were studied. The rate of thermal decomposition for each chelate was measured under the following conditions:

Temperature-290°C
pH 8.5 - 9.6 (adjusted with NH_4OH)
80 - 100 ppb hydrazine

The decomposition of the chelates studied followed first order kinetic decomposition. Therefore, relative thermo-stability of a chelate was determined by comparing its half-life to the half-life of other chelates. The half-life is defined as the time necessary for the chelates concentration to decrease to one-half the initial concentration. Table 3-1 shows the decomposition rate constants and the corresponding half-life's for the iron (II) chelates studied.

Table 3-1

Iron (II) •Chelate Thermostability in AVT Chemistry

Chelate	pH	Temperature (°C)	Rate Constant (hr^{-1})	Half-Life (hrs)
Fe(II)•NTA	9.52	290	Decomposed on heat-up	0.08
Fe(II)•EDTA	9.32	290	2.5	0.25
Fe(II)•EDTA	8.5	290	1.97	0.35
Fe(II)•HEDTA	9.60	291	0.247	2.8
Fe(II)•HEDTA	9.26	290	0.181	3.8
Fe(II)•DTPA	9.47	290	Decomposed on heat-up	0.08
Fe(II)•EDTA*	10.4	308	0.32	2.2

*Sodium Phosphate - Sodium Sulfite Chemistry (ref. 8)

Both Fe(II)·EDTA and Fe(II)·HEDTA show greater thermostability at lower pH's as shown in Table 3-1. PWR's are usually run between pH 8-9. These data suggest excellent stability at PWR operating conditions. Both Fe(II)·NTA and Fe(II)·DTPA decomposed almost completely during the reactor heat-up period indicating very short and unmeasurable half-lifes. Approximately 20 ppm of Fe(II)·NTA was detected in the first sample collected from the reactor (the first sample was collected at approximately the time the reactor reached 290°C). No Fe(II)·NTA was detected in subsequent samples. No Fe(II)·DTPA could be detected in the first sample. This implies that NTA is more stable than DTPA. But, neither chelant was considered suitable for further study.

Table 3-1 shows that the half-life of Fe(II)·EDTA in AVT water chemistry is less stable than Fe(II)·EDTA in sodium phosphate-sodium sulfite water chemistry.

Perhaps the most striking result was finding that Fe(II)·HEDTA exhibited one order of magnitude higher stability than Fe(II)·EDTA in AVT chemistry. Also the stability of Fe(II)·HEDTA appears to increase at lower pH's. These data indicate HEDTA may offer some advantages over EDTA in AVT chemistry.

3.1.2. CALCIUM CHELATE THERMOSTABILITY

The calcium chelates of EDTA and HEDTA were studied at various pH's and temperatures. Table 3-2 shows the results of these studies. Duplicate experiments were conducted with the Ca.HEDTA chelate, as shown in Table 3-2, to determine the reproducibility of the measurements. The reproducibility of the rate constants was + or - 0.5%.

Ca·EDTA was more stable in AVT water chemistry than in phosphate sulfite water chemistry. As Table 3-2 shows the Ca·EDTA chelate is even more stable at pH 8.5 than pH 9.5.

Table 3-2 shows the Ca·HEDTA chelate is more stable at higher temperatures than the Ca·EDTA chelate. The stability of the Ca·HEDTA chelate decreased directly with pH from pH 9.5 to pH 7.7 as shown in

Table 3-2

Calcium HEDTA and EDTA Chelates Thermostability

Chelate	pH	Temperature (°C)	Rate Constant (hr^{-1})	Half-Life (hrs)
Ca•HEDTA	9.5	290	0.179	3.9
Ca•HEDTA	9.5	290	0.178	3.9
Ca•HEDTA	9.5	300	0.220	3.2
Ca•HEDTA	9.5	310	0.267	2.6
Ca•HEDTA	8.7	290	0.223	3.1
Ca•HEDTA	7.7	290	0.283	2.4
Ca•EDTA	8.5	230	0.0885	8.1
Ca•EDTA	9.5	230	0.106	6.5
Ca•EDTA	9.5	250	0.414	1.7
Ca•EDTA	9.5	272	3.88	0.18
Ca•EDTA	9.3	230	0.19	3.6

*Phosphate-Sulfite Chemistry (ref. 9)

Figure 3-1. However, the slight loss of stability of Ca•HEDTA due to lower pH is small when compared to its excellent overall stability.

The Arrhenius plots were determined for Ca•EDTA and Ca•HEDTA and are shown in Figures 3-2 and 3-3 respectively. These plots predict the effect of temperature on the decoposition rate of Ca•EDTA and Ca•HEDTA.

The thermostability of both the Ca•EDTA and Ca•HEDTA chelates suggests that calcium ions can be transported through PWR's.

3.1.3 COPPER CHELATES THERMOSTABILITY

Table 3-3 gives the results of studies conducted on the thermostability of EDTA and HEDTA copper chelates. It was generally believed that

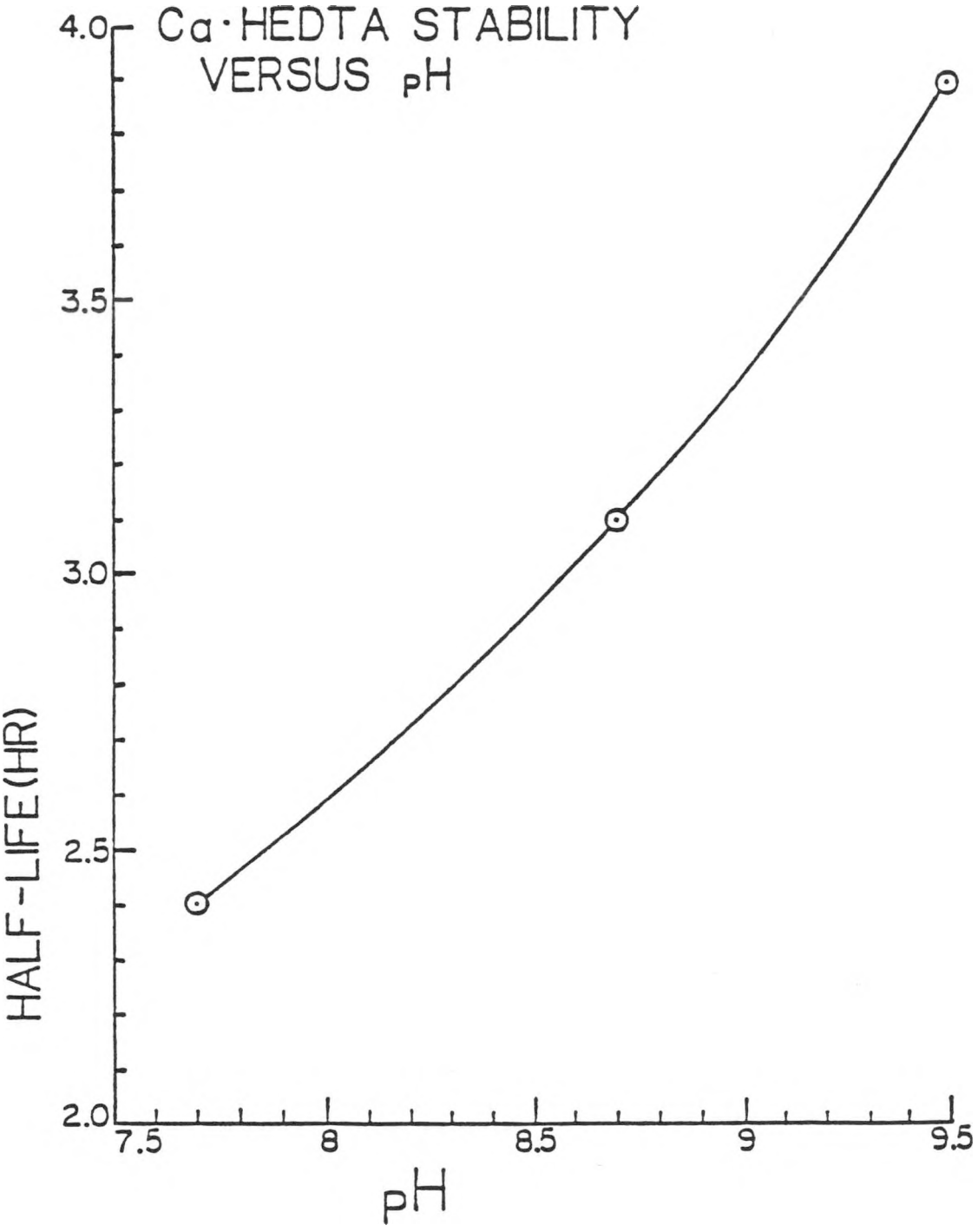

Ca·HEDTA STABILITY
VERSUS pH
4.0
3.5
3.0
2.5
2.0
HALF-LIFE(HR)
7.5
8
8.5
9
9.5
pH

FIGURE 3-1

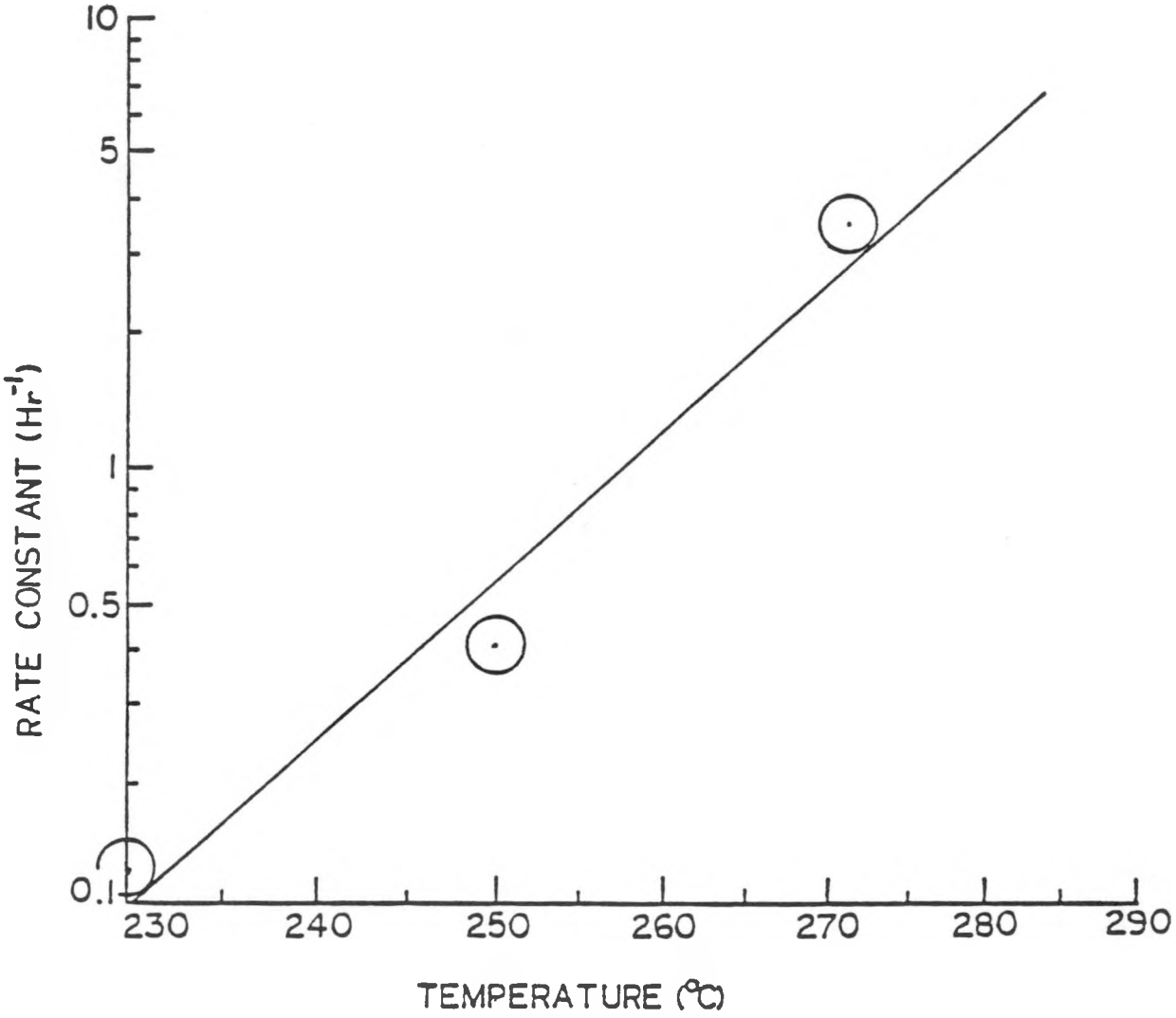


FIGURE 3-2

Ca^{+}(EDTA) ARRHENIUS PLOT

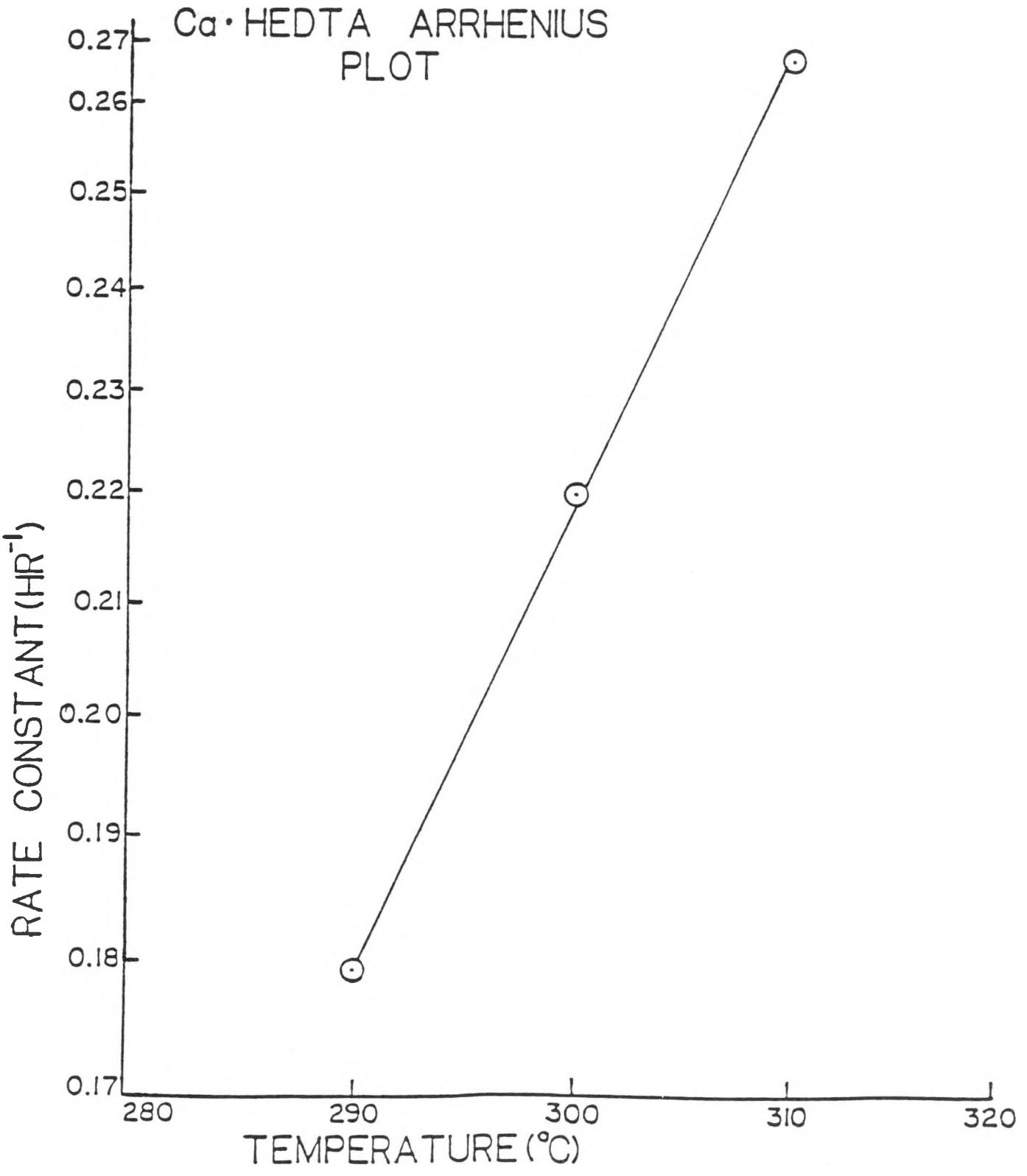

Ca·HEDTA ARRHENIUS PLOT
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.20
0.19
0.18
0.17
RATE CONSTANT (HR⁻¹)
280
290
300
310
320
TEMPERATURE (°C)

FIGURE 3-3

chelating agents cannot remove copper from operating steam generators. As table 3-3 shows, Cu·EDTA has a half-life of 0.1-0.2 hrs. This implies that copper may be transported through or cleaned from operating steam generators.

Table 3-3

Cu·HEDTA and Cu·EDTA Thermostability

Chelate	pH	Temperature (°C)	Rate Constant (hr^{-1})	Half-Life (hrs)
Cu·HEDTA	9.5	260	4.43	0.16
Cu·HEDTA	9.6	230	0.865	0.80
Cu·EDTA	9.6	270	3.80	0.18
Cu·EDTA	8.7	270	4.93	0.14
Cu·EDTA	8.1	270	4.20	0.17
Cu·EDTA	8.8	290	12.0	0.058

Table 3-2 shows the iron and calcium chelates of HEDTA to have much greater stability than the corresponding EDTA chelates. Table 3-3 shows that the Cu·EDTA chelate at 270°C has a half-life approximately the same as Cu·HEDTA chelate at 260°C. Thus the Cu·EDTA chelate is more stable than the Cu·HEDTA chelate. The thermostability of the Cu·EDTA chelate was not significantly effected by pH.

3.1.4 MAGNESIUM CHELATES THERMOSTABILITY

The stabilities of Mg·EDTA and Mg·HEDTA chelates were determined. Both Mg·HEDTA and Mg·EDTA chelates exhibit essentially the same stabilities at pH 9.5 and 290°C in AVT water chemistry as shown in Table 3-4. Figure 3-4 shows the effect of pH on Mg·HEDTA chelate. The optimum stability appears to occur at about pH 8.1. This is within the normal operating range of the steam generator, and suggests excellent Magnesium transport through steam generators.

Table 3-4

Magnesium HEDTA and EDTA Chelates

Thermostability

Chelate	pH	Temperature (°C)	Rate Constant (hr^{-1})	Half-Life (hrs)
Mg•HEDTA	9.5	290	0.400	1.7
Mg•HEDTA	8.1	290	0.147	8.8
Mg•HEDTA	8.85	290	0.117	5.9
Mg•HEDTA	7.3	290	0.103	6.7
Mg•HEDTA	9.5	290	0.497	1.4
Mg•HEDTA	9.5	290	0.510	1.4

3.1.5 EDTA DECOMPOSITION PRODUCTS

Samples from the thermostability studies, as well as samples obtained from CECo's Model Steam Generators, were analyzed using High Pressure Liquid Chromatography (HPLC), ion-chromatography, and GC-mass spectrometry. The results of these analyses were used to postulate decomposition pathways.

The following components have been qualitatively, but not quantitatively identified as being carried over in the steam:

CO_2
Methylamine and dimethylamine
Hydroxyethylamine and its methyl and dimethyl derivatives
Ethylenediamine and its methyl, dimethyl, trimethyl and tetramethyl derivatives
No CO was detected

There also appears to be relatively small amounts of the following substances in the liquid phase:

Methanol
Formaldehyde
N-substituted piperazines
1-piperazine carboxaldehyde

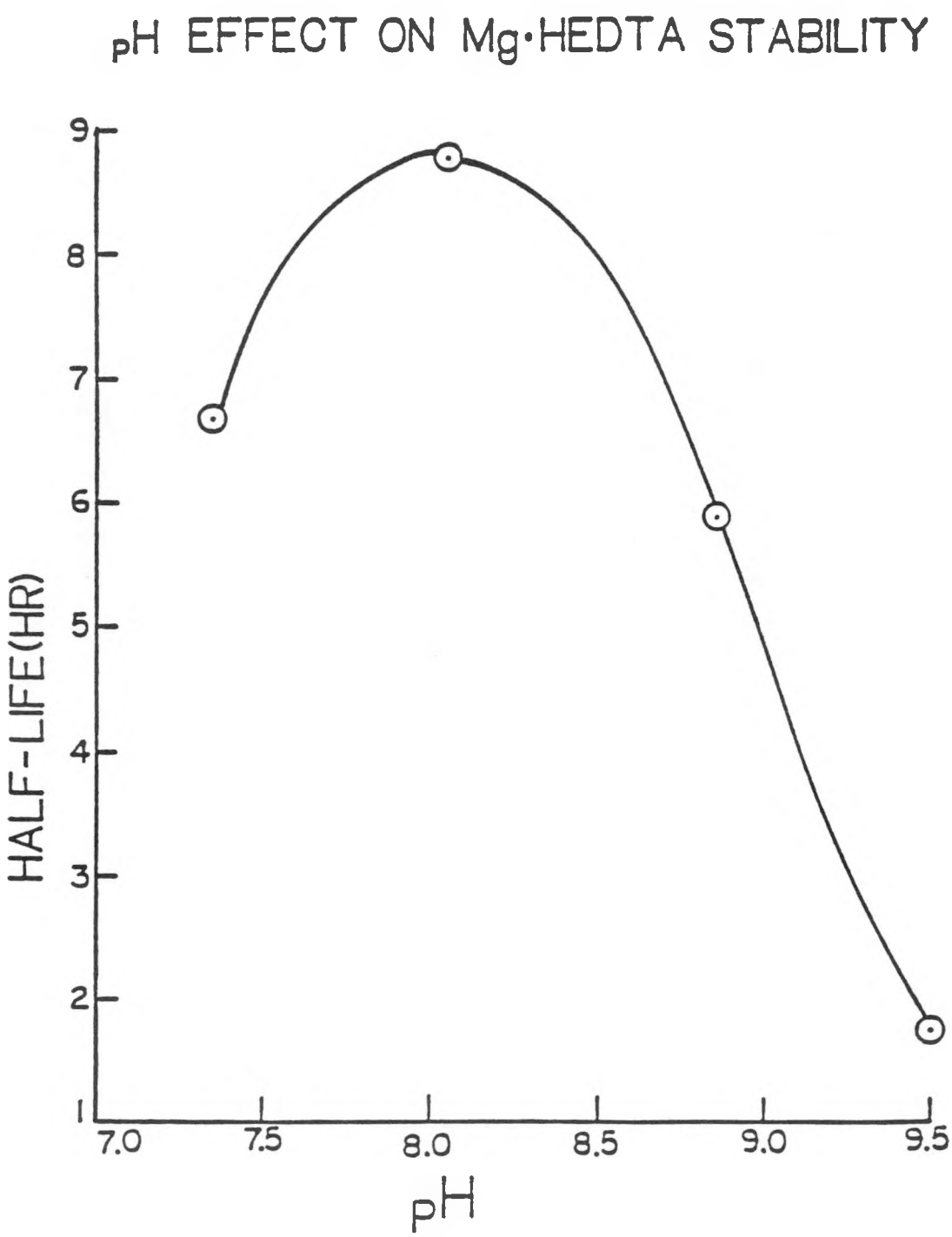

pH EFFECT ON Mg·HEDTA STABILITY
HALF-LIFE(HR)
9
8
7
6
5
4
3
2
1
7.0
7.5
8.0
8.5
9.0
9.5
pH

FIGURE 3-4

Decomposition appears to follow three mechanisms (ref. 9). The most prominent mechanism is the hydrolysis of the carbon-nitrogen bond. Equation 1, shows an example of the hydrolysis of EDTA.

Equation 1.

$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2 + H_2O \rightarrow HN(CH_2COOH)_2 + HOCH_2CH_2N(CH_2COOH)_2$$

Decarboxylation is another path that yields methylamines and CO_2. An example of this reaction is the decarboxylation of iminodiacetic acid shown in equation 2.

Equation 2.

$$HN(CH_2COOH)_2 \rightarrow CH_3HNCH_2COOH + CO_2$$

Equations 3 and 4 are examples of the third decomposition path. This pathway involves ammonification, i.e. decomposition to produce amines.

Equation 3.

$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2 + NH_3 \rightarrow H_2NCH_2CH_2N\ (CH_2COOH)_2 + HN(CH_2COOH)_2$$

Equation 4.

$$HOCH_2CH_2N(CH_2COOH)_2 + NH_3 \longrightarrow H_2NCH_2CH_2N(CH_2COOH)_2 + H_2O$$

All major decomposition products can be formed by combinations of these mechanisms. The mechanisms that cause the formation of the minor decomposition products, are not known and are left for future study.

3.2 TASK 2 - MATERIALS COMPATIBILITY

The corrosive effects of chelating agents were studied at the conditions encountered in PWR steam generators, i.e. temperature, pressure, residence time and chemistry. The following metals which are in direct contact with secondary water as well as several metals which contact only vapor were evaluated:

SA106 Gr. B (Feedwater system)

SA234 wpb Sec III Cl II (Feedwater system)

SA285 Gr. C (Steam generator internals)

SA333 Gr. 6 (Feedwater system)

SA508 Cl II (tube sheet, steam)

SA516 Gr. 70 S14 (Secondary manway)

SA533 Gr. A (1I (Stud barrel, lower shell barrel, transition cone, upper shell)

INCONEL 600 (tubes)

Tests which were performed included:

1. Exposure of flat plates to chelant solution. (General weight loss)
2. Exposure of stressed welds to chelant solution. (Welded U-bends)
3. Exposure of precracked and stressed specimens to chelant solution.
4. Exposure of galvanic couples.
5. Exposure of copper-plated flat specimens.

All tests were conducted in a dynamic loop. Fresh solvent was continuously introduced into the bottom of the autoclave and spend solvent was continuously removed from the top. The residence time of a PWR steam generator (approximately 4 hours) was simulated in the corrosion loop.

These data were used to predict the corrosion rates which should be expected in the secondary loop. The surfaces of selected specimens which had been exposed to chelant solutions were studied by techniques such as electron microscopy and X-ray defraction. The reported findings of Soviet researchers (ref. 5) on chelate-induced formation of an extremely protective iron oxide layer were verified.

A brief description of the test equipment and procedures used for the materials compatibility study can be found in Appendix A.2.

3.2.1 GENERAL WEIGHT LOSS (FLAT PLATES)

Table 3-5 gives test conditions for all general weight loss test runs.

Table 3-5

General Weight Loss Test Conditions

Test No.	Temperature, °C	Chemistry
1	290	0.1% EDTA/AVT
2	290	AVT only
3	290	0.1% EDTA/AVT/5 ppm Fe
4	290	0.1% EDTA/AVT/5 ppm Fe (coupons from Test 2)
5	290	0.1% HEDTA/AVT/5 ppm Fe

It was found that weight loss (corrosion rate) approached zero after a period of time. Further analysis of the data showed that the weight loss data fit an equation of the following form:

equation 3-1: $W = C(1-e^{-kt})$ where W is the weight loss at time t
C is maximum metal loss
k is a constant

The first derivative of this equation yields the corrosion rate (r) at any time t:

equation 3-2: $r = kCe^{-kt} \quad (t>0)$

The initial corrosion rate is then kC.

Figure 3-5 shows a typical plot of the weight loss data and Figure 3-6 shows the corresponding corrosion rate curve. The surfaces of the coupons turned black as the corrosion rates decreased indicating that active coupon surfaces became passivated with time. Thus, the corrosion rate curves, will be referred to as passivation curves which more accurately describes the observed phenomenon. The constant k in the equation 3-1 is the passivation constant.

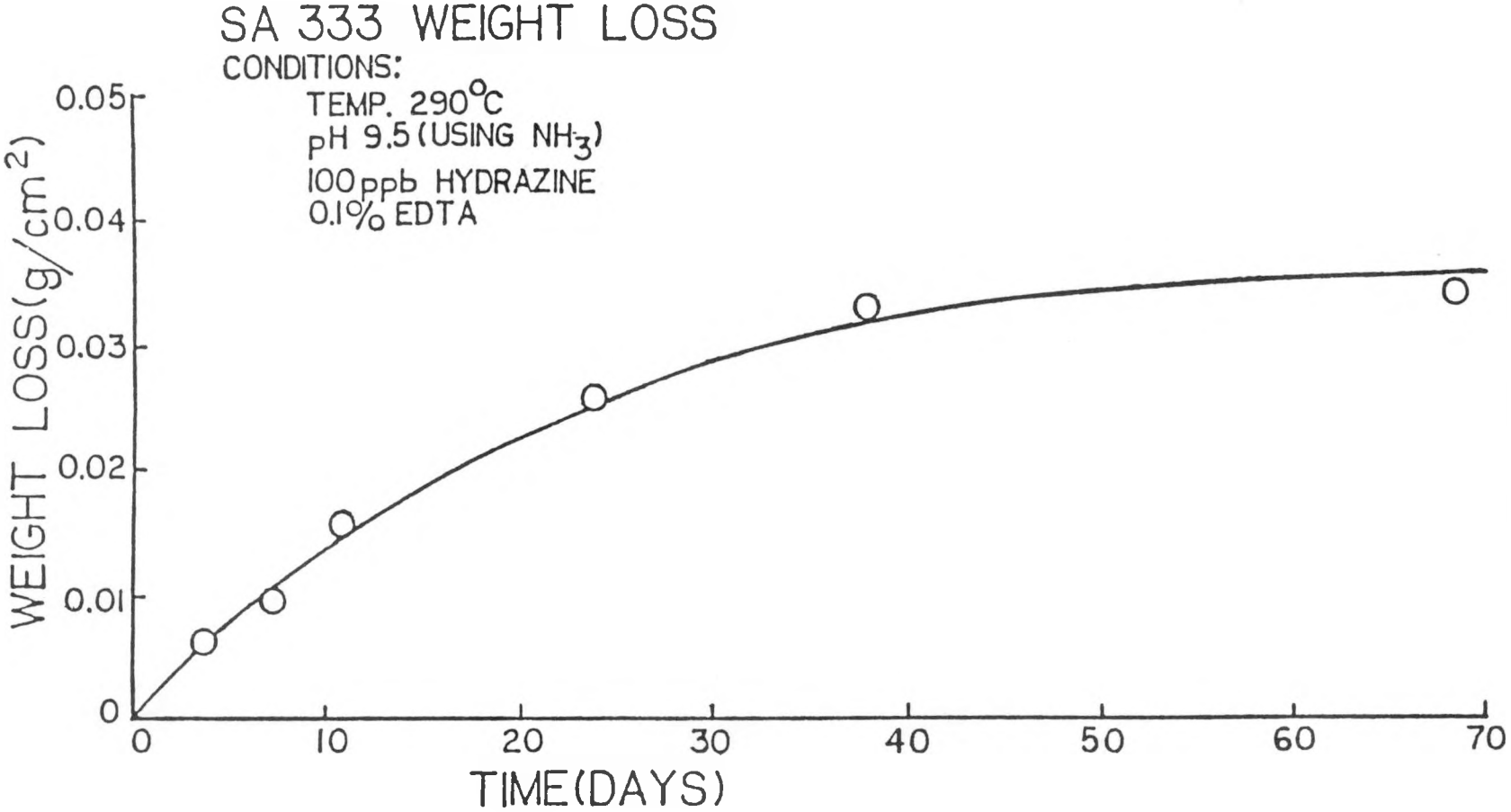

SA 333 WEIGHT LOSS
CONDITIONS:
TEMP. 290°C
pH 9.5 (USING NH3)
100ppb HYDRAZINE
0.1% EDTA
WEIGHT LOSS(g/cm²)
0.05
0.04
0.03
0.02
0.01
0
0
10
20
30
40
50
60
70
TIME(DAYS)

FIGURE 3-5

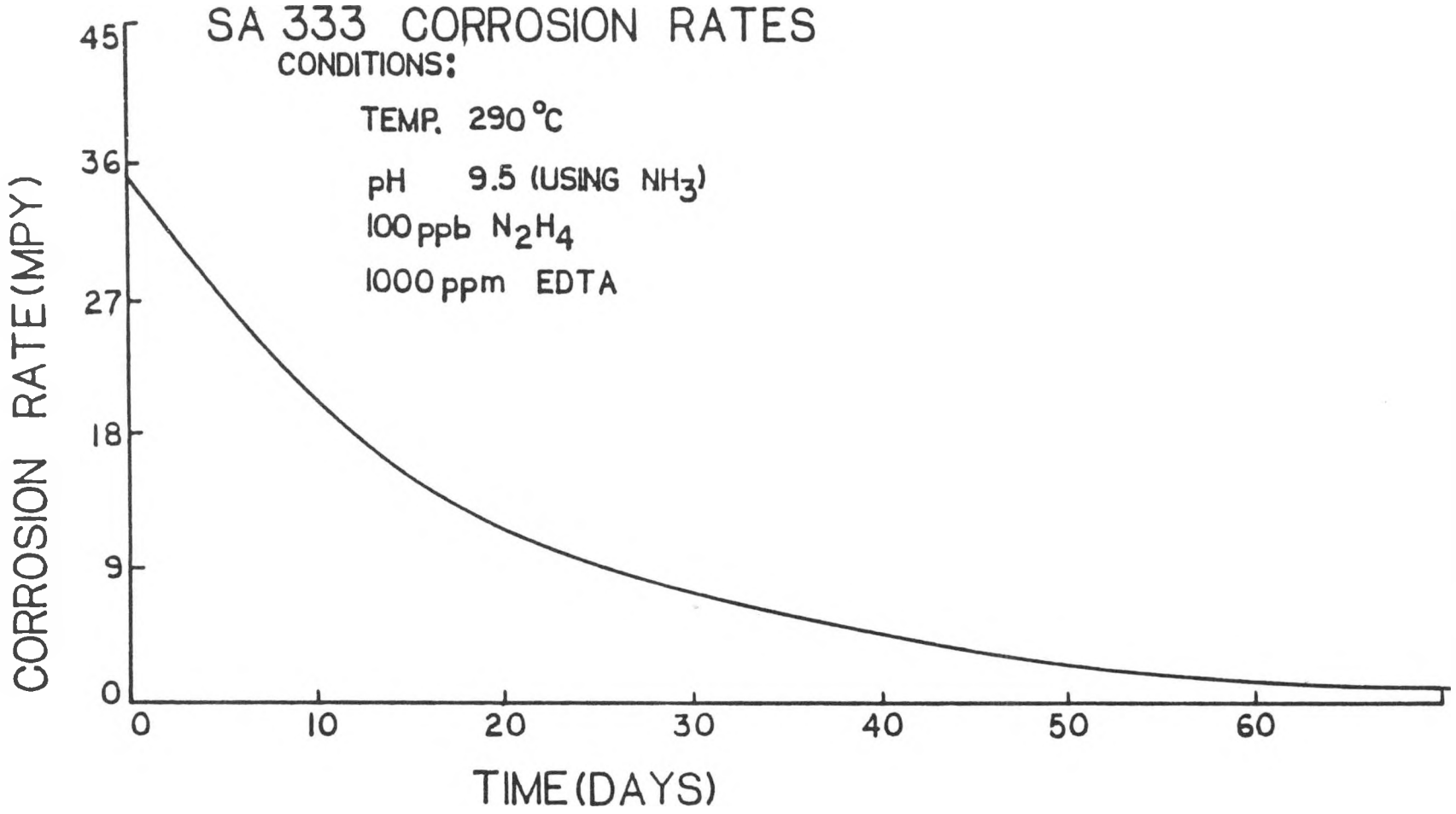

SA 333 CORROSION RATES
CONDITIONS:
TEMP. 290 °C
pH 9.5 (USING NH_3)
100 ppb N_2H_4
1000 ppm EDTA
CORROSION RATE (MPY)
45
36
27
18
9
0
0
10
20
30
40
50
60
TIME (DAYS)

FIGURE 3-6

Table 3-6 shows the passivation constants and maximum metal loss in Test 1. Fresh test solution entered the bottom of the test reactor and flowed upward and out the top of the reactor. Thus, the coupons located at the bottom of the test coupon rack were exposed to fresh EDTA without any iron, while the coupons located at the top of the test coupon rack were exposed to EDTA that was complexed with iron. Also, because of the time required for a given volume of test solution to pass from the bottom to the top of the test coupon rack, (See Appendix, A.2) the top row saw a lower concentration of EDTA due to thermal decomposition. As shown in Table 3-6, the coupons which were situated on the bottom row of the test coupon rack showed maximum metal loss of 1.6 - 2.4 mils for carbon steels and 0.45 mils for Inconel 600. The top row of the test coupon rack showed maximum metal loss of 0.20 - 0.36 mils for carbon steels and 0.06 mils for Inconel 600.

Because it appeared that iron was important for passivation, 5 ppm Fe was added to the 0.1% EDTA test solution used for Test 3. Table 3-7 shows the passivation rates and maximum metal loss for Test 3. A comparison of Tables 3-6 and 3-7 shows that corrosion of the coupons on the bottom row of the test rack was decreased by 20-50% as a result of the addition of a trace of iron. More importantly, Table 3-7 shows the passivation rates were nearly the same for all coupons regardless of location in the test rack. This indicates the importance of iron <u>in solution</u> for passivation with EDTA present.

The solution used during Test 2 consisted of AVT water chemistry only. Figure 3-7 shows results which are typical of Test 2. Note the initial weight loss followed by an apparent weight gain (negative weight loss). The scatter in the weight measurements is attributed to experimental measurement limitations. Table 3-8 shows the average total weight gain for the coupons. On two occasions, a black sludge clogged the pressure control valve of the test reactor. This suggests that corrosion occured. The overall trend however, is weight gain. This indicates scale formation and/or formation of a passive film.

Table 3-6

Test 1 Passivation Data

0.1% EDTA at 290°C

Metal	Coupon Number	Location On Test Rack	Passivation Rate (1/Days),k	Maximum Metal Loss (Mils),C
SA106	B04	Bottom	0.045	2.4
SA106	B05	Middle	0.044	0.39
SA106	B06	Top	0.11	0.28
SA234 wpb	K04	Bottom	0.045	2.3
SA234 wpb	K05	Middle	0.079	2.27
SA234 wpb	K06	Top	0.13	0.24
SA285C	P04	Bottom	0.041	2.4
SA285C	P05	Middle	0.028	0.61
SA285C	P06	Top	0.073	0.36
SA333	H04	Bottom	0.048	1.9
SA333	H05	Middle	0.10	0.27
SA333	H06	Top	0.12	0.25
SA508	Y04	Bottom	0.043	1.7
SA508	Y05	Middle	0.087	0.24
SA508	Y06	Top	0.14	0.20
SA516	L04	Bottom	0.048	1.7
SA516	L05	Middle	0.066	0.26
SA516	L06	Top	0.13	0.21
SA533	W04	Bottom	0.052	1.6
SA533	W05	Middle	0.090	0.26
SA533	W06	Top	0.11	0.21
Inconel 600	N04	Bottom	0.060	0.45
Inconel 600	N05	Middle	4.0	0.050
Inconel 600	N06	Top	4.0	0.064

Table 3-7

Test 3 Passivation Data

0.1% EDTA + 5 ppm Fe @ 290°C

Metal	Coupon Number	Location On Test Rack	Passivation Rate (1/Days),k	Maximum Metal Loss (Mils),C
SA106	B07	Bottom	0.10	1.4
SA106	B08	Middle	0.090	0.19
SA234 wpb	K07	Bottom	0.14	1.5
SA234 wpb	K08	Middle	0.12	0.19
SA285C	P07	Bottom	0.064	1.8
SA285C	P08	Middle	0.018	0.35
SA285C	P09	Top	0.061	0.21
SA285C	P10	Top	0.060	0.27
SA285C	P11	Top	0.055	0.32
SA333	H07	Bottom	0.12	1.4
SA333	H08	Middle	0.098	0.19
SA508	Y07	Bottom	0.095	1.0
SA508	Y08	Middle	0.074	0.20
SA508	Y09	Top	0.060	0.23
SA508	Y10	Top	0.089	0.20
SA508	Y15	Top	0.038	0.21
SA533	W07	Bottom	0.089	1.1
SA533	W08	Middle	0.056	0.23
SA533	W09	Top	0.11	0.19
SA533	W10	Top	0.14	0.19
SA516	L07	Bottom	0.10	1.4
SA516	L08	Middle	0.081	0.23
Inconel 600	N07	Bottom	0.076	0.21
Inconel 600	N08	Middle	1.055	0.070
Inconel 600	N07	Top	0.064	0.054

SA 333 WEIGHT LOSS
CONDITIONS:
TEMP. 290°C
pH 9.5 (USING NH3)
100 ppb HYDRAZINE
WEIGHT LOSS(10-4 g/cm2)
TIME(DAYS)
5
4
3
2
1
0
-1
-2
-3
-4
0
10
20
30
40
50
60
70

FIGURE 3-7

Table 3-8

Test 2 Weight Gain Data

AVT ONLY @ 290°C

Metal	Coupon Number	Location On Test Rack	Maximum Metal Loss (Mils),C
SA106	B09	Bottom	- 0.0001
SA106	B10	Middle	0.00004
SA333	H09	Bottom	0.0002
SA333	H10	Middle	0.0001
SA234 wpb	K09	Bottom	0.00013
SA234 wpb	K10	Middle	0.00011
SA516	L09	Bottom	0.00013
SA516	L10	Middle	0.00059
Inconel 600	N10	Bottom	0.00011
Inconel 600	N11	Middle	0.000037
Inconel 600	N12	Top	0.000034
SA285C	P12	Bottom	0.000080
SA285C	P13	Middle	0.00015
SA285C	P14	Top	0.00016
SA285C	P15	Top	0.000080
SA285C	P16	Top	0.00014
SA333	W11	Bottom	- 0.000037
SA333	W12	Middle	0.000019
SA333	W13	Top	- 0.00017
SA508	Y11	Bottom	0.00015
SA508	Y12	Middle	0.00019
SA508	Y13	Top	0.00017
SA508	Y14	Top	0.000040
SA508	Y15	Top	0.000029

The coupons, which had been exposed to AVT chemistry during Test 2, were reused for Test 4. This was to study the effect of EDTA/Fe on AVT passivated surfaces. Table 3-9 shows the results of Test 4. The passivation rates were somewhat greater than those seen in Test 3 which used coupons with active surfaces. The maximum metal loss, however, was essentially the same. These data suggest that the use of EDTA causes a more protective film to be formed on the surface of the coupons.

Table 3-10 shows the passivation rate constants (k) and the maximum metal loss (C) for Test 5 (coupons exposed to 0.1% HEDTA in AVT chemistry and 5 ppm Fe). A comparison of Table 3-7 (coupons exposed to 0.1% EDTA in AVT chemistry and 5 ppm Fe) to Table 3-10 shows that both k and C are greater for the coupons exposed to HEDTA. Figure 3-8 shows SEM data comparing the surfaces of coupons exposed to AVT chemistry alone with coupons exposed to 0.1% EDTA and 0.1% HEDTA in AVT chemistry and 5 ppm Fe. The coupons exposed to the chelants have sharp, well defined crystals on their surface. The coupons exposed to AVT chemistry alone have smaller, almost amorphous crystals. X-ray defraction showed these crystals to be magnetite (Fe_3O_4).

3.2.2 U-BEND WELDMENTS

Welded coupons, made by welding two pieces of SA106 Gr. B or SA508 together, were obtained from UNC Nuclear Industries, Inc. Details of the preparation of these coupons can be found in reference 6.

Three specimens of each metal were exposed for 30 days to a 0.1% EDTA in AVT water chemistry and 5 ppm Fe. After the exposure, all specimens were examined both visually, microscopically, and by using the MAGNAFLUX process.

The results of the exposure was that no cracking or pitting was found on any of the exposed specimens. The heat effected zones and the weld material showed no signs of any type of corrosion.

Table 3-9

Test 4 Passivation Data

Test 2 Coupons in 0.1% EDTA + 5 ppm Fe @ 290°C

Metal	Coupon Number	Location On Test Rack	Passivation Rate (1/Days),k	Maximum Metal Loss (Mils),C
SA106	B09	Bottom	0.39	0.36
SA106	B10	Middle	0.10	0.056
SA234 wpb	K09	Bottom	0.011	1.6
SA234 wpb	K10	Middle	0.15	0.062
SA285C	P12	Bottom	0.020	1.6
SA285C	P13	Middle	0.084	0.077
SA285C	P14	Top	0.047	0.020
SA285C	P15	Top	0.025	0.41
SA285C	P16	Top	0.043	0.21
SA333	H10	Bottom	0.012	1.2
SA333	H11	Middle	0.13	0.083
SA508	Y11	Bottom	2.3	0.28
SA508	Y12	Middle	0.30	0.036
SA508	Y13	Top	0.057	0.13
SA508	Y14	Top	0.045	0.17
SA508	Y15	Top	0.038	0.21
SA516	L09	Bottom	2.3	0.41
SA516	L10	Middle	0.12	0.076
SA533	W11	Bottom	0.053	0.20
SA533	W12	Middle	0.18	0.040
SA533	W13	Top	0.036	0.19
Inconel 600	N10	Bottom	0.17	0.29
Inconel 600	N11	Middle	1.8	0.0065
Inconel 600	N12	Top	2.0	0.070

Table 3-10

Test 5 Passivation Data

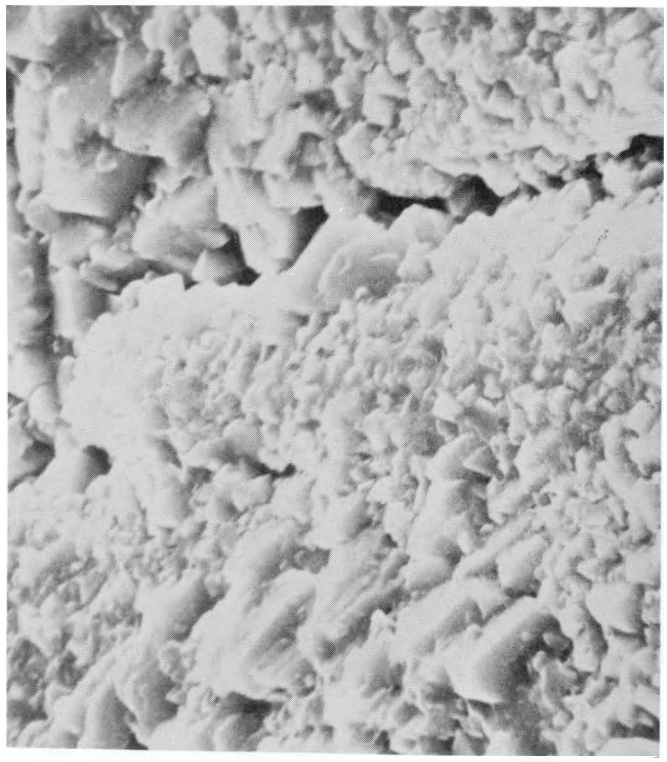
0.1% HEDTA + 5 ppm Fe @ 290°C

Metal	Coupon Number	Location On Test Rack	Passivation Rate (1/Days),k	Maximum Metal Loss (Mils),C
SA516	L13	Bottom	0.18	0.26
SA516	L14	Middle	0.20	0.27
SA516	L15	Top	0.21	0.39
SA508	Y17	Bottom	0.21	0.23
SA508	Y18	Middle	0.23	0.29
SA508	Y19	Top	0.22	0.24
SA508	Y65	Bottom	0.16	0.23
SA508	Y66	Middle	0.21	0.21
SA508	Y67	Top	0.20	0.27
SA285C	P88	Bottom	0.20	0.22
SA285C	P89	Middle	0.22	0.26
SA285C	P90	Top	0.16	0.36
SA533	W14	Bottom	0.16	0.26
SA533	W16	Middle	0.27	0.23
SA533	W17	Top	0.24	0.23
Inconel 600	N14	Bottom	2.2	0.015
Inconel 600	N15	Middle	2.4	0.012
Inconel 600	N16	Top	2.3	0.013
Inconel 600	N51	Bottom	4.0	0.0093
Inconel 600	N52	Middle	2.3	0.0081
Inconel 600	N53	Top	2.4	0.010
SA285C	P18	Bottom	0.17	0.24
SA285C	P19	Middle	0.20	0.29
SA285C	P20	Top	0.18	0.28

SCANNING ELECTRON
MICROGRAPHS
OF SA533

Exposed to
AVT only
2000X

Exposed to 0.1%
EDTA + 5 ppm Fe +
AVT 2000X



Exposed to 0.1%
HEDTA + 5 ppm Fe +
AVT 2000X

FIGURE 3-7

3.2.3 PRE-CRACKED STRESSED SPECIMENS

This test was designed in cooperation with Dr. Sheldon Mostovoy of the Illinois Institute of Technology (ref. 10). The test consisted of exposing three-point Bend Specimens to a solution of 0.1% EDTA in AVT water chemistry and 5 ppm Fe for 45 days and then examining the coupons for signs of corrosion. A description of the test equipment used for the environmentally assisted cracking tests can be found in Appendix A.3. Three fixtures containing 4 coupons each were exposed during the MSG operation.

The metallurgical examination of the specimens showed that the SA533 coupons were cracked at 90^{o} to the pre-crack. Subsequent examination revealed that the material used for the coupons had appreciable amounts of non-metallic inclusions. Therefore the SA533 results were disqualified. The materials showed no signs of environmentally induced stress corrosion. Also no other forms of corrosion were observed on any of the specimens. The specimens failed to passivate at the points where the coupons were held in place.

The results of this test indicate that there would be no environmentally induced stress corrosion problems using EDTA in PWR steam generators.

3.2.4 GALVANIC COUPLES

Table 3-11 shows the galvanic couples which were tested. Coupons of the two metals were placed face-to-face on the coupon test rack and exposed to 0.1% EDTA + 5 ppm Fe (as $FeSO_4$) in AVT water chemistry at $290^{o}C$, 1250-1300 psig for 30 days. After cleaning, the coupons were examined under a binocular microscope. No signs of pitting or other corrosion were detected. The coupons were black except where the two faces of the coupons made contact as shown in Figure 3-9.

Table 3-11

Galvanic Couples Tested

Inconel 600 - SA285C
Inconel 600 - SA508

SA285C/INCONEL®600
GALVANIC COUPLE
FIGURE 3-8

3.2.5 COPPER PLATED COUPONS

The flat metal coupons listed in Table 3-12 were cleaned and electrolytically coated with copper on one-half of the coupon. After a 30 day exposure to 0.1% EDTA + 5 ppm Fe (as $FeSO_4$) in AVT water chemistry at 290°C, 1250-1300 psig, the coupons were examined under a binocular microscope for signs of pitting or other corrosion. These coupons were not cleaned after exposure. No signs of pitting or any other types of corrosion were detected. However, as shown in Figure 3-10, 80-100% of the plated copper was removed.

Table 3-12

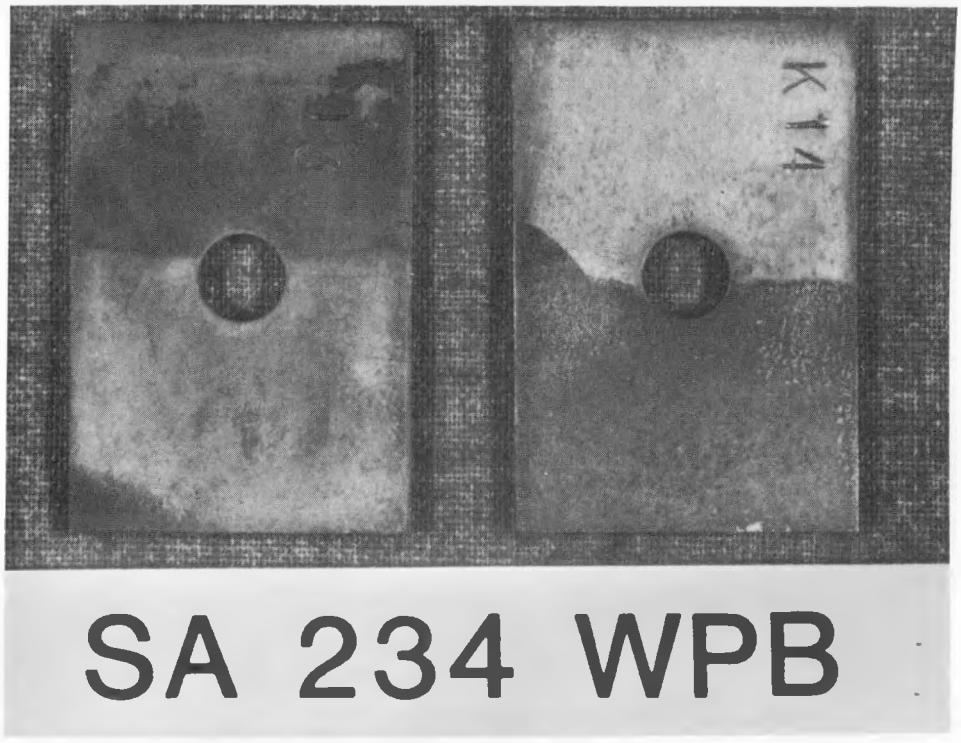
Copper Plated Coupon Metals

SA508
SA533
SA285C
Inconel 600
SA106
SA333
SA234 wbp

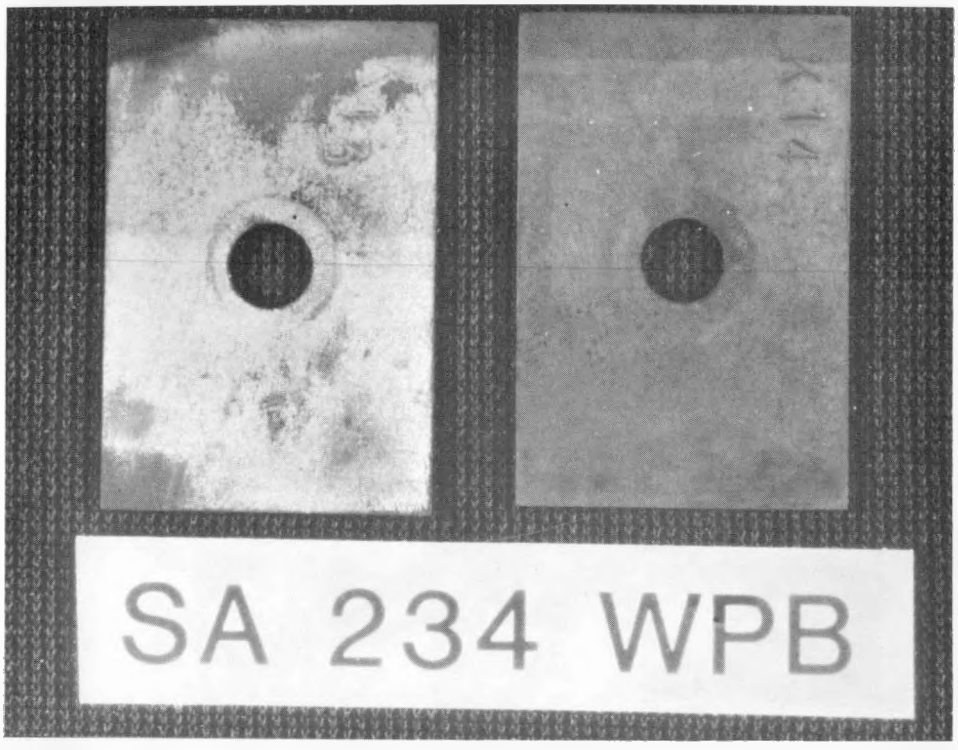
3.3 TASK 3 - MODEL STEAM GENERATOR TESTING

Commonwealth Edison Company (CECo) operated six model steam generators (ref. 10). Four of the MSG's were used in the evaluation of on-line chelant addition project. A brief description of the model steam generator test equipment is given in Appendix A.4. Dow researchers recommended both the specific chelating agent and the dosage, and analyzed water samples from the MSG's for organic components as reported in Section 3.1.

Although visual inspections yield the best data of a chelant's performance, another technique, which is based on monitoring metal ion transport through MSG, can yield results during operation. Metal ion



BEFORE EXPOSURE



AFTER EXPOSURE

Figure 3-9
SA234wpb COPPER PLATED
FLAT COUPONS

transport through a MSG is measured by means of a mass balance across the MSG as shown by the following equation:

$$\% \text{ Transport} = \frac{B(M)_B + S(M)_S}{F(M)_F} \times 100\%$$

where: F, B, and S are the mass flow rates of the feedwater, blowdown, and steam respectively (M) is the concentration of the metal ion of interest in the subscripted, F, B, S (Feedwater, blowdown, and steam respectively).

Interpretation of the data required knowledge of the MSG history and consideration of all metal ion transport data. If a metal ion shows less than 100% transport then deposition of that ion is occurring. When a metal ion has transport greater than 100%, then cleaning is occurring. If cleaning is occurring, the metal ion transport trend will eventually be reduced to 100% as the MSG is cleaned.

Iron transport data can give an indication of corrosion when compared to other metal ion transport data. Iron transport greater than 100% can indicate cleaning and/or corrosion. Corrosion is indicated when iron transport greater than 100% remain constant or increase as other metal ion transport begins to decrease.

3.3.1 MODEL STEAM GENERATORS (MSG) OPERATING ON SEA WATER FOULING

CECo conducted two accelerated-fouling, sea water in AVT water chemistry tests. The make-up water for these tests was adjusted with synthetic sea water (ASTM D1141) to obtain a concentration of 60 ppm Cl. One MSG (Unit 1) was fouled and dented prior to the start of EDTA addition. The second MSG (Unit 3) had EDTA addition started simultaneously with the fouling chemistry. The purpose of these two tests was to determine if EDTA could 1) clean a packed crevice or 2) prevent crevice packing, under accelerated fouling conditions.

Tables 3-13 and 3-14 show the transport data for the MSG's operated with salt water fouling. EDTA addition was started at the end of May, 1981 using a 1.2:1, EDTA:metal molar ratio. As shown in both Table 3-13 and Table 3-14 a significant lowering of the MSG's blowdown pH occurred after the start of EDTA addition. Also, these tables show Fe transport increased from approximately 150% to 5000%. This indicates either cleaning or corrosion.

Both MSG units experienced tube failures due to pitting corrosion, the detailed operation description for these MSG's can be found in reference 10. Examination of daily operating conditions showed that all failures of the Inconel 600 tubes occurred either during or immediately after wet layup periods with the water at pH 5.5-6.0 and 700-1000 ppm chloride concentration. These conditions are known to cause pitting of Inconel 600 (ref. 11). An extensive metallurgical examination conducted by CECo failed to show whether or not EDTA contributed to the Inconel 600 pitting.

An experiment was conducted to determine the role EDTA played in the lowering of the boilerwater pH. The experiment consisted of titrating 200 ml of 0.006 M metal salt (pH adjusted to 8.5 with ammonia) with 0.1 M EDTA (pH 8.5 with ammonia). The pH of the metal salt solution was measured after each addition of 1 ml of the EDTA solution. The metal ions tested were iron, magnesium, copper, and calcium. The metal salts tested consisted of the previously mentioned metal ions and the following anions:

chloride
sulfate
nitrate
hydroxide

Figure 3-11 shows the plot of the magnesium chloride titration. The results of these titrations show that chelation of magnesium and calcium ion will cause the pH to be lowered. Increasing the EDTA:metal ion ratio above 0.5:1 causes the pH to rise toward the initial pH of 8.5. This effect was also seen in the MSG's when the EDTA feed dosage was increased

Table 3-13

Materials Transport

Model Steam Generation Unit 1

Salt Water Prefouled

Month	Mass Overall	% Transport Fe	Cu	Ca	Mg	Na	Cl	Blowdown pH
March '81*	-	193	221	177	115	-	95	8.6
April '81*	-	112	84	62	105	-	112	8.6
May '81*	-	-	-	-	-	-	-	-
June '81	100	9,780	175	57	90	99	101	6.0
July '81	99	4,298	271	76	95	109	92	5.5
August '81	99	5,152	146	65	129	103	93	5.6
September '81	109	3,833	252	70	86	58	50	7.9
October '81	-	8	20	30	69	10	13	8.2

November '81 New tube bundle installed

*Na transport number assumed to be 100.

Table 3-14

Materials Transport

Model Steam Generation Unit 3

Salt Water Fouled

Month	Mass Balances	% Transport						Blowdown pH
		Fe	Cu	Ca	Mg	Na	Cl	
March*[1]	-	67	-	79	83	-	133	8.5
April*[2]	-	26	30	80	83	-	-	8.5
May*[2]	-	180	60	189	105	-	-	8.4
June	100	3,880	150	100	308	107	104	6.2
July	104	5,989	132	82	6,414	95	90	5.8
August	100	6,418	114	95	100	100	98	5.6
September	-	2,809	56	76	75	95	74	5.5
October	99	1,090	80	15	15	14	12	8.8
November	88	856	-	6	8	8	6	9.0

*Na transport assumed to be 100.

[1]Only 12 days fouling.

[2]No fouling during this period.

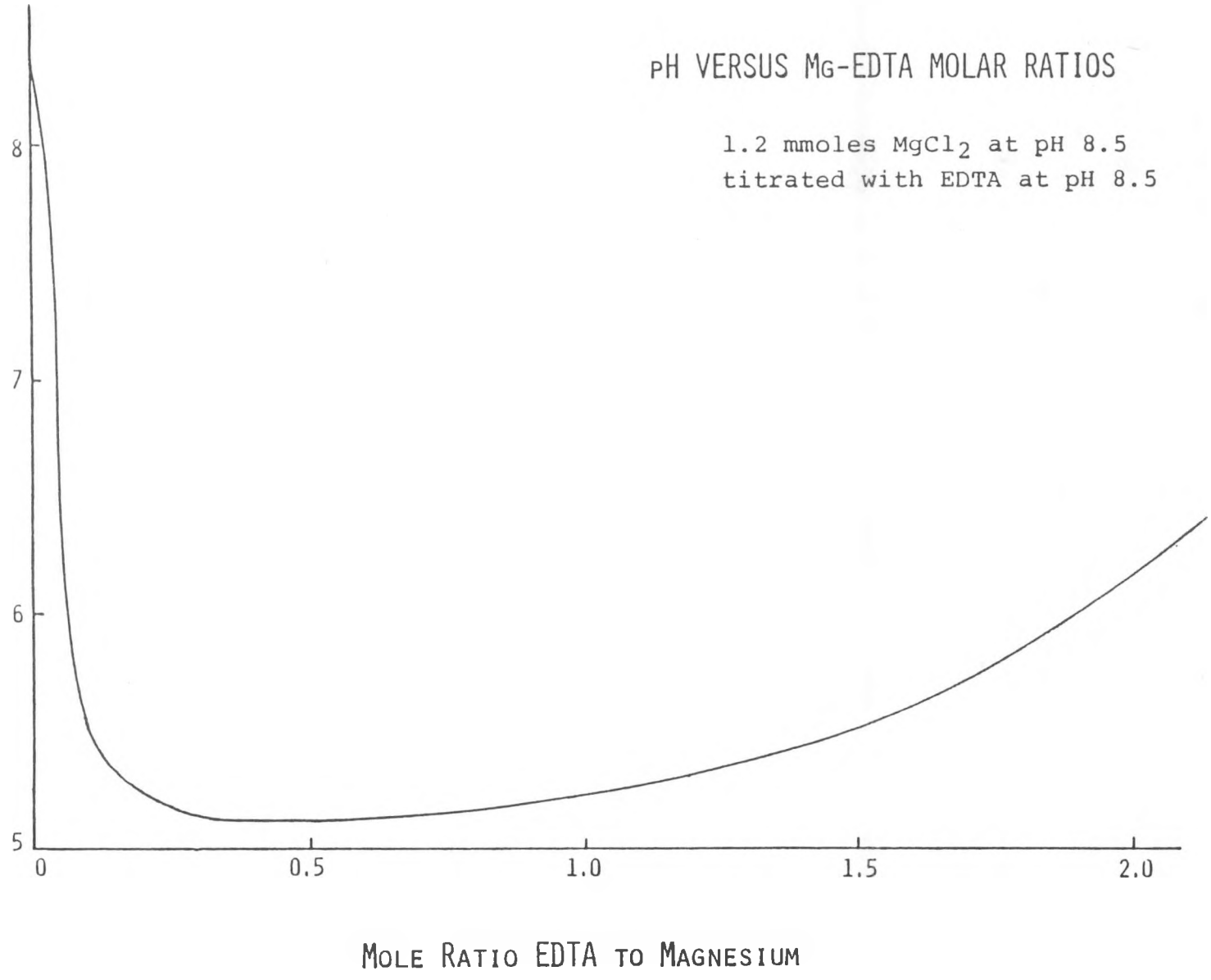

pH VERSUS Mg-EDTA MOLAR RATIOS
1.2 mmoles $MgCl_2$ at pH 8.5
titrated with EDTA at pH 8.5
pH
8
7
6
5
0
0.5
1.0
1.5
2.0
Mole Ratio EDTA to Magnesium

FIGURE 3-11

in September, 1981. There was no change in pH measured for any of the iron or copper salts tested. None of the anions tested affected the pH.

During September 1981, the EDTA:total metal ion mole ratio was increased from 1.2 to 2.2:1. During this phase of operation, the sludge on the bottom of the MSG was removed. Since Fe transport numbers remained at about 5000%, corrosion appeared to occur. General corrosion may have been the result of the following:

1. Low pH causing the protective Magnetite film to be destroyed, and acid induced corrosion to occur.
2. Corrosion from the high chloride levels (700-1000ppm). The role of EDTA in this increase in corrosion should be studied in the future.

3.3.2 MODEL STEAM GENERATORS OPERATING ON LAKE WATER FOULING

Tests similar to those described in Section 3.3.1 were conducted concurrently using a lake water fouling chemistry. The fouling solution was prepared by putting approximately 10 gallons of raw Lake Michigan water into 500 gallons of make-up water. The MSG feed water thus contained 0.5 ppm Fe, 0.1 ppm Cl 0.4ppm Ca, 0.1 ppm Mg, 2.4 ppm ammonia hydroxide, 3.2 ppm hydrazine and had pH of 9. MSG unit 2 was fouled prior to the start of EDTA addition. The fouling required 80 days of operation with the fouling chemistry. A second MSG, unit 4, had EDTA addition started at the same time as the fouling chemistry was started. EDTA addition, to both units, was initiated at the end of May, 1981.

The transport data for these units are shown in Tables 3-15 and 3-16. The low sodium (Na) transport numbers seen in tables 3-15 and 3-16 suggest an error in either sampling, analysis, or MSG operation. Correcting the metal transport numbers of the other metals for the error suggested by Na transport, the following average transport numbers were generated:

MSG Unit 2

Metal	% Transported
Fe	65
Cu	83
Ca	109
Mg	144

MSG Unit 4

Metal	% Transported
Fe	480
Cu	75
Ca	105
Mg	63

These estimated transport numbers suggest good to excellent transport of all metal ions.

Although MSG unit 2 (pre-fouled) had no open crevices at the end of the trial, the sludge that had been at the bottom of MSG unit 2 had been removed. After 169 days of operation with EDTA and fouling chemistry, MSG unit 4 had completely open crevices and had accumulated no sludge.

3.4 TASK 4 - PLANT DEMONSTRATION

If the results of the first three Tasks had been favorable, the Commonwealth Research Corporation was to operate one secondary loop of a PWR plant using an on-line chelate program.

The plant demonstration was deferred for several reasons which include the following:

1. Determination of possible effects of the chelant and its decomposition products on steam turbines.

2. Pitting was observed in the salt water fouled MSG's and the role of EDTA is unclear.

3. Inconclusive results of the SA533 environmentally-induced-stress-cracking test.

Future study must address these concerns prior to application of this process to a full size steam generator.

Table 3-15

Materials Transport

Model Steam Generator Unit 2

Lake Water Pre-Fouled

Month	Mass Balance Overall	% Transport					
		Fe	Cu	Ca	Mg	Na	Cl
March*	-	51	54	68	22	-	-
April*	-	32	32	99	29	-	-
May*	-	12	27	23	35	-	-
June	97	239	30	73	24	67	-
July	94	51	66	44	27	26	-
August	101	10	15	51	18	47	-
September	-	11	21	36	85	43	-
October	99	23	21	32	85	33	-
November	-	-	-	62	-	10	-
December	100	-	23	55	251	26	-

*Na transport number assumed to be 100.

Table 3-16

Materials Transport

Model Steam Generator Unit 4

Lake Water Fouled

Month	Mass Balance Overall	% Transport					
		Fe	Cu	Ca	Mg	Na	Cl
July	99	582	40	58	54	40	47
August	-	126	27	83	25	49	-
September	-	200	46	65	54	15	74
October	100	448	48	21	22	97	-
November	-	-	-	-	-	-	-
December	88	-	-	27	28	23	-

3.5 TASK 5 - CHELATE REMOVAL

The purpose of this task was to conduct a lab-scale feasibility study to explore methods of removing metal chelates from the blowdown of PWR's. Ion-exchange resins were studied for their ability to remove metal chelates. Details of the experimental apparatus and procedures can be found in reference 12.

The specific resins evaluated are listed in Table 3-17. As shown in Table 3-17, the SAX resins had excellent capacity for chelate removal. The WAX resins tested had a much smaller capacities. None of the cation exchange resins tested showed any ability to remove metal chelates. The ion-exchange resins used for this study are resins normally sold for nuclear service. Based upon this data, it is feasible to use demineralization for removal of the metal chelates from steam generator blowdown. However, engineering studies would have to be performed to obtain design information prior to actually using ion-exchange resins to remove metal chelates.

3.6 CONCLUSIONS

The feasibility of using an on-line chelant for treatment of PWR steam generator water has been demonstrated by this project. Additional study will be required of some aspects of this treatment process prior to a full scale demonstration.

Results obtained in this project support the following conclusions:

1) Metal complexes of EDTA and HEDTA are sufficiently stable to allow transport of typical metal ions (Fe, Ca, Mg, Cu) from the steam generator prior to deposition. Results of the thermostability testing indicate that HEDTA complexes are more stable than EDTA complexes. Copper chelates have adequate stability to allow transport from the steam generator.

Table 3-17

Ion-Exchange Resin Test Results

Resin	Type	Form	Time of Breakthrough(hr)	Capacity meg/ml
DOWEX SBP-P-OH Nu.Gr.	SAX (gel)	OH^-	16.5	0.20
DOWEX MSA-1	SAX (hard bead)	OH^-	16.3	0.20
DOWEX MWA-1	WAX (macroporous)	OH^-	0.25	$3.1x10^{-3}$
DOWEX WGR	WAX (hard bead)	OH^-	0.25	$3.1x10^{-3}$
DUOLITE C-464	WCX (hard bead	H^+	0	0
DOWEX MSC-1	SCX (macroporous)	H^+	0	0
DOWEX HCR-S-H Nu.Gr.	SCX (gel)	H^+	0	0

2) On-Line addition of EDTA can prevent packing of crevices in a freshwater fouled MSG. One MSG operated successfully for 169 days with accelerated lake water fouling/EDTA water chemistry with no signs of crevice packing and no signs of corrosion. An identical MSG, Unit 2 had packed crevices after 80 days of operation with lake water fouling and without chelant addition. This suggests that EDTA will prevent crevice packing and related corrosion from occurring in lake water cooled PWR steam generators. EDTA failed to stop crevice packing with accelerated seawater fouling condition.

3) Chelants have the ability to remove sludge deposits containing iron and copper from MSG's. EDTA cleaned existing sludge and prevented sludge formation from all MSG's, but crevices packed with corrosion deposits were not cleaned during the test period.

4) Chelants may play a role in the pitting of Inconel 600 tubing under severe sea water fouling conditions. Inconel 600 tubes did experience pitting when exposed to a stagnant, low pH, high chloride,

deaerated water solution containing EDTA. EDTA's role could not be determined by metallographic examination. Future work should address EDTA's role in the pitting corrosion seen in the units operating with accelerated salt water fouling chemistry.

5) Corrosion rates were low and no localized corrosion problems were identified with the following exceptions:

   a) No conclusions can be drawn regarding the behavior of stressed SA533 because of problems with the specimens of this material.

   b) The relationship of EDTA to the pitting observed in the severely fouled sea water must be determined.

   Highly stressed weldments were not attacked when exposed to 0.1% EDTA + AVT water chemistry. All parts of the weldment underwent passivation during exposure to 0.1% EDTA + AVT water chemistry at 290^{o}C, 1250-1300 psig.

   Notched-precracked-stressed specimens of SA508 and SA285C exposed to 0.1% EDTA + AVT water chemistry showed no environmentally-induced-stress- corrosion. No pitting or general corrosion was observed when galvanic pairs or copper plated coupons were exposed to 0.1% EDTA + AVT water chemistry.

6) A more protective film was apparently formed when using EDTA + AVT water chemistry, than was formed using AVT alone. All coupons tested were passivated in less than 80 days when exposed to 0.1% solutions of either EDTA or HEDTA in AVT water chemistry. AVT showed greater passivation rates than either EDTA or HEDTA. However, sludge formation was observed with AVT, whereas, the EDTA and HEDTA treated systems had no sludge.

Trace amounts of iron were shown to significantly increase the rate of passivation with EDTA or HEDTA treatment low concentrations of iron in the PWR feedwater system are normally present. This would accelerate passivation of all high temperature surfaces in the feedwater system and steam generator.

7) Chelant-metal complexes can be removed from solution using anion demineralizer resin.

4.0 DILUTE CHEMICAL CLEANING PROCESS

The dilute chemical cleaning process was developed by UNC Nuclear Industries. The development of this process is detailed in this section according to the task description detailed in Section 1.2.2.

4.1 TASK 1 - PLANT INSPECTIONS

The objective of Task 1 was 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 chemical cleaning concept.

UNC personnel visited the Zion plant in August, 1980, to obtain an overview of the general plant layout and construction features. The information obtained is reported in detail in Reference 6.

Based upon this inspection, the total sludge loading for a dilute solvent process was estimated (Table 4-1). This solvent sludge loading was then used in the process development and pilot plant demonstration phases of the program.

4.2 TASK 2 - PROCESS DEVELOPMENT

The objective of Task 2 was to develop and qualify a dilute solvent and an application process for steam generator chemical cleaning. This task included the development and demonstration work needed to identify an acceptable dilute solvent process and to determine the feasibility of applying the process to clean an operating PWR steam generator.

Process development proceeded in five phases. These were:

1) Materials Test Program
2) Inhibitor Selection
3) Solvent Development
4) Recirculating Loop Tests
5) Pilot Scale Cleaning Demonstration

Table 4-1

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.

Work performed during the first three phases of process development is described in detail in References 6, 7 and 13, and is summarized in Sections 4.2.1, 4.2.2 and 4.2.3 of this report.

The fourth phase of process development utilized a bench-top, recirculating test system to model the process and to establish operating parameters for application of the inhibited solvent. The parameters were established by a series of ten recirculation tests. Test conditions and results for the first seven tests were reported in Reference 7. The remaining three tests were conducted for optimization of pH control, refinement of solvent application temperature, and verification of the complete process before performing the model steam generator cleaning demonstrations. These tests are reported in detail in Reference 13. These results are summarized in Section 4.2.4.

The last phase of process development was the demonstration cleaning of two model steam generators installed at the CECo State Line station. This work is detailed in Reference 13 and summarized in Section 4.2.5.

4.2.1 MATERIALS COMPATABILITY

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

The materials test program utilized three types of coupons:

1) Uniform corrosion test coupons
2) U-Bend stress corrosion test specimens
3) Precracked, 3-point bend 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). Details regarding the fabrication of these test specimens can be found in reference 6.

4.2.1.1 UNIFORM CORROSION & U-BEND STRESS CORROSION

The materials compatibility evaluations were conducted in conjunction with the solvent development and the process development tasks. Results of the uniform corrosion and U-Bend stress corrosion testing are reported in Sections 4.2.3, 4.2.5 and 4.2.6.

4.2.1.2 STRESS CORROSION AND CRACK PROPAGATION

As part of the materials test program for the Steam Generator Chemical Cleaning Project, precracked, three-point bend specimens were prepared to study crack propagation and stress corrosion cracking during exposure of materials to the dilute chemical cleaning solution. The specimens were exposed during the demonstration cleaning of Unit No. 5. The materials tested were SA508, SA533A, SA285C and turbine disc material. (See Figures 4-31 and 4-32.)

After exposure to solvent during the 5-1/2 day test, the precracked specimens were evaluated by the Commonwealth Edison Company, System Materials Analysis Department. No environmentally assisted stress corrosion cracking was found. The uniform corrosion rate of the precracked specimens was 4 mils/day, as calculated from weight loss measurements.

This general corrosion rate is significantly higher than the typical corrosion rate of 1 mil/day or less, measured for UNC test coupons. The difference is attributed to the influence of the stainless steel holder

used for stressing the specimens. Stainless steel in galvanic contact with carbon steel has produced similar high general corrosion rates in other organic solvent studies. The corrosion rate of stressed SA533A coupons, galvanically coupled to stainless steel, was increased by factors of 24 to 40 above that of insulated coupons in testing with concentrated EDTA solvents (Reference 15). Thus, the factor of 4 corrosion increase observed in the model generator cleaning is not unexpected considering the specimens are galvanically coupled to a large stainless steel coupon holder and exposed to a low pH, dilute organic solvent.

It should be noted that stainless steel is not used as a construction material for the secondary side of PWR steam generators. Carbon steel test specimens in galvanic contact with the Inconel 600 steam generator tube material did not exhibit abnormal uniform corrosion.

Conclusions from the precracked 3-point bend specimen data are:

1. The dilute solvent developed and demonstrated in this project does not cause crack propagation or stress corrosion cracking.

2. Further corrosion studies on site-specific materials are necessary before using this dilute solvent process in systems which contain carbon steel galvanically coupled to stainless steel.

4.2.2 INHIBITOR SELECTION

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.

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

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 tests were carried out in 4-liter glass kettles, each containing 3 liters of solvent with the candidate inhibitor. Temperature was maintained at 93 $\pm$ 2°C for 8 hours. Three materials of construction (SA285C, SA533A, and IN600) and 5.6 g of PWR steam generator sludge were included in each test. Pelletized 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.

Corrosion measurements were taken at frequent intervals during the 8-hour test period using a Corrator* probe fitted with AISI 1010 carbon steel electrodes. Total corrosion was also measured for three major SG alloys from weight loss calculations for coupon specimens.

The observed degree of sludge dissolution and corrosion rates are given in Table 4-2, together with a calculated value for inhibitor efficiency relative to DETU. Table 4-2 data shows 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.

Within the context of these results it is evident that:

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

---

*Registered trademark of Rohrback Corporation.

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.

Table 4-2

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 surfactants have been known to affect ion-exchange processes, they will be deleted from future dilute solvent formulations.

4.2.3 SOLVENT DEVELOPMENT

The objective of this portion of the work was to develop a regenerable, dilute solvent formulation using complexing organic acids at concentrations of approximately 0.5 wt%. The solvent should be capable of dissolving at least 90 wt% of the bulk sludge, while maintaining a corrosion rate of 1 mil/day.

As indicated in Reference 6, dilute solvents containing chelates are not regenerable by ion-exchange because of the high stability of the chelate iron complex. As a result, complexing organic acids (citric acid, gluconic acid, etc.) were included in the dilute cleaning solvent. Complex organic acids of this type are known to be capable of regeneration by ion-exchange.

The screening studies were usually carried out in sets of six using 4-liter glass kettles. These assembled kettles were maintained at operating temperature in an insulated and thermostatically controlled water bath.

4.2.3.1 EFFECT OF INHIBITOR CONCENTRATION

Six kettle tests were conducted to evaluate the effect of inhibitor concentration on sludge dissolution and corrosion in a dilute solvent containing 0.1% Citric Acid and 0.1% Gluconic Acid at pH 3.2. The concentration of cinnamonitrile was varied from 0 to 0.3 wt%. The results of these tests are shown in Figure 4-1. The reducing environment was established by adding hydrazine to the solvent, and maintained by sparging nitrogen gas through the dilute solvent at 200 cc/min to exclude oxygen. The nitrogen also provided agitation of the dilute solvent.

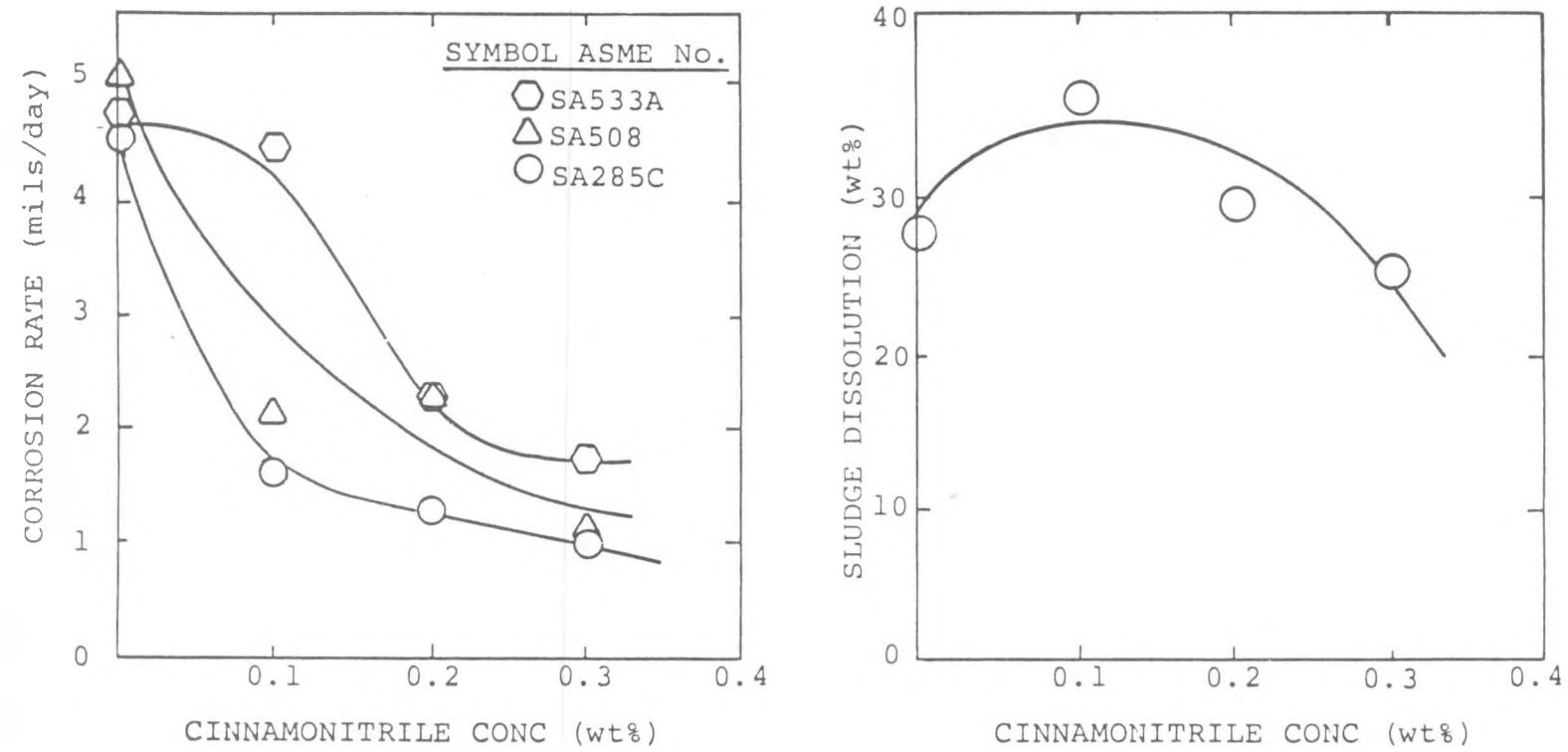


FIGURE 4-1 Effect of Inhibitor Concentration on Corrosion Rate and Sludge Dissolution.

Effect of Inhibitor Concentration on Corrosion Rate and Sludge Dissolution.

The data in Figure 4-1 indicate that the cinnamonitrile concentration must be at least 0.3 wt% to keep the corrosion rate of the materials of construction near the 1 mil/day level. It also appears that in this solvent, which contains 0.1 wt% citric acid and 0.1 wt% gluconic acid, the presence of cinnamonitrile at 0.3 wt% also reduced the amount of sludge dissolved during the 6-hour contact at 95°C.

As a result of this series of tests it was concluded that:

1. Dilute complexing acids are relatively effective solvents for sludge dissolution.

2. Cinnamonitrile concentration needs to be at least 0.3 wt% to reduce the corrosion rate to a level of 1 mil/day.

3. The penalty of slightly reduced sludge dissolution at higher inhibitor concentrations was acceptable considering the significantly lowered corrosion rate.

4.2.3.2 EFFECT OF INITIAL pH

Ten kettle tests were performed to determine the effect of initial pH, on the sludge dissolution effectiveness and corrosivity of the dilute solvent. The initial solvent pH was varied from 3.2 to 6.4 by adjustment with ammonium hydroxide. A reducing environment was established by addition of hydrazine, and the final pH adjustment in each case was made with ammonium hydroxide. These studies were performed with and without inhibitor (0.2 wt% cinnamonitrile) in the reference solvent, 0.1% Citric Acid and 0.1% Gluconic Acid.

The effectiveness of sludge dissolution as a function of solvent pH is illustrated in Figure 4-2. The data show solvent effectiveness is significantly reduced at greater than pH 4. A pH range of 3.5 to 4.0 was selected for use in future testing.

4.2.3.3 EFFECT OF SOLVENT CONCENTRATION AND MOLAR RATIO

The objectives of this series of static kettle tests were:

1. Evaluate the relative effect of complexing acid concentration on sludge dissolution and corrosion.

2. Evaluate the advantage, if any, of changes in the molar ratio of citric acid to gluconic acid for sludge dissolution and corrosion.

The effect of solvent concentration was evaluated by two approaches. First, kettle tests were performed by varying the total complexing organic acid concentration from 0.2 wt% to 0.5 wt% while maintaining a fixed molar ratio of 1.0 for citric acid to gluconic acid. Second, kettle tests were performed at a fixed total acid concentration of 0.2 wt%, and the molar ratio of citric acid to gluconic acid was varied from 0.5 to 3.0. The tests were conducted at 94°C and were all uninhibited.

The corrosion results are graphically presented in Figure 4-3. As expected, without inhibitor the corrosion was found to increase almost directly as a function of the solvent concentration. It also appears that the corrosion rate is dependent on the molar ratio and increases as the fraction of citric acid is increased.

Sludge dissolution, shown in Figure 4-4, also depends on the solvent concentration, showing a definite decrease in effectiveness below a total acid concentration of 0.3 wt%. The molar ratio, however, has little effect on the degree of sludge dissolution.

As a result of these tests, it was concluded that the total organic acid concentration should be less than or equal to 0.3 wt% and the molar ratio of citric acid to gluconic acid should be about 1.0. Maintaining solvent compositions within these ranges was considered to offer the best potential for controlling corrosion to less than 1 mil/day when 0.3 wt% cinnamonitrile is used as inhibitor.

4.2.3.4 ASCORBIC ACID VERSUS HYDRAXINE

Reducing conditions were established in the previous kettle tests by the presence of hydrazine (180 mg/l) and maintained by sparging with N_2 gas,

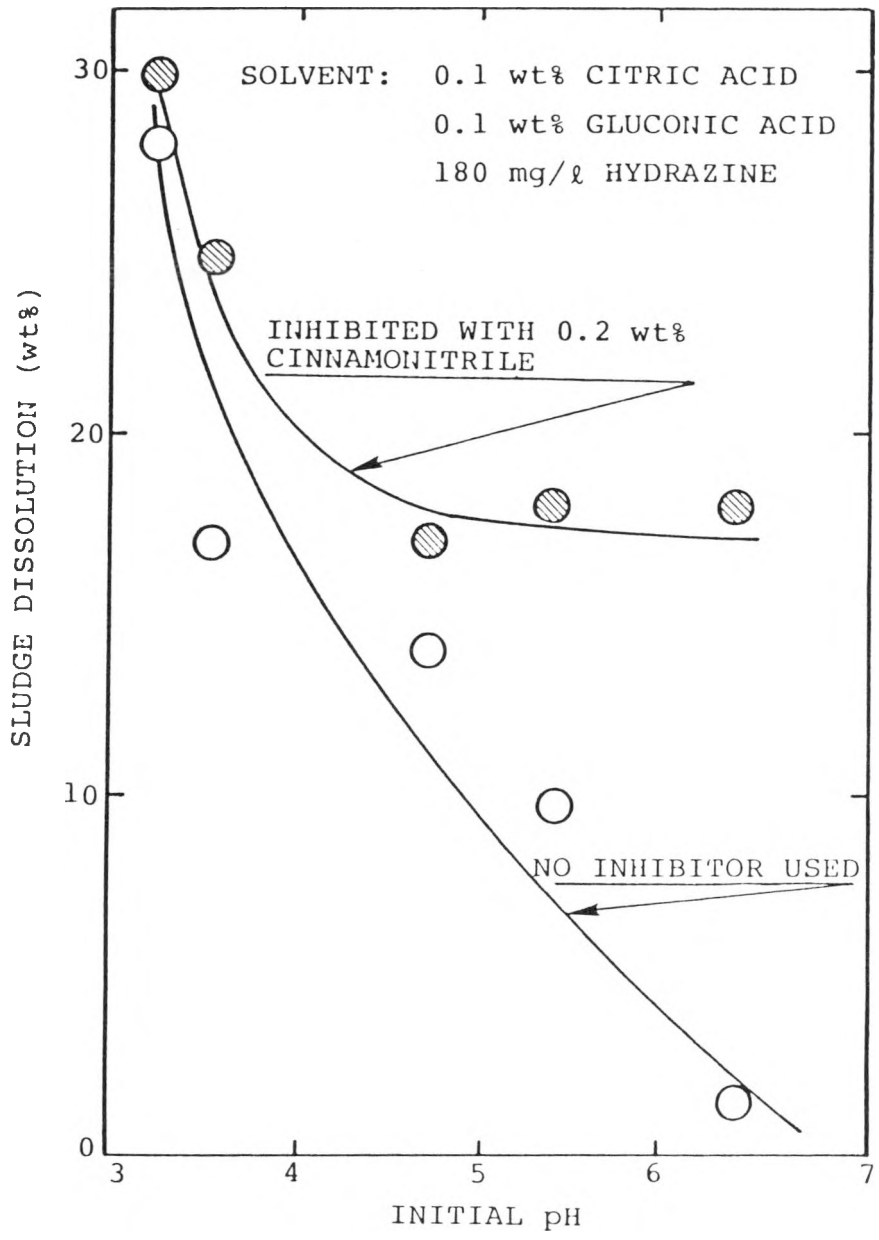


FIGURE 4-2 Effect of Initial pH on Sludge Dissolution

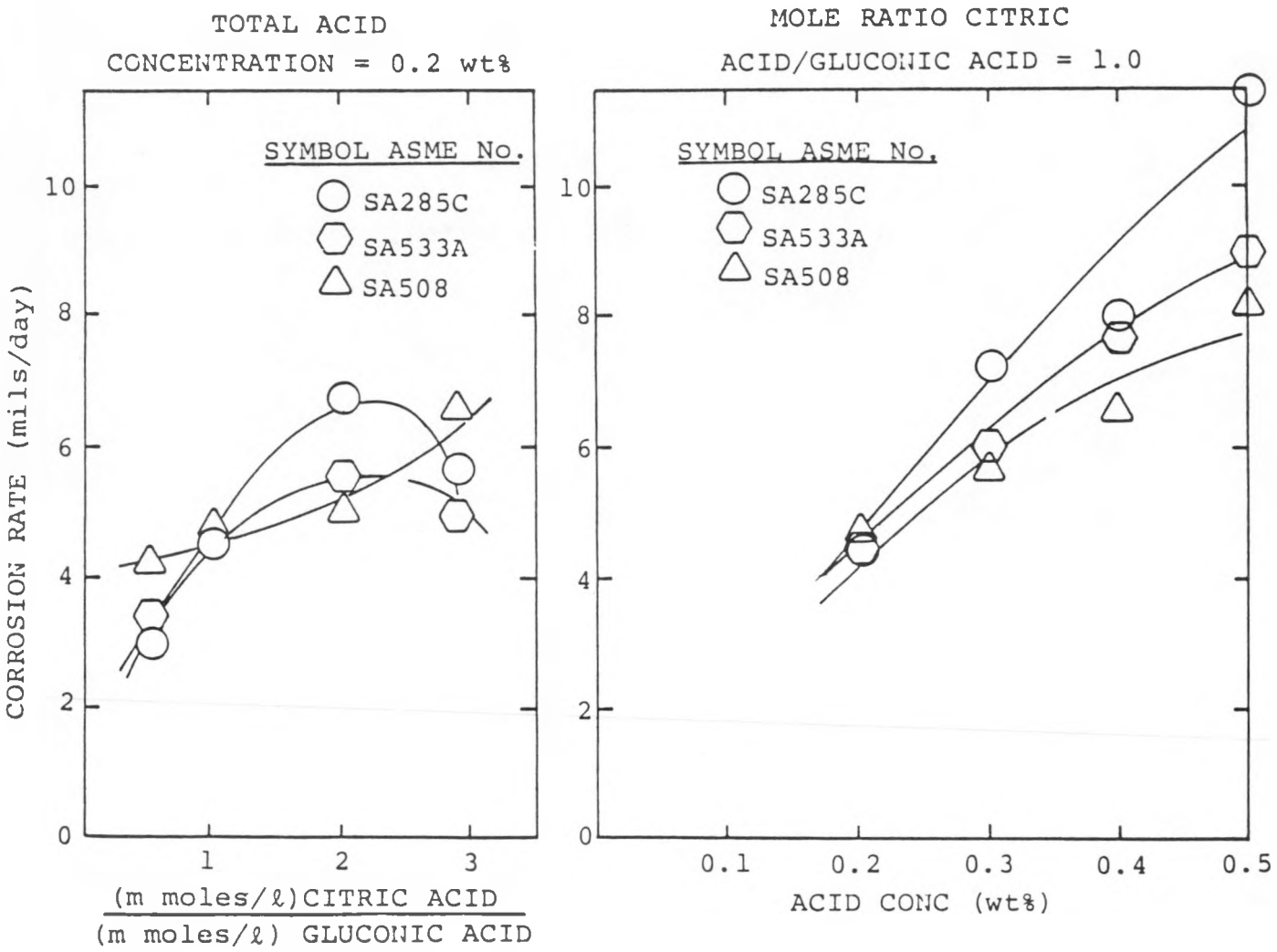


FIGURE 4-3 Effect of Mole Ratio and Acid Concentration on Corrosion Rate

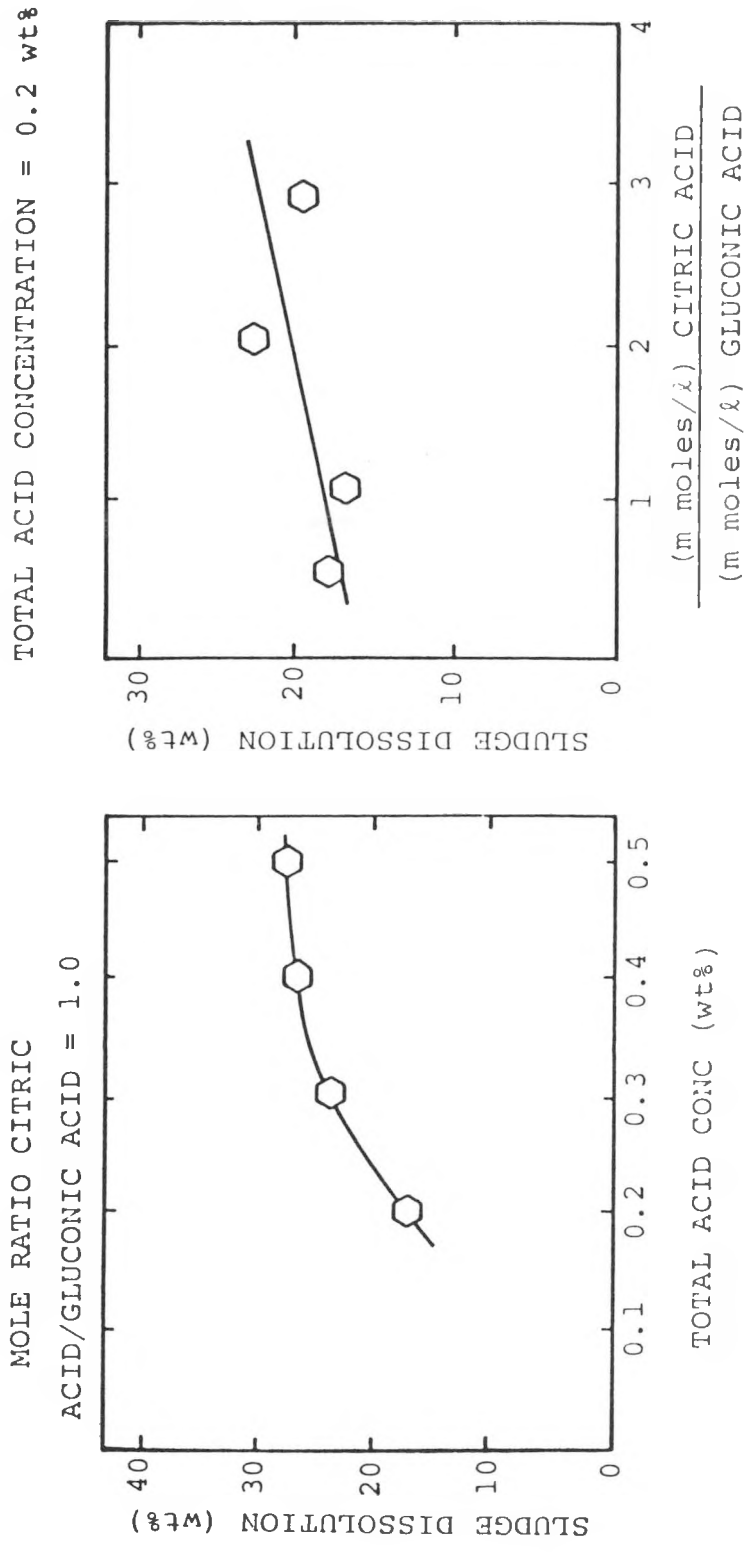


FIGURE 4-4 Effect of Acid Concentration and Mole Ratio on Sludge Dissolution.

for O_2 exclusion. Previous testing (Reference 6) had shown that hydrazine accelerated corrosion, especially for SA533A, at concentrations above 200 ppm.

A set of tests was carried out in which ascorbic acid, a reducing organic acid, was substituted for hydrazine. The objective was to evaluate if ascorbic acid could be substituted for hydrazine without increasing corrosion rates or decreasing sludge dissolution. Ascorbic acid would be preferrable to hydrazine because it is regenerable by ion-exchange, whereas hydrazine is removed by ion-exchange.

The test observations are shown in Figure 4-5. For the conditions of this test, the sludge dissolution with 0.1 wt% ascorbic acid was essentially equivalent to that obtained with hydrazine at a concentration of 180 mg/l. Higher concentrations than 0.1 wt% should be avoided since the corrosion rate is increased without a corresponding increase in sludge dissolution.

It is evident that ascorbic acid at a concentration of 0.1 wt% can be substituted for hydrazine without compromising the dilute solvent effectiveness for dissolving sludge. Although, under the conditions of these tests, uniform corrosion for 0.1% ascorbic acid appeats slightly higher than for 180 mg/l hydrazine, it is apparent that SA533A does not exhibit the same degree of corrosion sensitivity with ascorbic acid as was observed for hydrazine concentrations above 200 mg/l.

4.2.3.5 CONCLUSIONS FOR SOLVENT SCREENING TESTS

Based on the preceding screening tests the following dilute solvent formulation was selected for use in further testing:

0.1 wt% citric acid
0.1 wt% gluconic acid
0.1 wt% ascorbic acid
0.3 wt% cinnamonitrile
pH 3.4-3.8 adjusted with NH_4OH

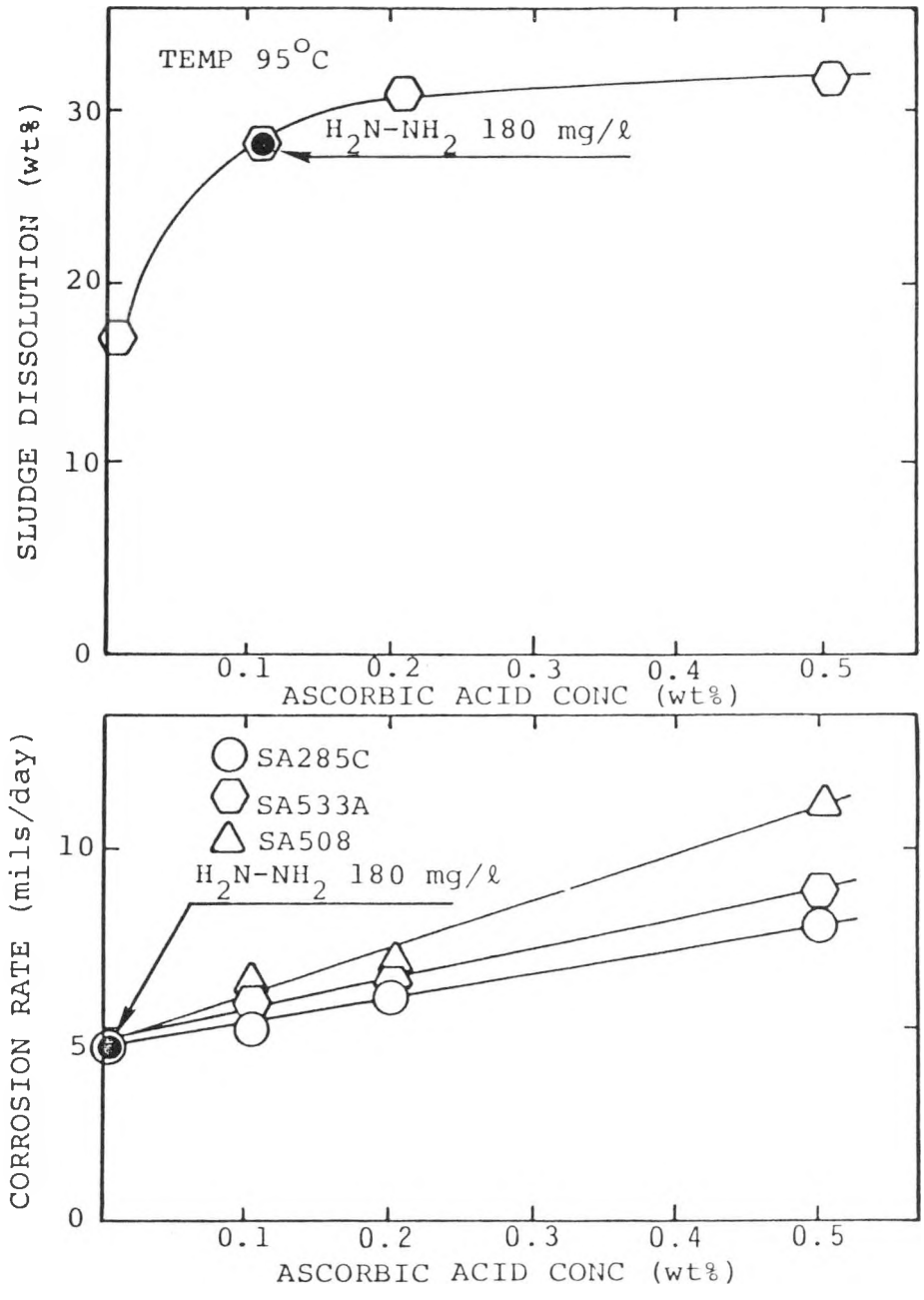


FIGURE 4-5 Ascorbic Acid Versus Hydrazine.

This dilute solvent formulation was used exclusively for the testing described in the following sections of this report.

4.2.4 SOLVENT REGENERATION

Several laboratory tests were conducted to establish the effectiveness of ion-exchange regeneration of spent solvents containing complexing acids, and to evaluate the relative effect of several corrosion inhibitors on the ion-exchange process. Once-through ion-exchange runs was made at room temperature with partially spent dilute solvent and several candidate inhibitors. The inhibitors were cinnamonitrile, trimidodiazoline, and diethylthiourea. A detailed description of the test method and appartus used are provided in Reference 6.

Each solution, with inhibitor as indicated, was partially spent by adding sludge (1 g/L) and allowing it to reflux for about 16 hr at 90°C. The synthetic sludge used contained 95 wt% Fe_3O_4 and 5 wt% CuO. The partially spent dilute solvent was filtered and analyzed. It was then used as the influent to the cation resin columns. The ion-exchange flow rates were approximately 4 gpm/ft, which is twice the normal flow rate for water treatment practice. The effluent was sampled for analysis at frequent intervals during each run.

Using the influent and effluent iron concentrations and the volume of solvent processed, the capacity of the ion-exchange resin was calculated as follows for each run:

$$\frac{(Fe_{in} - Fe_{out})\ V_p}{V_r} = \text{Capacity (meq/ml)}$$

Where:

Fe_{in} = Influent Iron Concentration, meq/ml
Fe_{out} = Effluent Iron Concentration, meq/ml
V_p = Solution Volume Processed, ml
V_r = Resin Bed Volume, ml

The results are shown in Table 4-3. The data show that Cinnamonitrile had the least effect on the cation exchange capacity for iron, and that diethylthiourea ranked second. The regeneration of the partially spent dilute solvent is evidenced by the nearly quantitative removal of iron from the organic complex.

Using a conservative design capacity of 1.5 meg Fe^{+3}/ml of resin and an estimate of 100 lb of magnetite in the Zion steam generator support plate crevices, the amount of strong acid cation exchanger required is calculated to be:

$$\frac{100\ \text{lb} \times 453.6\ \frac{\text{g}}{\text{lb}} \times 1000\ \frac{\text{mg}}{\text{g}} \times \frac{3(55.85)}{231.5}}{1.5\ \frac{\text{meg}}{\text{cm}^3} \times 18.6\ \frac{\text{mg}}{\text{meg}} \times 28300\ \frac{\text{cm}^3}{\text{ft}^3}} = 41.6\ \text{ft}^3$$

For every 100 lb of surface sludge dissolved by the solvent, an additional 42 ft^3 of cation exchanger material will be required.

The once-through ion-exchange studies provided the following conclusions:

1. Ion-exchange regeneration of spent dilute solvents containing organic complexing acids is effective, using cation resins in either the H^+ or NH_4^+ form.

2. At the expected application concentration of 0.3 wt% necessary for corrosion inhibition, cinnamonitrile shows the least reduction of capacity for ion-exchange regeneration of spent dilute solvents.

3. Using a design capacity of 1.50 meq/ml for sizing ion-exchange units, the resin quantities required for regeneration are reasonable for plant use.

Table 4-3

Relative Capacity of Strong Acid Cation Exchanger in the Presence of Inhibitor

Cation Exchanger: Dowex 50

Inhibitor	Conc (wt%)	Capacity (meq/mL) H^+ Form	Capacity (meq/mL) NH_4^+ Form
None	0	1.87	1.75
Cinnamonitrile	0.2	1.44	--
	0.3	1.53	1.50
Triimidotriazoline	0.1	0.78	--
	0.5	0.77	0.78
Diethylthiourea	0.1	1.26	1.66

4.2.5 RECIRCULATING LOOP TESTS

A benchtop system was assembled to translate the data from the static test kettle tests to a dynamic recirculating system and to evaluate operating parameters for such a system. Initial tests, discussed in Reference 7, were carried out to compare:

a) Sludge dissolution
b) Corrosion effects
c) Spent solvent regeneration
d) Final mixed bed cleanup

It was found that sludge dissolution was equal to or better than that found in the static tests. The regeneration of the spent solvent was confirmed on the recirculating system, and C/S corrosion levels in the recirculating system did not increase compared to kettle testing when 0.3 wt% cinnamonitrile inhibitor was used.

After the premilinary tests had confirmed the feasibility of the process when used in a recirculating loop, the loop was modified to simulate the conditions in a typical steam generator. The Inconel and C/S alloy surface areas were adjusted to simulate the volume-to-surface ratios expected in the steam generator, as shown in Table 4-4. In addition, the sludge concentration was increased to about 6.0 g/l to simulate to steam generator sludge loading of about 1100 lb. Several dilute process tests were conducted using the modified recirculating test loop and sludge loadings of 6 g/l. Test conditions and the parameters for ths test series are summarized in Table 4-5.

4.2.5.1 INITIAL CLEANUP WITH MIXED BED RESIN

In simulating conditions in a typical steam generator, it was considered that a full-scale cleaning process will begin with the steam generator in a water-filled, wet lay-up condition. The wet lay-up liquid contains hydrazine which must be removed to minimize SA533 corrosion during cleaning.

Table 4-4

Comparison of Laboratory System
And Typical Steam Generator

		Steam Generator Volume 22,140 gal.		Laboratory Volume 1.056 gal.	
Structure	Alloy	Area (ft^2)	Ratio (gal/ft^2)	Area (ft^2)	Ratio (gal/ft^2)
Tubes	IN600	51500	0.43	2.79	0.38
Tube Sheet	SA508	77	288	0.0062	285
Support Plates	SA285C	1622	13.7	0.074	14.1
Wrapper	SA285C	2572	8.61	0.121	8.75
Shell	SA533A	1383	16.0	0.062	16.9

Table 4-5

Summary of Recirculation Loop Test Parameters

	SYSTEM VOLUME (mL)
Test Vessel	4000
Tubing	800
Ion-Exchangers	400
TOTAL VOLUME	5200

	TEST NO.		
SOLVENT	19-4	19-5	20
Citric Acid wt%	0.1	0.1	0.1
Gluconic Acid wt%	0.1	0.1	0.1
Ascorbic Acid wt%	0.1	0.1	0.1
Cinnamonitrile wt%	0.3	0.3	0.3
pH Control	By IX	By IX	By IX
SLUDGE			
Concentration (g/L)	6.024	5.789	6.000
OPERATION			
Temperature (^{o}C)	94 $\pm$ 2	Variable	80 $\pm$ 2
Recirc Rate (mL/min)	100	120	250
Turnover Time (min)	52	43.3	23
CIX Form	H^+ and NH_4^+	H^+ and NH_4^+	H^+ and NH_4^+
Time at Temp (hr)	47	100	143

Removal of the hydrazine from wet lay-up conditions was accomplished by recirculating the loop water through the H-OH form mixed-bed at room temperature. The degree of clean-up was monitored by measuring the loop water conductivity, pH, and hydrazine concentration as a function of recirculation time. The data (Table 4-6) indicate that the hydrazine is removed from the recirculating water by the mixed-bed ion-exchanger, and that the removal can be achieved with about three system turnovers.

4.2.5.2 pH CONTROL WITH ION-EXCHANGE RESINS

Data reported in Table 4.3 showed conclusively that iron removal could be achieved with either H^+ form or NH_4^+ form cation exchange resins. It was recognized that parallel operation of H^+ and NH_4^+ form ion-exchangers could be used to control steam generator pH and eliminate the need for auxiliary pH control equipment. The bench-top loop was modified as shown in Figure 4-6 to accommodate parallel ion exchanger operation. Tests were performed in which the test vessel pH was controlled by operating the two ion-exchange units in parallel.

During test run 19-4, pH measurements were made in the test vessel, at the H^+ form resin column outlet, at the NH_4^+ resin column outlet, and in the return line to the test vessel. These measurements were made as a function of operating time and corrected to 25^oC for comparison purposes. Flowrates through each cation exchange column were recorded during the operating period of 48 hours. The data are given in Table 4-7. The same technique was used for pH control in test 19-5 (100-hr) and test 20 (143-hr) with equal success.

As a result of the pH control evaluation in tests 19-4, 19-5 and 20, the model steam generator cleaning was performed with parallel H^+ and NH_4^+ form cation exchange column. An auxiliary chemical addition system for pH control was not required.

4.2.5.3 EFFECT OF APPLICATION TEMPERATURE

An investigation was performed using the bench-top recirculating loop to determine the effect of temperature or process performance in the range of 50^oC to 95^oC.

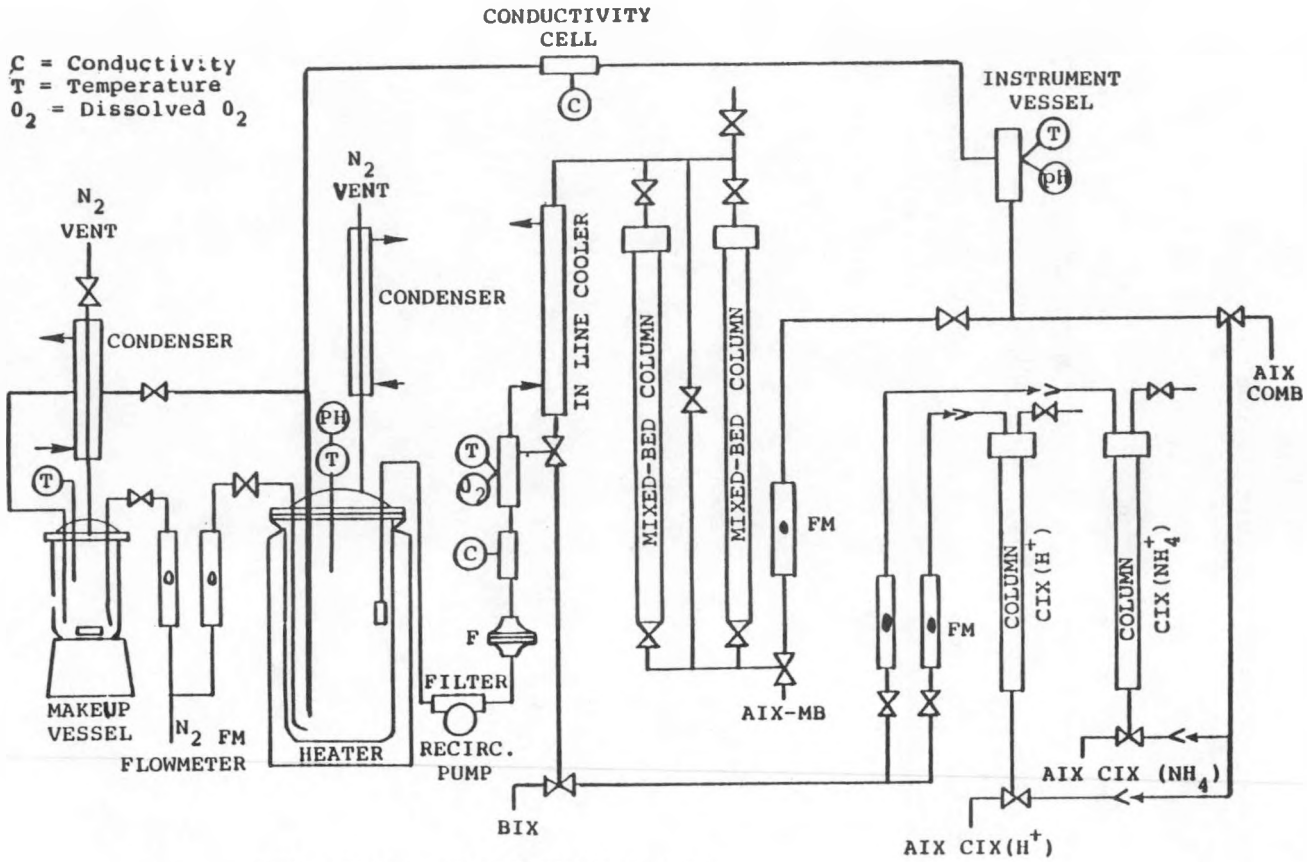
Table 4-6

Use of Mixed-Bed Resin for Initial Clean-up

Test Run No.		19-4			19-5			20		
Operating Time		Conductivity		H_2NNH_2	Conductivity		H_2NNH_2	Conductivity		H_2NNH_2
Hour	Periods[a]	(umho/cm)	pH	(g/L)	(umho/cm)	pH	(g/L)	(umho/cm)	pH	(g/L)
0	--	38	9.1	460	50	9.1	870	--	10.2	--
0.25	0.45	37	--	440	46	--	730	42	10	590
0.50	0.9	27	8.9	200	27	--	200	41.5	9.7	590
0.75	1.35	12.2	--	27	16.5	9.0	51	29	9.6	240
1	1.8	5.2	8.6	5.2	12	--	27	15	9.0	39
1.25	2.25	--	--	--	--	--	--	8.5	8.7	14
1.5	2.6	3.7	8.2	3.0	8.0	8.9	13	4.1	8.4	4
1.75	2.95	--	--	--	7.3	8.5	10	--	--	--
2	3.4	--	--	--	7.3	8.5	10	--	--	--
2.25	3.85	--	--	--	7.7	8.3	8	--	--	--

[a] Circulation rate = 120 mL/min

$$\text{Period} = \frac{\text{mL/min} \times \text{oper. min}}{\text{vessel vol (mL)}}$$



BIX = BEFORE ION EXCHANGE SAMPLE

AIX = AFTER ION EXCHANGE SAMPLE

MB = MIXED BED

CIX(H^+) = CATION RESIN HYDROGEN FORM

CIX(NH_4^+) = CATION RESIN AMMONIUM FORM

Loop for Recirculation Tests.

FIGURE 4-6. Loop for Recirculation Tests

Table 4-7

pH Control During Test 19-4

Recirculation Time (hr)	Ionic Form of Cation Resin: H^+ Flow (mL/min)	H^+ Effluent pH	NH_4^+ (mL/min)	NH_4^+ Effluent pH	Return Line pH	Test Vessel pH
0.5	20	2.3	100	3.0	3.4	3.4
1	10	2.4	100	3.8	3.6	3.5
3	20	2.4	100	3.3	3.7	3.6
5	0	--	120	3.2	3.7	3.5
6	0	--	120	3.3	4.5	3.7
10	10	1.3	100	3.4	3.7	3.6
21	20	2.8	100	3.9	4.4	3.5
25	20	2.8	100	4.3	4.0	3.8
31	10	2.7	110	3.7	4.1	3.6
35	15	2.5	100	3.8	4.0	3.5
40	10	2.3	110	3.8	3.8	3.5
45	10	2.1	110	3.0	3.9	3.6
47	10	2.2	110	3.7	4.3	3.5

The relative efficiency of the dilute solvent as a function of temperature is illustrated in Figure 4-7. Calculation of the solvent efficiency ratio is explained in Reference 7. The results show good agreement with the corresponding temperature data for the static kettle tests. The data from both tests series show that the best solvent utilization is realized at about 80°C. This temperature was used in the demonstration cleaning on the DOE/CRC model generators at the CECo State Line Facility.

4.2.5.4 EFFECT OF EXTENDED SOLVENT APPLICATION TIME

Test 20 was carried out to evaluate long-term effects of the dilute solvent on sludge dissolution rates and on corrosion of welded coupons. The test period was 248-hr, which allowed time for performance of all the steps in the process. The steps involved, together with the parameters described for each step, are given in Table 4-8.

In order to maintain the test vessel pH between 3.4 and 3.8, the total loop flow of 250 mL/min was split between an ammonium form cation exchanger and a hydrogen-form cation exchanger, with flow adjustment to each column. At the recirculation rate of 250 mL/min, the test vessel turnover rate was approximately one volume every 16 minutes. The initial sludge loading, final sludge recovered, and weight percent dissolution for the 248-hr operating time are given in Table 4-9.

This test was the first to include welded C/S coupons. Two unwelded coupons (SA 285C and SA 533A) from the last recirculation test were also included in this test to compare the corrosion rate of passivated surfaces with that of unpassivated surfaces. The coupon designations and their corrosion rates (in mils/day) are listed in Table 4-10.

The data in Table 4-11 for SA285C and SA533A coupons clearly show that fresh C/S surfaces will have higher corrosion rates than surfaces of the same alloy that have been passivated by the copper step. Although only

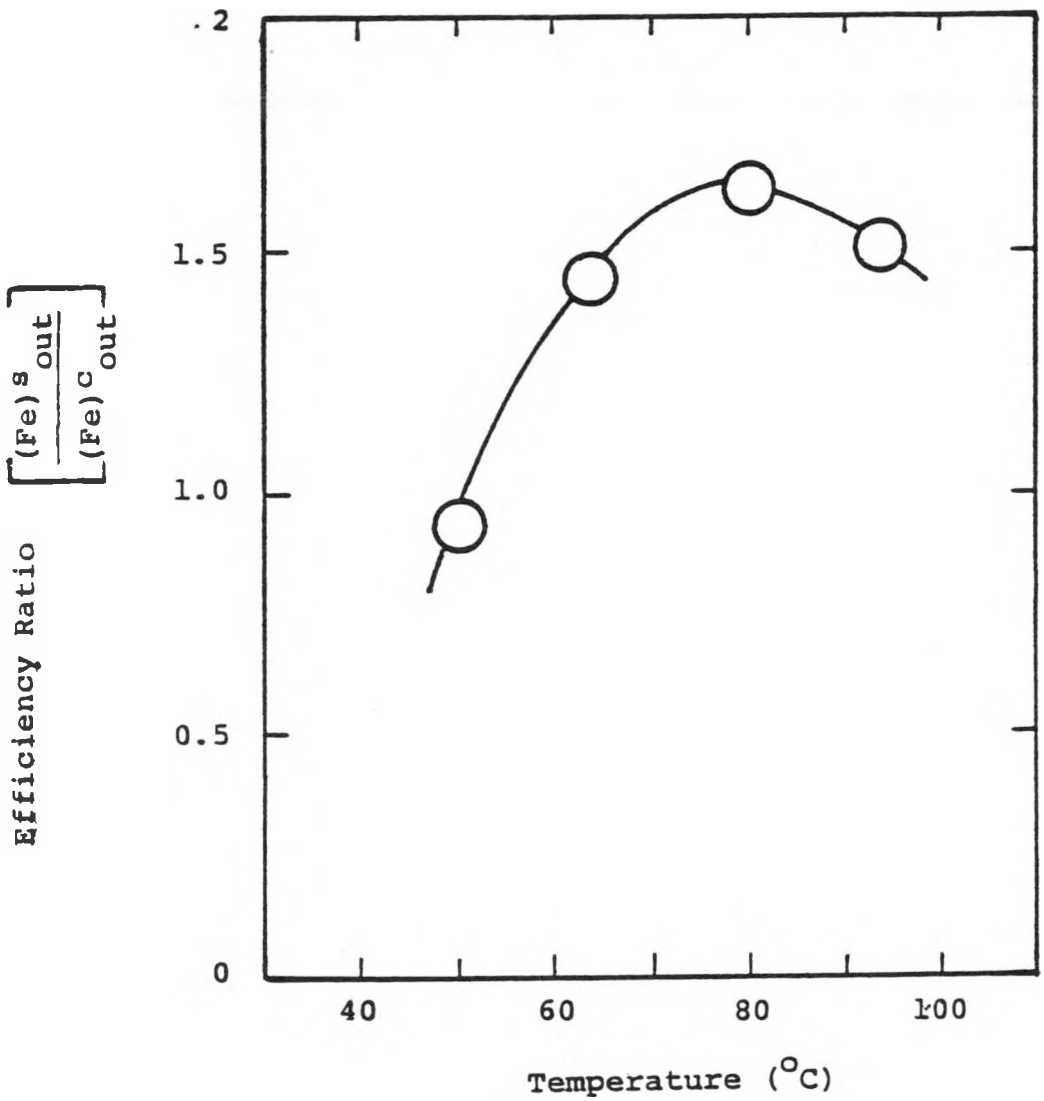


FIGURE 4-7. Solvent Efficiency as a Function of Temperature.

Table 4-8

Process for Dilute Chemical Cleaning

Description	pH Range	Temp (°C)	Purge Gas	Time (hr)
Initial Clean-up	9.5- 8.0 [a]	40	N_2	2.5
Copper Step I	10.0-10.2	40	Air	4.5
Intermediate Clean-up	10.2- 8.0 [a]	40-80	N_2	11.5
Sludge-Iron Step I	3.4- 3.8 [b]	80	N_2	70
Intermediate Clean-up	3.8- 6.0 [a]	80-40	N_2	1
Copper Step II	10.0-10.2	40	Air	2.5
Intermediate Clean-up	10.2- 8.0 [a]	40-80	N_2	2.5
Sludge-Iron Step II	3.4- 3.8 [b]	80	N_2	143
Intermediate Clean-up	3.8- 6.0 [a]	80-40	N_2	1.5
Copper Step III	10.0-10.2	40	Air	4
Final Clean-up	10.2- 9.5 [a]	40	N_2	5
Total Continuous Hours			248	

[a] All clean-up steps used H-OH form mixed bed resins.

[b] pH control on Sludge Iron steps was achieved with parallel operation of H^+ and NH_4^+ cation resins.

Table 4-9

Sludge Dissolution Characteristics

Oper. Time	248 hours
Oper. Temp.	80°C Sludge-Iron Step.
	40°C Copper Step

	Sludge as Loaded	Sludge Recovered
Total wt (g)	23.895	3.765
(g/L)	5.973	0.941
wt% Fe_3O_4	94.8	99.3
wt% CuO	5.2	0.7

Dissolved (wt%) 84.3[a]
83.4[b]

[a] Dissolved (wt%) = $\frac{(23.895 - 3.765) \times 100}{23.895}$

[b] Corrected for particulate matter recovered from ion-exchange columns.

Table 4-10

General Coupon Corrosion for 248 Hour Recirculation Test

ASME Number	Type	Weight Loss (mg/sq in)	Corrosion Rate (mils/day) (b)	(c)
SA285C	(a)	310.5	0.23	0.27
	W/o weld	459.2	0.33	0.39
	welded	279.8	0.21	0.25
	welded	327.7	0.24	0.28
SA533A	(a)	2046.3	1.54	1.80
	w/o weld	3196.6	2.40	2.81
	welded	2062.1	1.55	1.81
	welded	1642.4	1.20	1.40
SA508	welded	1193.6	0.89	1.04
SA106	welded	723.1	0.54	0.63
SA333	welded	279.1	0.21	0.25
SA234WPB	welded	327.1	0.24	0.28
IN600	welded	1.07	0.0080	0.0094

(a) Passivated coupon from previous test.
(b) Based on total time, 248 hours (10.3 days).
(c) Based on time at 80°C, 213 hours (8.8 days).

Table 4-11

Effect of Passivation and Prefilming

Oper. Time - 213 hours

Oper. Temp. - 80°C (Sludge Iron Step)

Surface Condition	Corrosion (mils/day) SA285C	SA533A
Passivated	0.27	1.80
Nonpassivated	0.39	2.81
Ratio = Passivated / Nonpassivated	0.69	0.64

Table 4-12

Comparison of Welded and Nonwelded Corrosion Rates

ASME No.	SA285C		SA533A	
Type	Welded	Nonwelded	Welded	Nonwelded
Average Corrosion (mils/day)	0.26	0.39	1.60	2.18
Ratio[a]	0.67		0.73	

[a] Ratio = (mils/day) welded / (mils/day) nonwelded

one specimen of each condition was included in this test, it appears that for the alloys tested, passivation will reduce the amount of corrosion by 31% to 36%.

This test also provided a comparison of welded and nonwelded corrosion rates for SA285C and SA533A, as reflected in Table 4-12. The average corrosion for welded coupons was slightly lower than for the same alloys exposed as non-welded materials, primarily due to the corrosion resistance of the weld metal. However, visual examination of the weld coupons showed varying degrees of selective attack in the weld heat affected zone (HAZ). Micrometer thickness measurements were taken to quantify the extent of corrosion penetration in the HAZ for each alloy. The micrometer measurements are presented in Table 4-13 with the original nominal coupon thickness shown for comparison. HAZ corrosion was very high for the SA533A and SA508 coupons and moderate for the other weld coupons tested.

Solvent pH was controlled in the range of 3.4 to 3.9 during the 248-hr test period by using separate NH_4^+ form and H^+ form strong acid cation-exchange columns. Regeneration and pH control were achieved by splitting the 250-mL/min recirculating flow between the two cation columns. Averaged over the whole run, the flow rate through the NH_4^+ form cation exchanger was about 90% of the total available flow.

A resin sample from each column removed from the operating loop was cleaned to remove particulate material and colorimetrically analyzed for iron by eluting the sample with hot (180°C) 2N hydrochloric acid. The results are presented in Table 4-14. The relatively poor utilization shown for the H^+ form cation columns is attributed to conversion of the H^+ cation resin to the NH_4^+ form by available NH_4^+ ion in the dilute solvent. This depletion of the H^+ form resin necessitated premature column changeout because it was no longer useful for pH control.

Table 4-13

Preferential Corrosion in HAZ[(a)]

Nominal Coupon Thickness = 62 mils

		Measured Thickness (mils)		
ASME No.	Coupon No.	Weld[(b)]	HAZ[(a)]	General Surface
SA285C	P334	61.3	53.5	61.1-61.6
	P328	60.9	58.5	61.4-61.5
SA533A	W314	58.3	23.5	58.6-60.8
	W312	59.0	14.2	58.5-60.7
SA508	Y308	59.5	33.0	50.2-51.5
SA106	B346	60.6	46.7	58.8-59.9
SA333	H336	61.8	61.0	61.4-61.8
IN600	N346	61.9	51.0	51.0-51.6

(a) HAZ = Heat Affected Zone

(b) Measurement made at two points on estimated center line of weld

Table 4-14

Iron Capacity of Cation Columns

New Resin Capacity = 2.10 meq/mL

Resin Ionic Form	Resin Column No.	Resin Column Vol (mL)	Process Vol (L)	Iron (meq/mL)(a)	Utilization (%)(b)
NH_4^+	I	214	320	1.79	85
	II	216	410	2.02	96
	III	219	470	2.11	101
	IV	219	330	1.76	84
	V	220	350	2.01	96
	VI	220	330	2.08	99
	VII	219	180	1.45	69
	VIII	196	230	1.35	64
	IX	216	190	1.58	75
	X	210	97	0.63	30
H^+	I	206	61	0.13	6
	II	200	67	0.23	11
	III	208	39	0.21	10
	IV	198	45	0.17	8
	V	200	34	0.43	20
	VI	214	8	0.31	15

(a) Based on the exchange of Fe(III) ion

(b) $\%\ \text{utilization} = \frac{\text{meg Fe(III)/mL} \times 100}{2.10}$

4.2.5.5 COPPER REMOVAL/PASSIVATION

A modified copper dissolution passivation and step (Reference 14) was employed three times during the extended operating period of 248 hr. Following each sludge iron step, a mixed bed clean-up step was performed. When cooling was complete, the copper step was conducted by the following procedure:

1. Add NH_4OH to adjust pH to 9.0.

2. Add ethylenediamine (EDA) to adjust the pH from 9.0 to 10.5.

3. Continue recirculation for 30 minutes to distribute chemicals. Start air sparge at 200 cm^3/min.

4. Add hydrogen peroxide to produce a final concentration of 3% H_2O_2 while maintaining the temperature at 40°C.

5. Continue recirculation at 40°C for at least 2 hr, and add hydrogen peroxide as needed to hold the concentration at about 0.5 wt%.

6. After 2 hr, increase the temperature to 94°C to destroy the excess hydrogen peroxide.

7. Reduce temperature to 40°C, turn off air sparge, and start nitrogen sparge at 200 cm^3/min.

8 Recirculate through a mixed-bed ion-exchange column until the conductivity is 10 umhos.

The amount of copper in solution and the approach to equilbrium as a function of operating time are shown for each copper step in Figure 4-8.

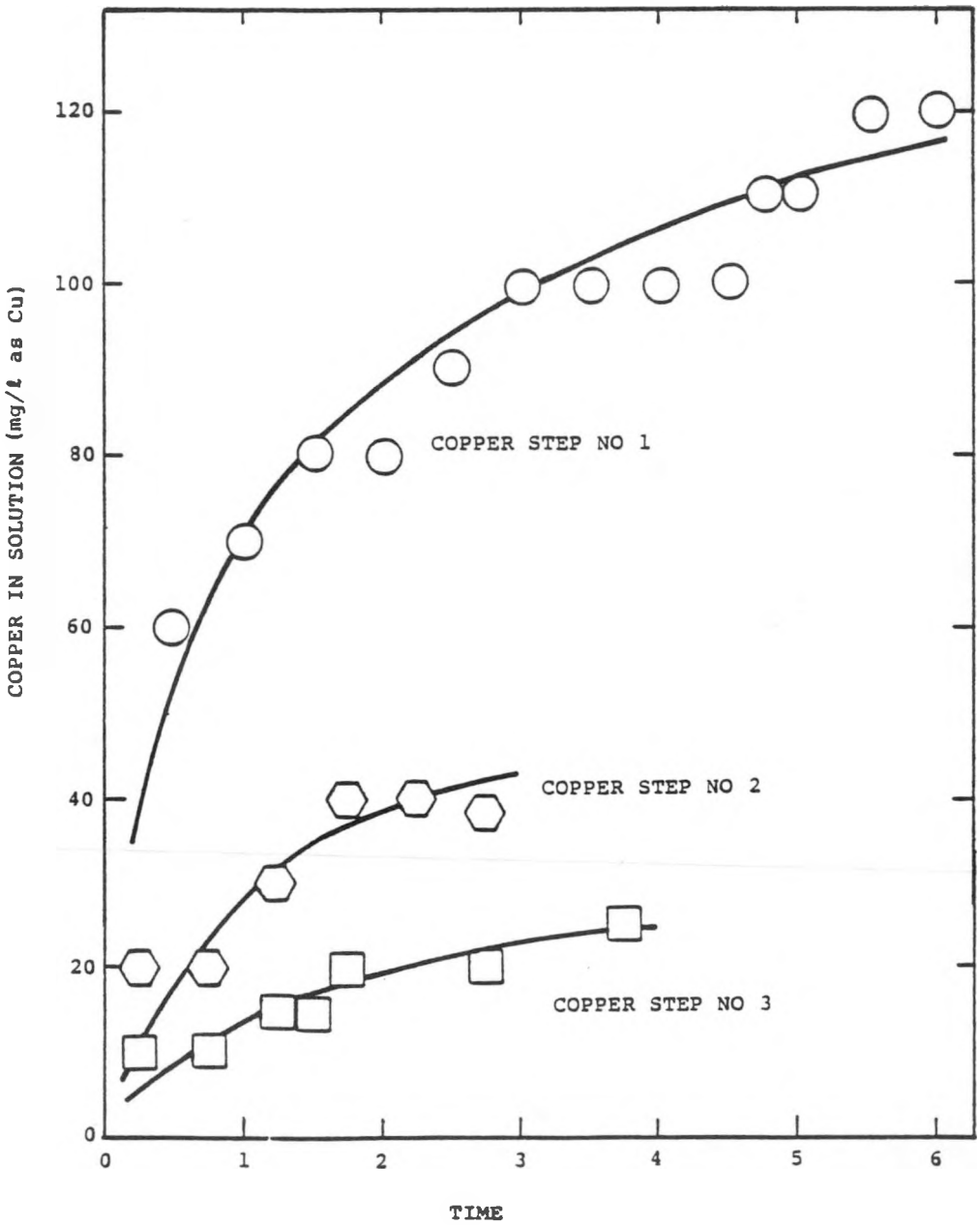


FIGURE 4-8. Dissolution of CuO and Cu From Sludge

Three earlier recirculation tests (Reference 7) were used to develop the copper/passivation step. In this development process, chemical analysis of the sludge was performed before and after each exposure and corrosion coupons were included to determine the effect of the copper/passivation step on steam generator materials of construction. The results are summarized in Table 4-15, and show that the copper/passivation step is both effective for copper removal and non-corrosive to the alloys tested. Visual observations also confirmed that copper which was plated on C/S surfaces during the iron dissolution step was completely removed.

4.2.5.6 CREVICE CLEANING

Dilute solvent effectiveness for cleaning fully packed and partially packed crevices in the reverse dent configuration was evaluated in the 100-hr and 248-hr bench top tests (Tests No. 19-5 and 20). The degree of crevice cleaning was determined by using a "Bubble Point Measurement" taken from ASTM E128-61. This measurement is an estimate of the maximum pore diameter in a porous solid. The pore diameter is related to the gas pressure required to form a bubble in the following way:

$$D_{max} = \frac{(13.53)\ (30)\ (T)}{P - P_c}$$

Where Dmax = Maximum pore diameter in microns

T = Surface tension (water at $20^{o}C$ = 72 dynes/cm)

P = Pressure to form a bubble expressed as mm of H_2O

Pc = Pressure correction for water layer over surface (1-in. = 25.4 mm of H_2O)

Sensitivity of the test procedure was verified by forcing successive 150-ml portions of hot ($90^{o}C$ to $95^{o}C$) dilute solvent through a partially packed reverse dent, and determining the bubble point after each incremental volume of solvent was passed through the crevice. The results, shown in Figure 4-9, demonstrate that the effectiveness of solvent disolution of the crevice corrosion can be measured by this

Table 4-15

Effect of Passivation on Sludge Composition and Corrosion Rate

Test Number	19-3		19-4		19-5	
Time(hr)	5.25		6.5		6	
Sludge Composition	Before	After	Before	After	Before	After
Fe_3O_4 (wt%)	94.8	97.3	97.3	99.7	95	99.5
CuO (wt%)	5.2	2.7	2.7	0.3	5	0.5
Dissolution (wt%)						
ASME No.	mils/day[(a)]		mils/day[(a)]		mils/day[(a)]	
SA285C					0.016	
SA533A	0.012		0.008		0.049	
SA508			0.008		0.090	
SA106					0.033	
	0.005				0.001	

(a) Uniform nonwelded corrosion coupons.

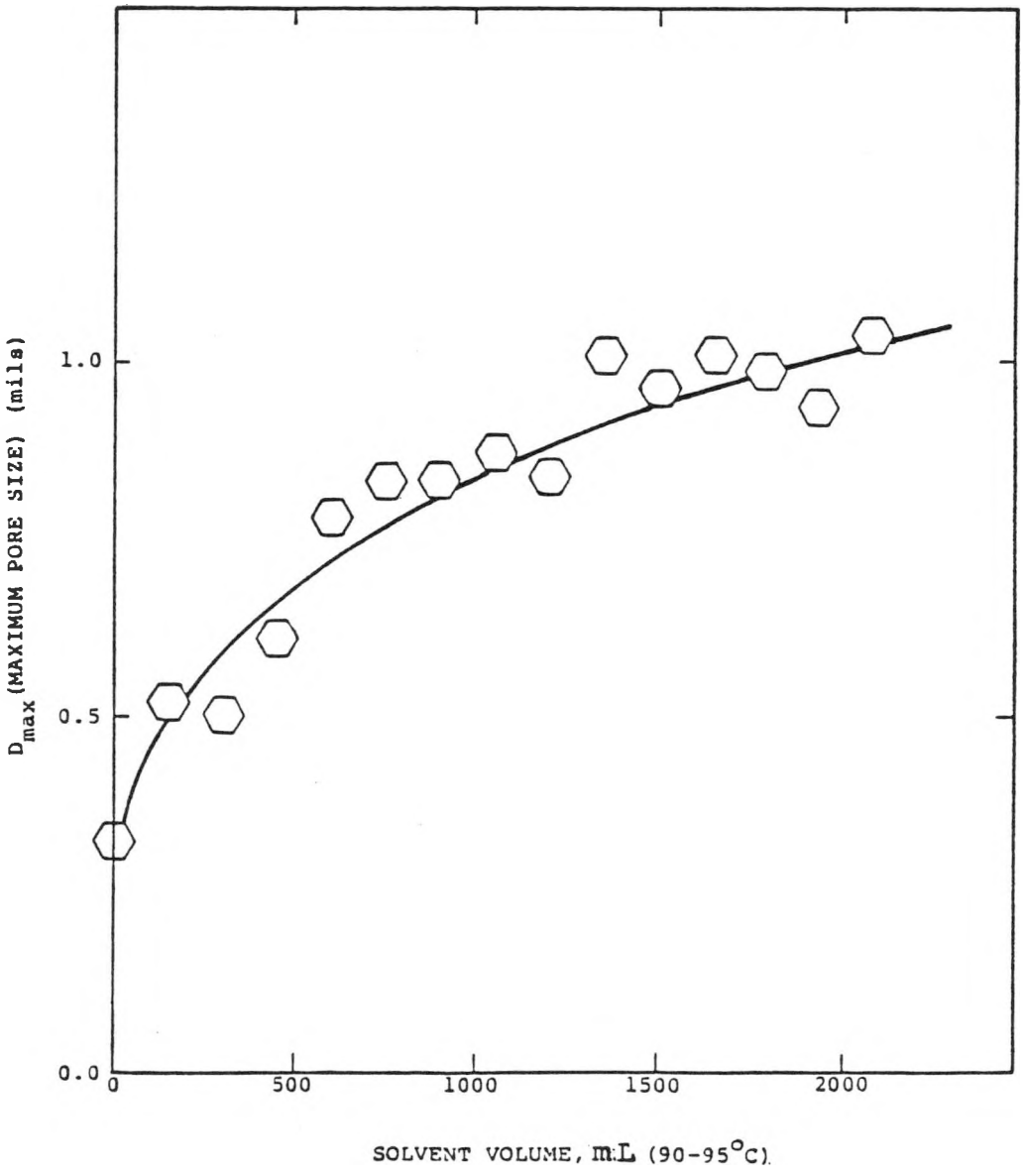


FIGURE 4-9. Effect of Hot Dilute Solvent on Pore Size in a Reverse Dent.

technique. The bubble point method will detect cleaning action when visual observation will not because the solvent flow is labyrinthian and frequently no visual light path is established until the dented sample is mostly cleaned. The reverse dents exposed during the 100-hr and 248-hr recirculation tests were characterized by bubble point measurement before and after exposure and the data are given in Table 4-16. All three reverse dents had visible openings at the end of the test period. the carbon steel slugs in the fully impacted reverse dents (3/8-in.) were loose and easily fell out of the Inconel tube. The 3/4-in. reverse dent showed several paths open to the passage of light and the corrosion product deposit appeared to be loose and unconsolidated.

The above results and observations indicate that the dilute solvent at 80°C is potentially applicable for cleaning blocked or slightly dented crevices. Later tests were equally successful for removing deposits from blocked crevices but less successful for cleaning dented crevices.

4.2.5.7 FINAL CLEANUP WITH MIXED BED RESINS

Mixed-bed ion-exchange resin was used for cleanup after each solvent step and for final cleanup of the recirculating loop. Typical performance of the mixed-bed ion-exchanger following a sludge-iron step is shown in Figure 4-10. The cleanup process after a copper removal/passivation step is longer than after an iron removal step because of the presence of residual ethylenediamine (EDA), which is difficult to remove by ion-exchange.

Results of a typical cleanup step based on reduction of the coolant conductivity to 10 umhos/cm are given in Table 4-17. The reduction of organic carbon concentration in the mixed-bed effluent verifies that the ion-exchange bed has removed all solvent organic components, including dissolved nonionic species.

Additional test results confirm that mixed-bed ion-exchange cleanup can be used to restore the water quality, after cleaning, to 10 umhos and 5mg/L residual iron. When the cleanup process is applied after a copper/passivation step, restoration of water quality will take about twice as long as cleanup from a sludge iron step.

Table 4-16

Crevice Cleaning During Recirculation Tests

Solvent:	Citric Acid	0.1 wt%
	Gluconic Acid	0.1 wt%
	Ascorbic Acid	0.1 wt%
	Cinnamonitrile	0.3 wt%
	pH	3.6 (NH_4OH)

Temperature: 80±2°C

Description	3/4-in. Thick, No Measurable Denting		3/8-in. Thick, Fully Dented Estimated Deformation (2-3 mils)			
Time (hr)	248		248		101	
	Before	After	Before	After	Before	After
Weight (g)	52.603	50.819	25.312	22.273	27.311	26.787
Thickness (in)	0.7167	0.7014	0.3185	0.2925	0.377	0.368
Bubble Point (mm H_2O)	110	22±5	850	66±2	285±14	16±2
D_{max} *(microns)	280	1800	34	488	104	3000
Weight Loss (mg)	1784		3039		525	

$$*D_{max} = \frac{13.53 \times 30 \times 72}{p - \frac{25.4}{4}}$$

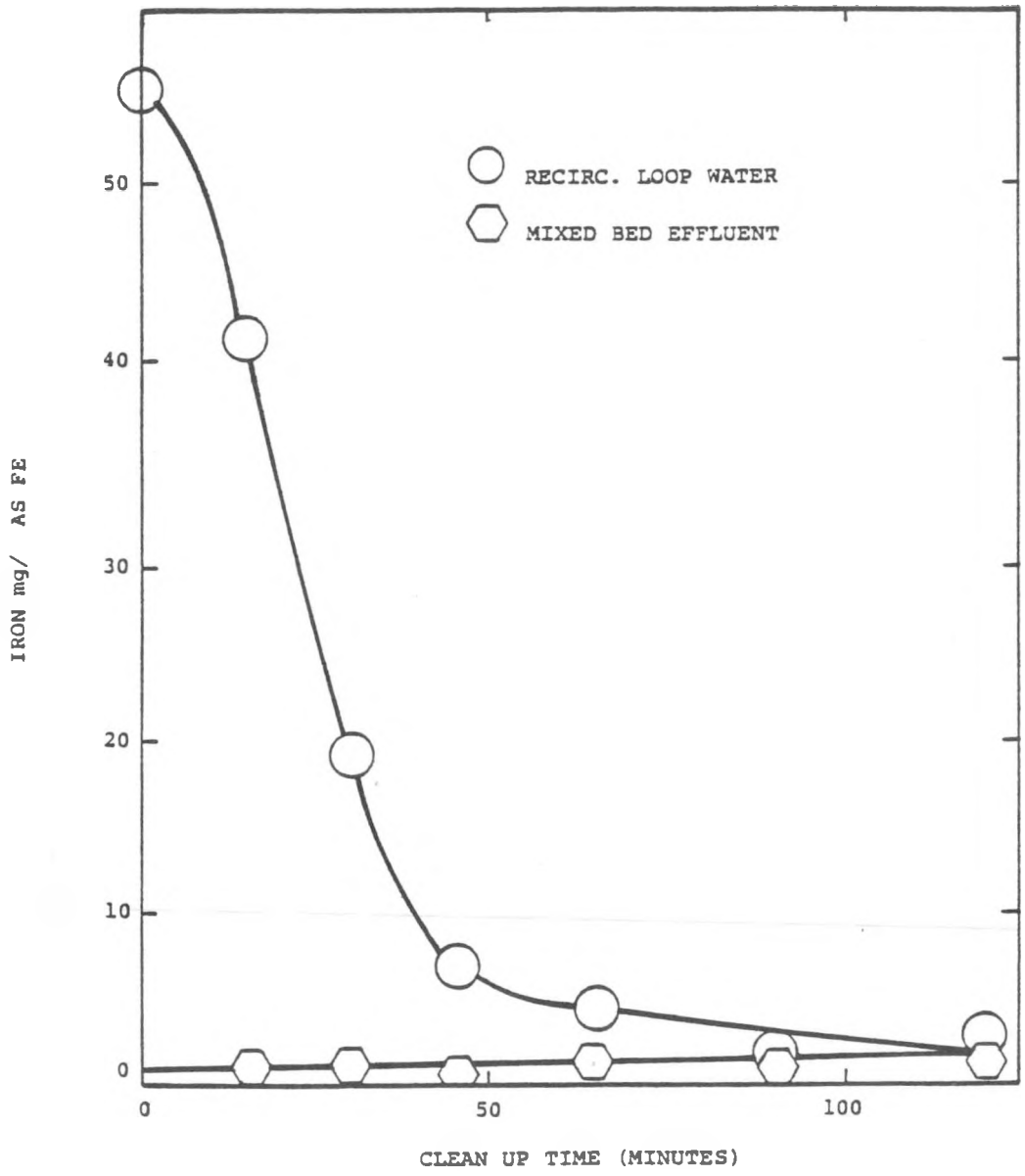


FIGURE 4-10. Typical Mixed-Bed Cleanup After Sludge Iron Step.

Table 4-17

Mixed-Bed Cleanup After Passivation

Time (min)	Recirculation Loop Sample	Mixed-Bed Effluent	Organic Carbon (mg/L)
0	11,000	-	1,000
30	2,700	0.22	250
90	325	0.46	125
120	260	0.77	ND
180	110	0.41	75
210	50	1.3	ND
240	20	1.2	ND
270	10	1.5	ND

ND = None Detected

4.2.6 MODEL STEAM GENERATOR CLEANING DEMONSTRATION

After the pilot-scale system (Appendix A.5) had been fabricated and tested, it was transported to Commonwealth Edison Company's State Line Station and was used in the successful demonstration of the dilute chemical cleaning process on two model steam generators. This section discusses the dilute chemical cleaning demonstration performed at the State Line Power Plant.

Inspections of Unit 5 and Unit 6

Prior to cleaning, the tube bundles and shrouds of Unit 5 and Unit 6 model generators were inspected and photographed. The units had a very similar appearance, with a reddish-brown film on all surfaces that had been exposed to the fouled water chemistry operation. The quantity of sludge and scale in the annular crevices was assessed by backlighting the crevices and estimating the percentage of crevice open to the passage of light. Unit 5 had been operated for 48 days on sea-water fouled chemistry with an average chloride content of 60 ppm. Unit 6 had been operated for 112 days on coolant fouled with 1% Lake Michigan water.

The units had been operated with daily additions of 1 to 2 g of synthetic sludge to aid in producing a fouled condition simulating full-size steam generator sludge conditions. Sludge added to Unit No. 5 was 80 wt% Fe_3O_4 and 20 wt% CuO. Sludge added to Unit 6 was 91.2 wt% Fe_3O_4 and 8.7 wt% CuO. The composition of Unit 6 sludge simulated low copper content steam generator sludge.

Neither of the units had measurable denting. Unit 6 was the least fouled and was cleaned first. An initial copper step was not performed in Unit 6 because the sludge added was a low-copper sludge and visual inspection showed no significant copper plateout after the fouling operation.

Cleaning of Unit 6

The process for cleaning Unit 6 proceeded as follows:

a. Coolant cleanup from model generator wet layup chemistry was accomplished by recirculation through the mixed bed ion-exchange column. Cleanup continued until the coolant conductivity was reduced to 10 umho/cm. Nitrogen sparge was used for oxygen control, and coolant was heated to 175°F during recirculation.

b. The mixed-bed ion-exchange was bypassed, corrosion inhibitor was added, and concentrated solvent chemicals were added to the coolant to establish the dilute solvent concentration levels for sludge dissolution.

c. Solvent pH was adjusted to 3.6 with NH_4OH and flows through the H^+ and NH_4^+ cation columns were adjusted to maintain pH at 3.6 $\pm$ 0.2.

d. Sludge dissolution continued for 60 hours. Operating parameters for the sludge dissolution step were maintained as follows:

Temperature, °F	175-178
Solvent Flow, total, cm^3/min	500
H^+ Cation Column Flow, cm^3/min	75-100
NH_4^+ Cation Column Flow cm^3/min	425-400
N_2 Sparge Rate, Total, cm^3/min	1500
Sparge Recirculation Rate, cm^3/min	100-1300
N_2 Makeup Rate, cm^3/min	500-200
pH, Depleted Solvent from Generator	4.0 $\pm$ 0.4
pH, Regenerated Solvent	3.6 $\pm$ 0.3
Dissolved Oxygen, ppm	0.2
Conductivity, umho/cm	1000-3000

e. Cleanup for the copper step was started by beginning cooldown and diverting solvent flow through the mixed-bed ion-exchanger. (The mixed-bed heat exchanger maintained the influent temperature below 140°F for ion-exchange resin protection and later provided cooling to reduce temperature to 100°F for the copper step.) Cleanup continued until the solvent conductivity was reduced to 35 umhos/cm.

f. The ion-exchanger was bypassed and a one-to-one mixture of ethylenediamine (EDA) and NH_4OH was added to adjust solvent pH to 10.4.

g. The sparge was switched from nitrogen to air, and hydrogen peroxide was added to initiate copper dissolution.

h. On completion of copper dissolution, as evidenced by stabilization of the copper concentration in the recirculating solvent, the solvent was heated to 160°F to destroy excess hydrogen peroxide.

i. Copper solvent cleanup flow was established through the mixed-bed ion-exchanger and recirculation continued until conductivity was reduced to 10 umhos/cm.

j. Hydrazine was added to a concentration of 200 ppm and the model generator was left in wet layup until disassembly for inspection.

During sludge dissolution, the equilibrium level of dissolved, complexed iron was determined by sampling and analysis of the recirculating dilute solvent at frequent intervals (approximately 2 hrs). The curve of dissolved iron concentration vs. time is shown in Figure 4-11. An initial high iron concentration occurred 3/4-hr after solvent injection and is attributed to a short period of operation at low pH before correction by adjustment of the NH_4^+ cation column flow. The second peak at 10-hr is attributed to dissolution of the most readily exposed surface deposits. Beyond 20-hr, the equilibrium iron concentration is a combination of base metal corrosion and dissolution of the less exposed deposits, including corrosion products in the tube-to-support plate crevices.

The sludge iron step was followed by a copper step to remove any copper plated on the carbon steel surfaces and to passivate the descaled surfaces. The final concentration of dissolved copper was 45 ppm for a total copper removal of 0.54 grams.

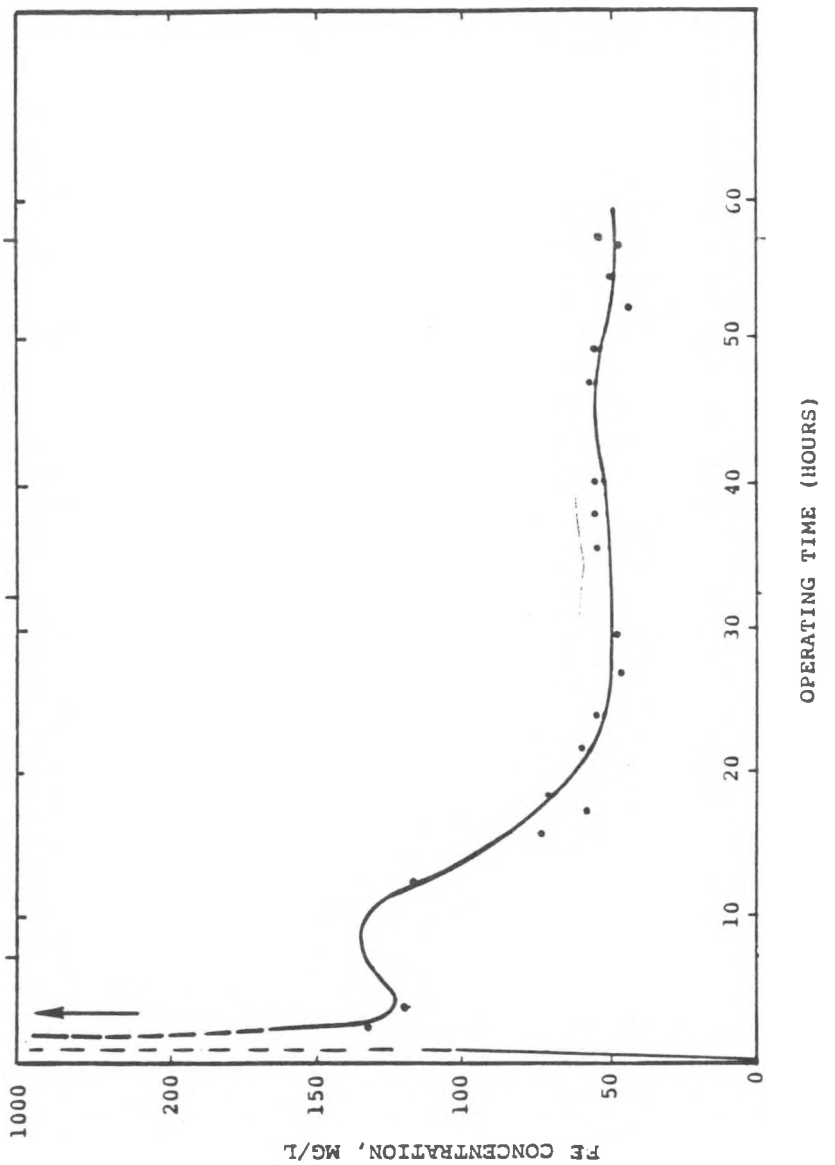


FIGURE 4-11. Unit 6 Soluble Iron Versus Operating Time.

Disassembly of the model generator for inspection revealed the tubes and shroud assembly had been very effectively cleaned. Figures 4-12 and 4-13 show the condition of the shroud and tubes before cleaning. Figures 4-14 and 4-15 show the condition after cleaning. After cleaning, the Inconel tubes were mirror bright, and the shroud was clean, with a gray passivated surface. A ring of particulate material had been deposited on the tubesheet, concentric with the shroud, suggesting some surface deposits had been loosened but not completely dissolved by the solvent. The undissolved particulate material was concentrated in the annular space between the shroud and outer shell. This area was essentially stagnant due to the central location of the blowdown ports through which the solvent and sparge gas were introduced.

Figure 4-16 portrays the visually estimated tubesheet sludge deposits and support plate crevice conditions for pre- and post-cleaning comparison. The crevice blockage was estimated by observing light passage when the support plates were backlighted from the bottom. There were no deposits remaining on the support plate surfaces after cleaning, and the plates were passivated to a gray color. Seven of the eight tube-to-support-plate annular crevices showed significant cleaning action. Corrosion products remaining in the crevice annuli were primarily loosely held scale and flakes. The eighth tube-to-support-plate crevice was the only completely blocked crevice prior to cleaning, and it remained completely blocked.

Four reverse dent crevice specimens were mounted in the gas-liquid separator during cleaning. Two of these reverse dents were 3/8-in. long specimens which had been prepared with 2 to 3 mils of denting. Both 3/8-in. specimens were fully cleaned (the carbon steel plug was free from the tube). Some loose scale remained in the crevice of one specimen but the solid plug dropped out of the tube during inspection. The remaining two reverse dents were 3/4-in. long specimens which were not dented, but the crevices were fully packed. Of these, one was sufficiently cleaned to show several paths visually open to light. The remaining scale in the crevice was loose and unconsolidated. The other specimen showed no paths visually open to light, but the crevice deposits appeared loose and

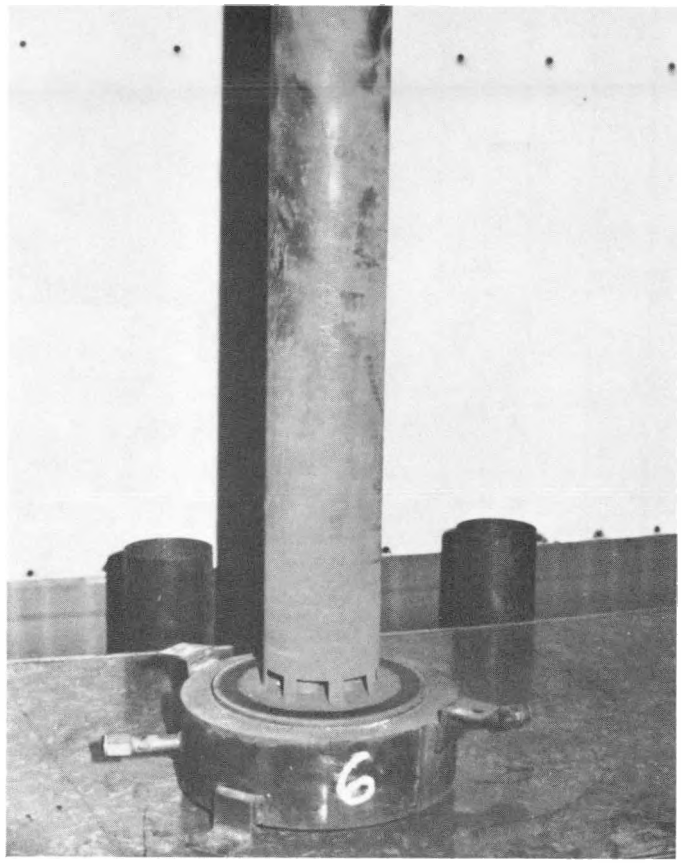


FIGURE 4-12. Unit 6 Before Cleaning (Shroud).

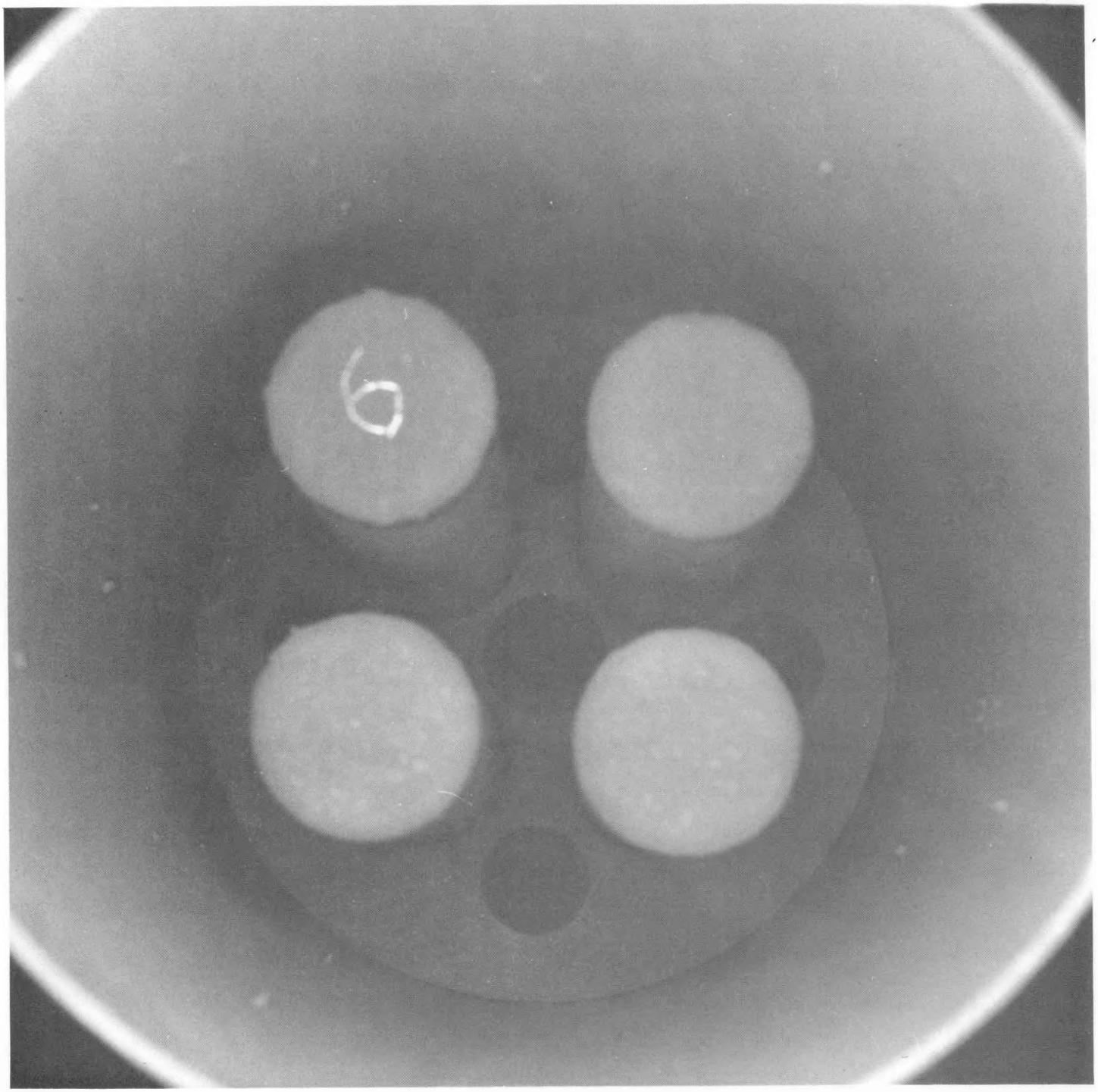


FIGURE 4-13. Unit 6 Before Cleaning (Tubes).

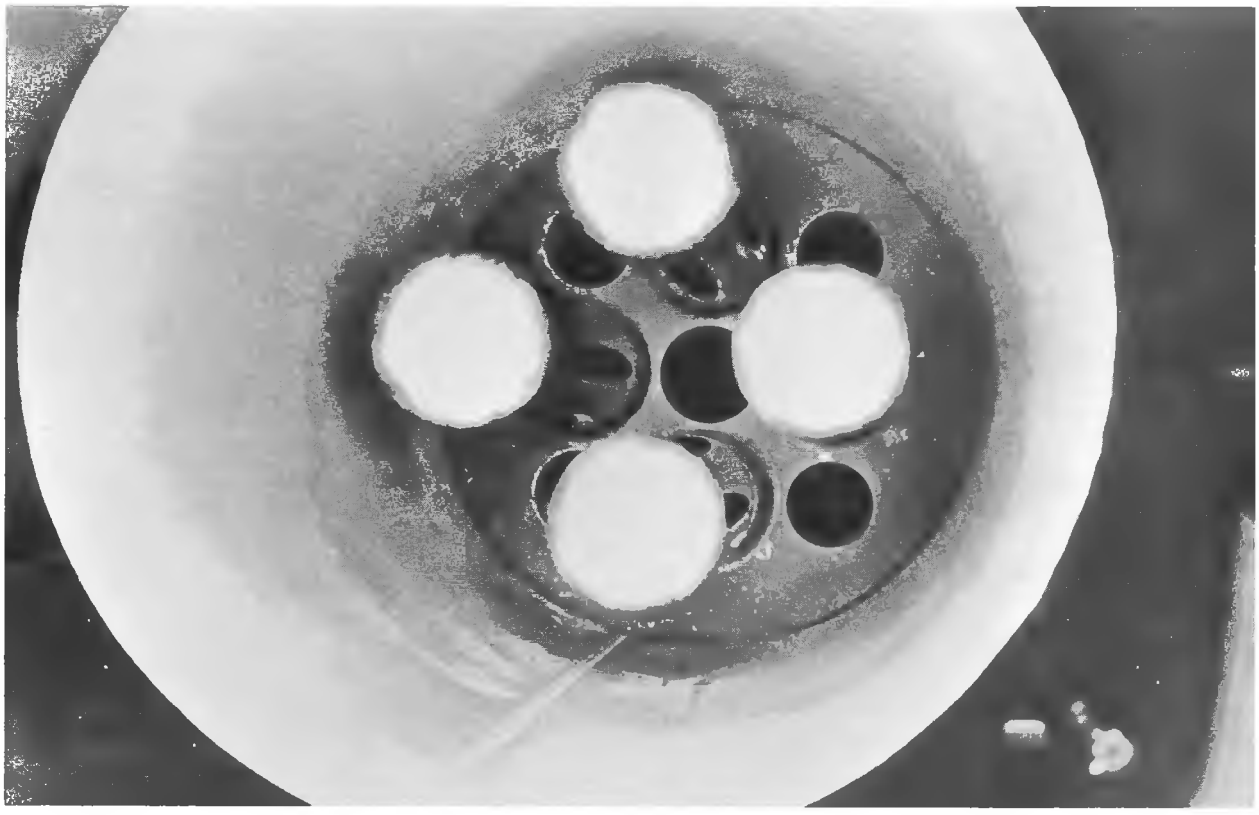


FIGURE 4-14. Unit 6 After Cleaning (Tubes).

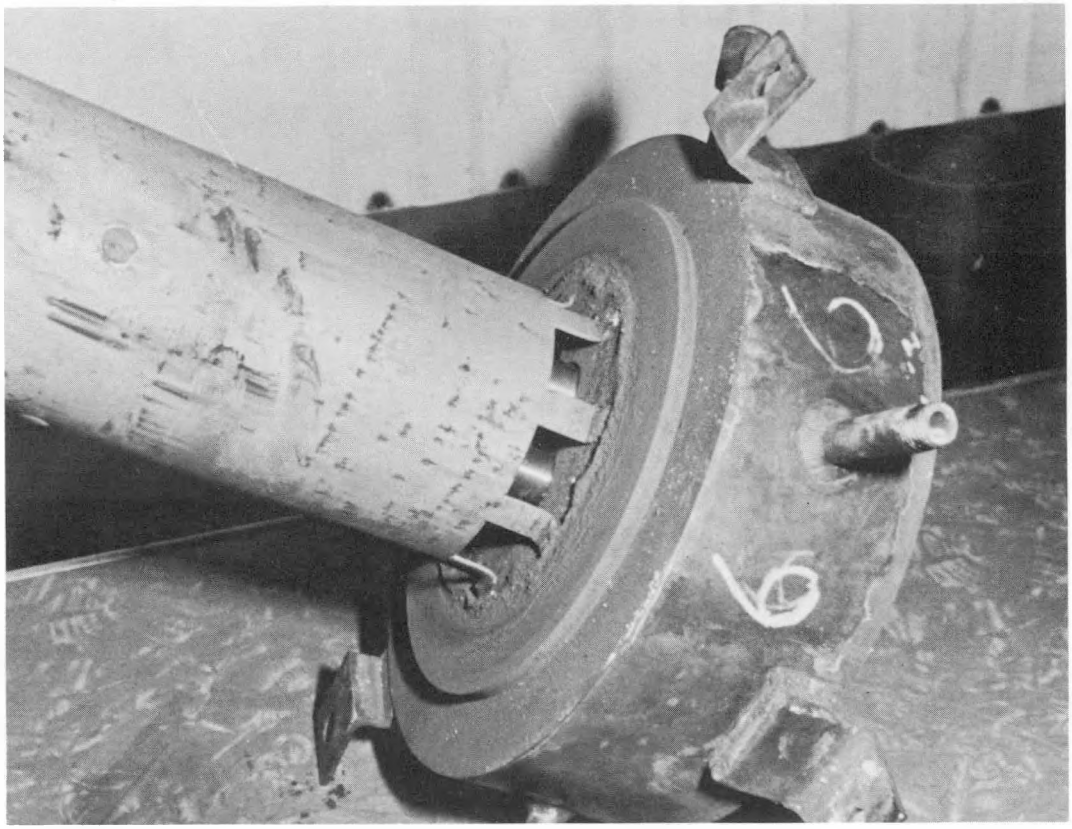


FIGURE 4-15. Unit 6 After Cleaning (Flange).

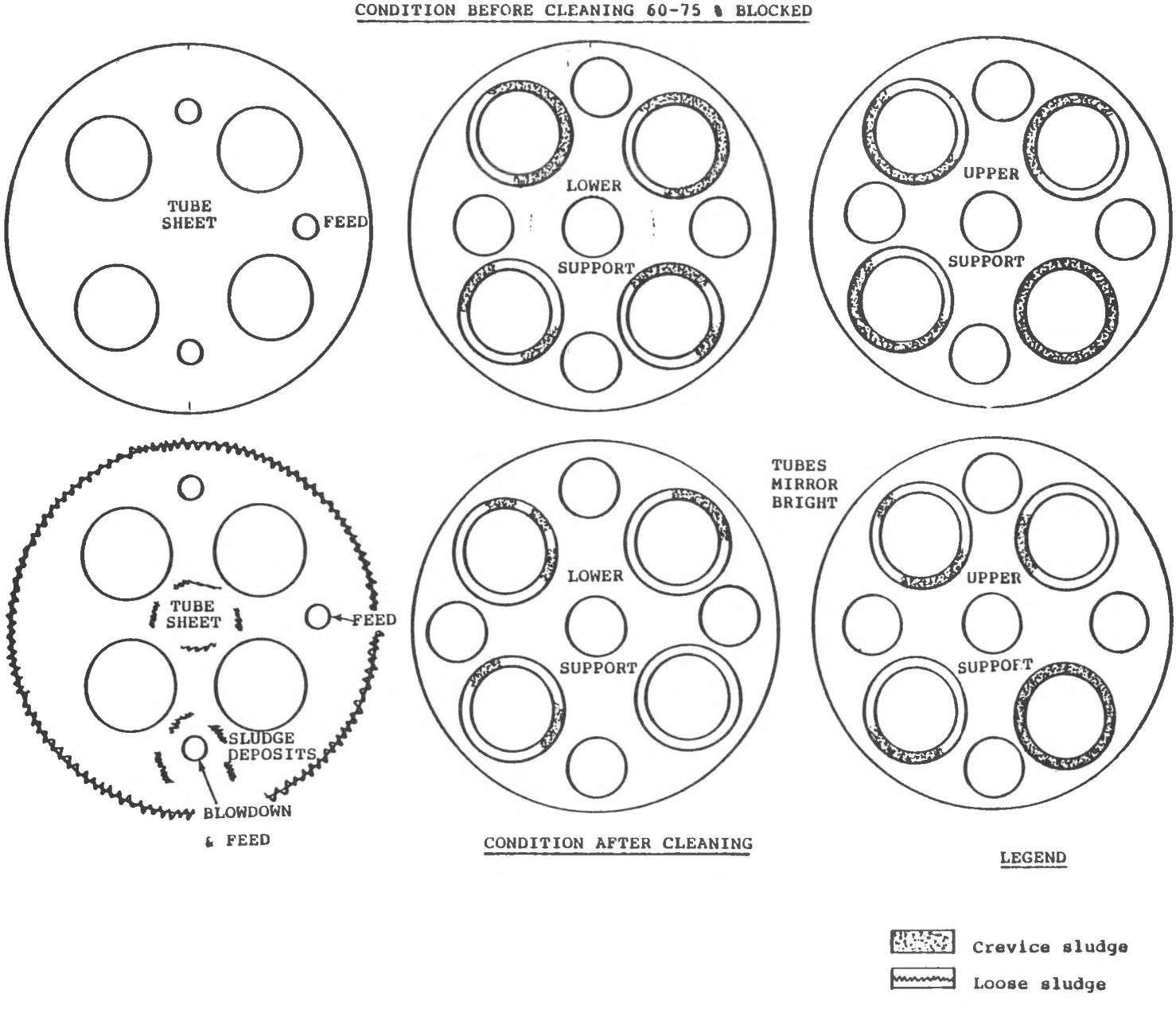


FIGURE 4-16. Unit 6 Pre- and Post-Cleaning Comparison.

unconsolidated. Figure 4-17 shows the crevice condition of the reverse dent specimens after cleaning.

The relative effectiveness of crevice cleaning for the four reverse dent specimens was evaluated by determination of the "Bubble Point" (Reference 7) before and after cleaning. The data are presented in Table 4-18. The weight loss data for each reverse dent are also included in Table 4-18, but cannot be used to accurately evaluate crevice cleaning effectiveness.

Uniform and stressed U-Bend corrosion specimens had been installed in the gas-liquid separator prior to initial cleanup and were removed for evaluation after final wet layup chemistry was established. Average corrosion rates for each type of specimen are presented in Table 4-19. The corrosion rate was calculated from the total coupon weight loss over the total contact time of the sludge iron step, where essentially all of the corrosion occurs during the cleaning process.

Corrosion of the vapor phase specimens was very low, averaging 0.003 mil/day, indicating that the process does not produce corrosive vapors. This is a significant result, since corrosive vapors would attack unprotected carbon steel surfaces in the vapor space of steam generators.

There was no evidence of cracking of the stressed U-Bend specimens. Visual inspection showed no accelerated uniform corrosion or pitting of the weld metal or HAZ on either the welded U-Bends or the unstressed weld specimens. The only apparent difference was a darker shading of the HAZ.

Cleaning of Unit 5

Unit No. 5 was cleaned by the same process as Unit 6 except for the addition of a copper step prior to the sludge iron step and the extention of the sludge iron step from 60 to 132 hr. The initial copper step was used to simulate the process sequence that would be needed for a steam generator with a high copper content in the sludge. Unit No. 5 had been operated with sludge additions containing 20% CuO to simulate high-copper sludge conditions.

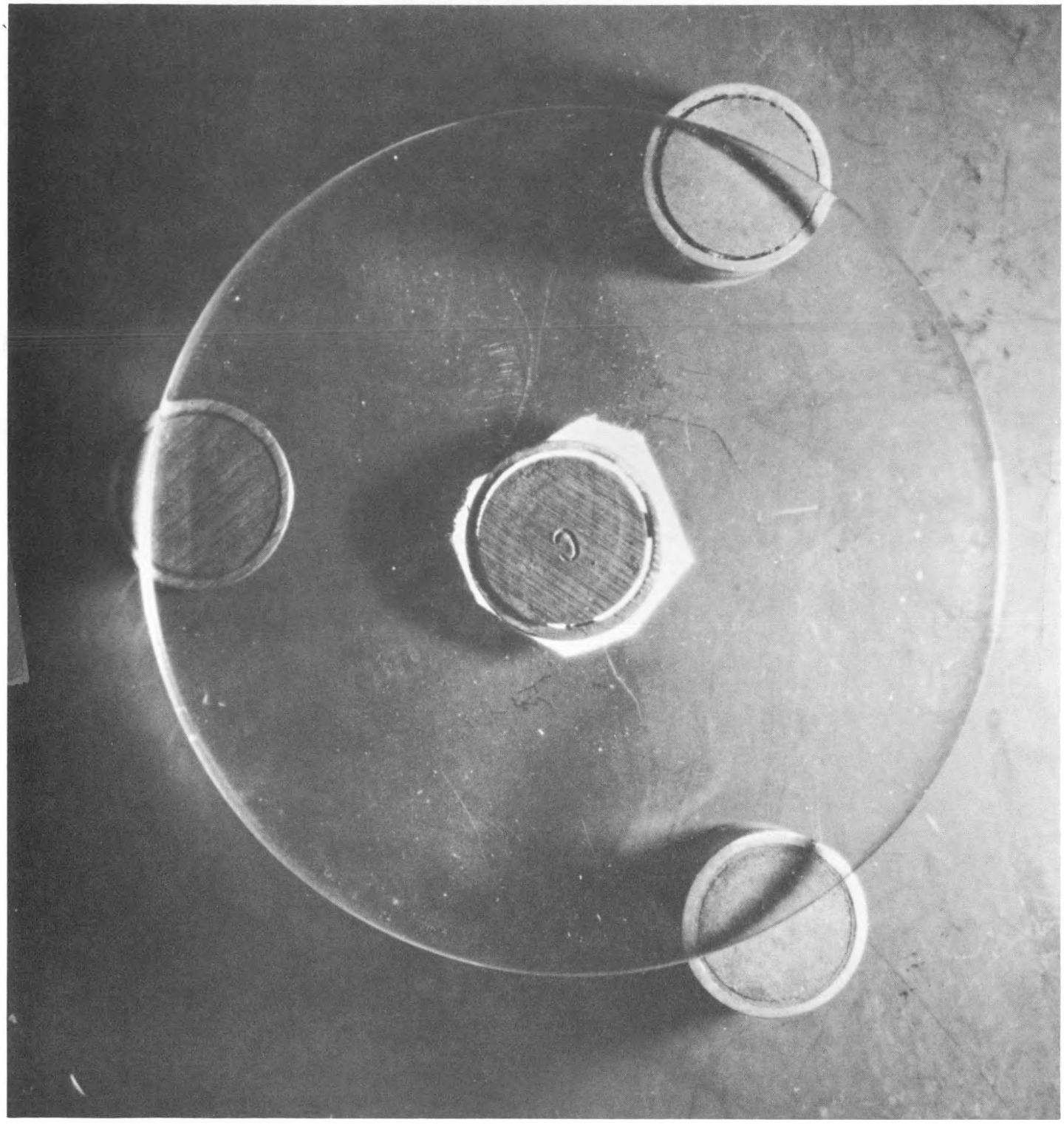


FIGURE 4-17. Reverse Dent Specimens From Unit 6 After Cleaning.

Table 4-18

Crevice Changes Observed for Unit 6
Dilute Chemical Cleaning

Reverse Dent Description	Nominal 3/8-in. Thick Fully Packed and Dented to 2-3 mils		Nominal 3/4-in. Thick Partially Packed Without Denting	
Specimen No.	C	D	4	16
Before				
Weight (g)	25.8803	28.6802	51.4340	53.6367
Bubble Point (mm H_2O)	890	890	400	355
After				
Weight (g)	25.2822	28.4900 (a)	51.0574	53.3270
Bubble Point (mm H_2O)	126		400	3.6

(a) Carbon steel core was loose and Inconel was clean (see Figure 4-17).

Table 4-19

Average Corrosion Rates Observed for Unit 6
Dilute Chemical Cleaning

ASME No.	Coupon Type	Corrosion Rate (mils/day) Vapor Phase	Liquid Phase
SA285C	Welded	0.003	0.23
	Welded U-Bend	--	0.16
	Nonwelded	--	0.26
SA533A	Welded	0.004	0.91
	Nonwelded U-Bend	--	0.96
SA508	Welded	0.002	0.56
	Nonwelded	--	0.44
SA106	Welded	--	0.63
	Nonwelded	--	0.94
SA333	Welded	--	0.29
SA23WPB	Welded	--	0.17
	Nonwelded	--	0.21
SA516	Welded	--	0.69
	Nonwelded	--	0.89
IN600	Welded	--	0.005
	Welded U-Bend	--	0.002
	Nonwelded	--	0.005

The process for cleaning Unit 5 proceeded as follows:

a. Coolant cleanup from model generator wet layup chemistry was accomplished by recirculating flow through the mixed-bed ion-exchanger for 45 minutes.

b. The mixed-bed ion-exchanger was bypassed and an EDA/NH_4OH mixture at a 1:1 weight ratio was added to adjust pH to 10.8.

c. The N_2 sparge was switched to an air sparge and H_2O_2 was added to initiate copper dissolution.

d. Upon completion of copper dissolution, as evidenced by stabilization of the copper concentration in the solvent, the solvent was heated to 160°F to destroy excess hydrogen peroxide.

e. Copper solvent cleanup was accomplished by recirculation through the mixed-bed ion-exchanger until successive samples showed the solution conductivity was reduced to 11 umho/cm.

f. The iron step was initiated by injecting inhibitor after bypassing the mixed-bed ion-exchanger. The inhibitor solution was recirculated for 40 minutes to ensure dispersion of the inhibitor while the solvent was being heated.

g. Concentrated solvent chemicals were added to attain the desired chemical concentration (0.3 wt%) for dissolution of sludge. Solvent pH was 4.6. Flow through both cation exchangers was adjusted to maintain pH control and to accomplish solvent regeneration.

h. Sludge dissolution continued for 132 hr with periodic sampling and change-out of cation exchange columns as they became depleted. The pH was controlled by adjusting the flow ratio between the H^+ form and NH_4^+ form cation resin columns. The following operating parameters were maintained:

Temperature, ^{o}F	175 to 178
Solvent Flow, Total, cm^3/min	500
H^+ cation column flow cm^3/min	75 to 200
NH_4^+ cation column flow, cm^3/min	425 to 300
N_2 Sparge rate, total, cm^3/min	1500
Sparge recirculation rate, cm^3/min	500 to 1300
N_2 makeup rate, cm^3/min	1000 to 200
pH, depleted solvent from generator (BIX)	4.0 $\pm$ 0.3
pH regenerated solvent (AIX)	3.5 $\pm$ 0.3
Dissolved oxygen, ppm	0.1 to 0.2
Conductivity, umho/cm	500 to 1500

i. Cleanup for the final copper step was started by initiating cooldown and establishing flow through the mixed-bed ion-exchanger. Conductivity was reduced from 1400 umhos/cm to 90 umhos/cm after 1.25 hr of cleanup flow.

j. The pH was adjusted to 10.3 with a 1:1 mixture of NH_4OH and EDA after bypassing the mixed-bed ion-exchange column.

k. Hydrogen peroxide was added to initiate copper dissolution, and the sparge was switched from nitrogen to air.

l. After 3 hrs, the copper solvent contained 50 ppm H_2O_2 but no copper was detected. The dissolution, with periodic H_2O_2 additions, was continued for another hour. A heatup to destroy H_2O_2 and a switch to nitrogen sparge completed the copper step.

m. Cleanup was started with mixed-bed ion-exchange flow and was accomplished in 2.25 hrs.

n. The mixed-bed resin was bypassed and hydrazine was added to a concentration of 200 ppm for wet layup. Recirculation was continued for 20 minutes to disperse the hydrazine. The unit was left in wet layup until disassembly for inspection.

When Unit No. 5 was opened for inspection, there was excellent cleaning of surface areas and tube-to-support plate crevices. The heavy surface film had been completely removed. The Inconel tubes were mirror bright. Figures 4-18 through 4-21 show the pre- and post-cleaning conditions of the shroud and tubes. The deposit of loose scale on the tubesheet directly below the shroud-to-outer-shell annulus appeared in Unit 5 as it did in Unit 6. The scale deposit can be seen in Figure 4-19.

The support plate crevices in the model generator were all fully cleaned. Figure 4-22 provides representation of pre- and post-cleaning conditions in the tube-to-support plate annuli. There was a small amount of loose scale flake trapped where the tube alignment caused contact with the inside diameter of the support plate penetration.

The four reverse dent specimens in the gas-liquid separator were cleaned less effectively in Unit 5 than in Unit 6. The bubble point measurements for the reverse dent specimens are given in Table 4-20. One 3/8-in. dented specimen was fully cleaned. The other three specimens showed, by visual examination and bubble point evaluation, little or no cleaning improvement.

The equilibrium levels of dissolved iron in the solvent are shown by Figure 4-23. During the sludge cleaning, the initial iron dissolution peaked about 20 hrs after injection of chemicals, and the major quantity of sludge was dissolved during the first 37 hrs. The initial iron peak reflects the rapid dissolution of exposed surface deposits. The very high iron peak that occurred during the first 2 hr of Unit 6 cleaning is absent because the pH of the concentrated solvent used for Unit 5 was adjusted to pH 3.5 with NH_4OH prior to injection into the system.

A further comparison of the iron equilibrium curves for Unit 6 cleaning (Figure 4-11) and Unit 5 cleaning (Figure 4-23) shows notable differences. For Unit 5, the data show wide scatter and an increase in iron concentration after forty hours. Unit 6 data are less scattered and show the iron

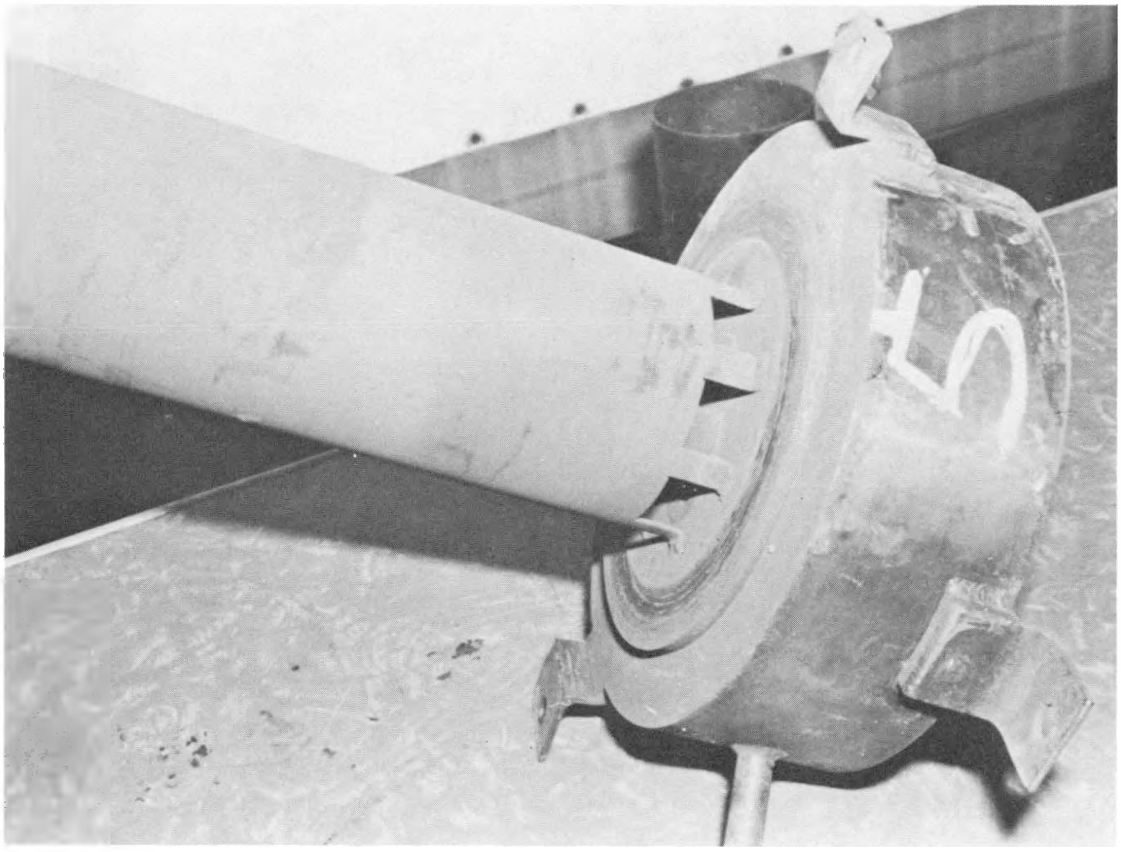


FIGURE 4-18. Unit No. 5 Before Cleaning (Flange and Shroud).

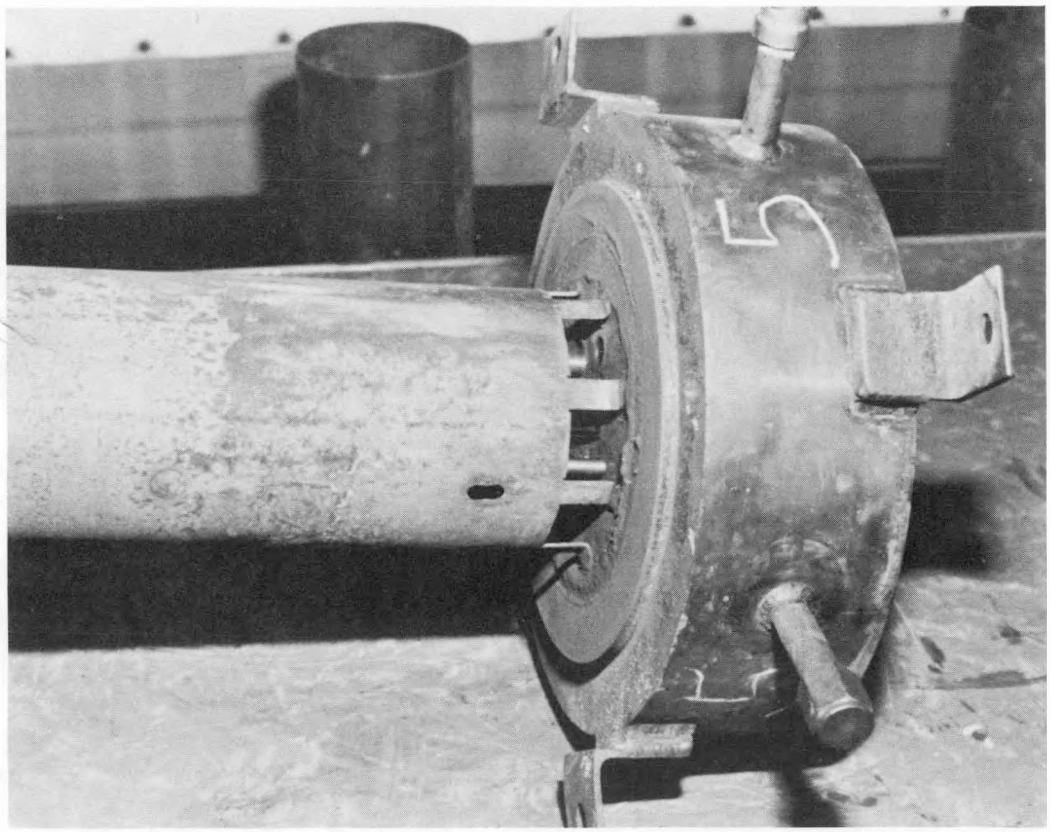


FIGURE 4-19. Unit No. 5 After Cleaning (Flange and Shroud).

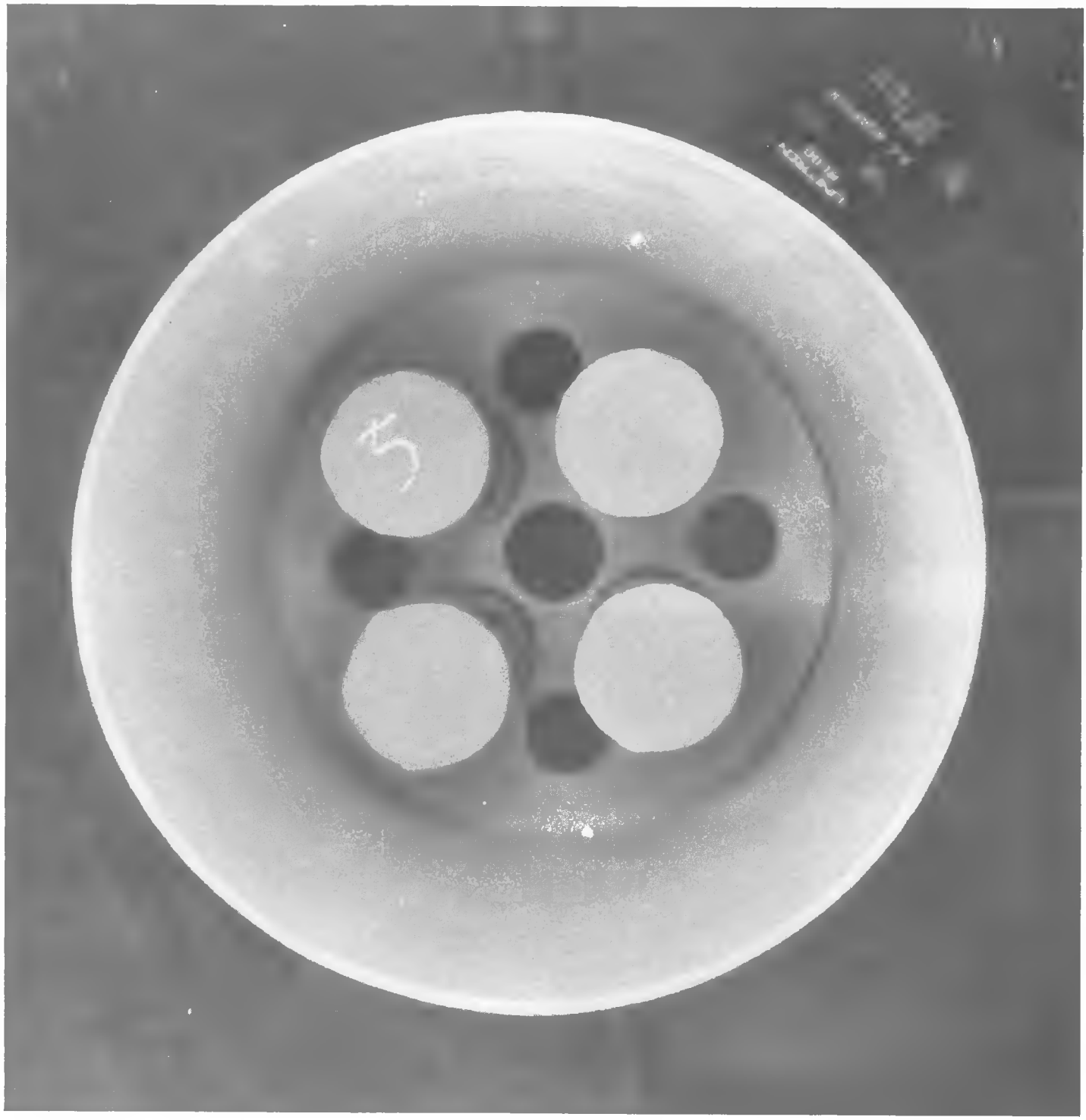


FIGURE 4-20. Unit No. 5 Before Cleaning (Tubes).

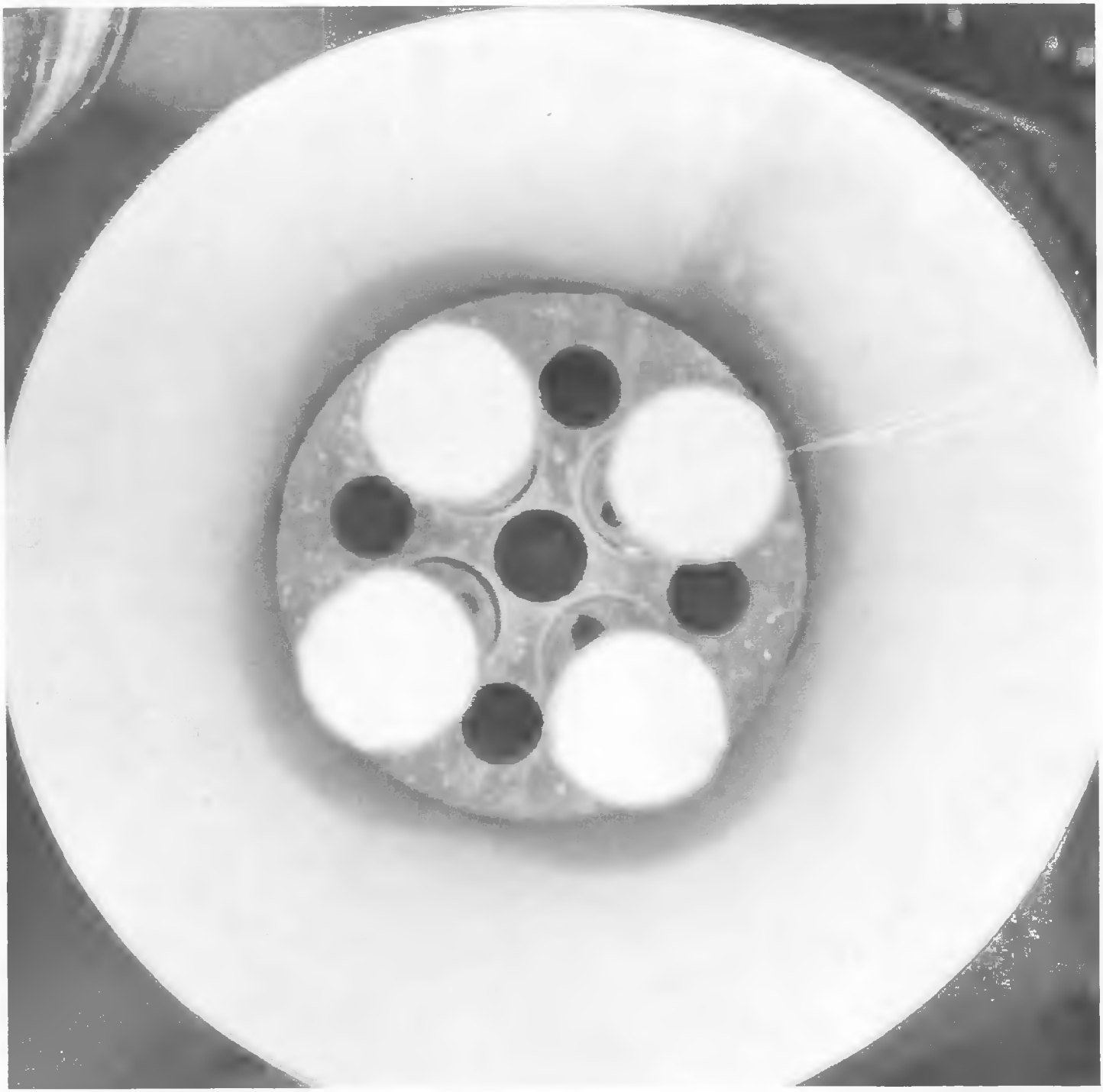


FIGURE 4-21. Unit No. 5 After Cleaning (Tubes).

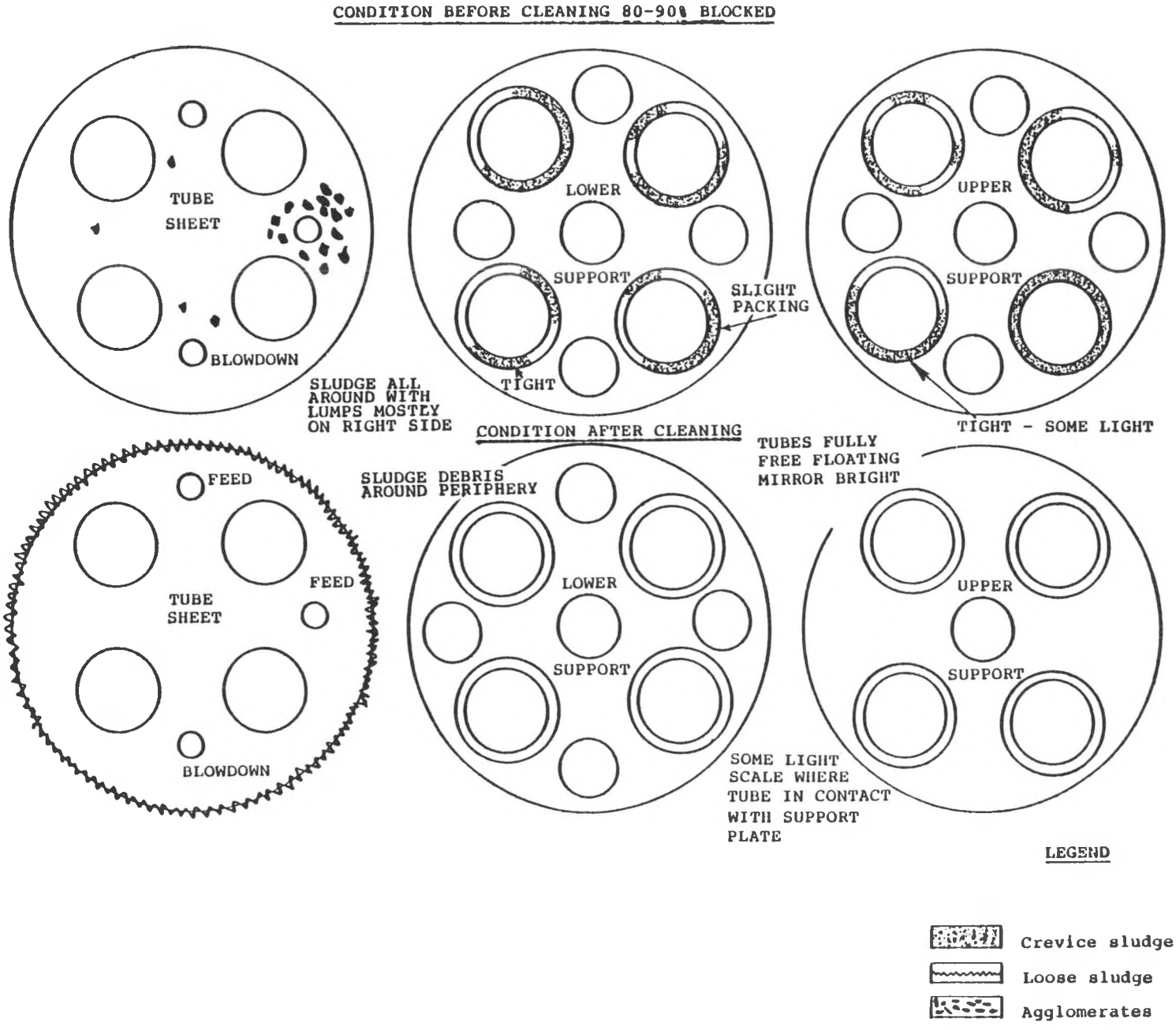


FIGURE 4-22. Unit No. 5 Pre- and Post-Cleaning Comparison.

Table 4-20

Crevice Changes Observed for Unit 5
Dilute Chemical Cleaning

Reverse Dent Description	Nominal 3/8-in. Thick Fully Packed and Dented to 2-3 mils		Nominal 3/4-in. Thick Partially Packed Without Denting	
Specimen No.	A	B	9	12
Before				
Weight (g)	24.2042	24.3586	53.5451	54.4124
Bubble Point (mm H_2O)	890	890	390	600
After				
Weight (g)	23.1900	23.8660 (a)	52.4493	53.5098
Bubble Point (mm H_2O)	837		390	600

(a) Carbon steel core was loose.

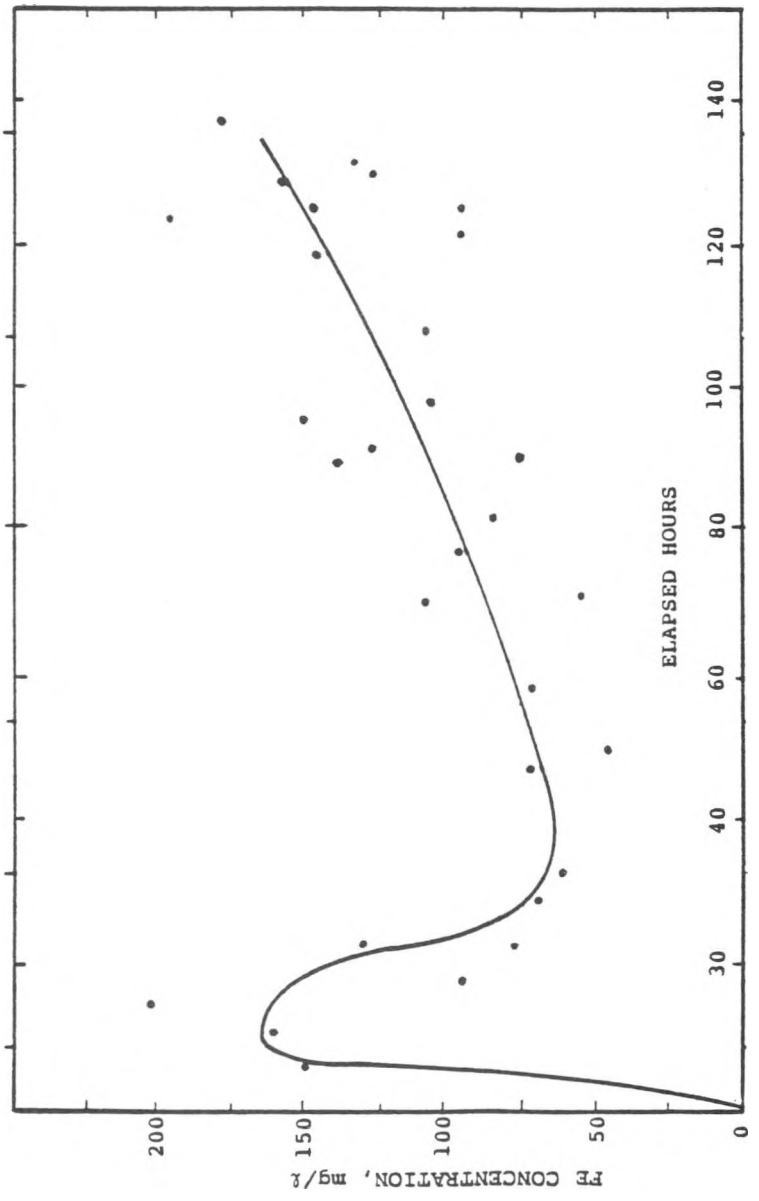


FIGURE 4-23. Unit No. 5 Soluble Iron In Equilibrium With Cleaning Solvent.

concentration was stable after about 20-hr. A possible explanation of these differences may be that for Unit 5, two sets of stressed, pre-cracked specimens were included in massive stainless steel holders, resulting in a significant amount of corrosion iron being released to the solvent due to galvanic corrosion effects. The specimen holders were mounted near the level of the solvent effluent port. Consequently they were alternately washed by the frothing action of the nitrogen sparge, submerged in cleaning solvent, or exposed to the generator gas phases because of changing solvent levels. These specimens were found to have corroded at a rate four times higher than totally submerged specimens. The combination of high corrosion rates and occasional vigorous washing of the specimens may well have resulted in sporadic release of corrosion iron to the solvent, resulting in scattered data and unexpectedly high iron concentrations. The holders and pre-cracked specimens mounted in Unit 5 are shown in Figure 4-24 and 4-25.

Average corrosion rates for specimens installed in the gas-liquid separator of Unit 5 are shown in Table 4-21. The corrosion rates are comparable to the rates of the Unit 6 cleaning. Alloy SA533A was the most sensitive to corrosion, but all rates were <1 mil/day. Corrosion of specimens in the vapor space was very low, as in the Unit 6 cleaning, with SA533A corrosion of 0.016 mils/day as the highest. There was no evidence of cracking of stressed U-bend specimens. Visual inspection of weld HAZ of corrosion specimens showed the beginning of selective attack and incipient pitting when compared to non-welded specimens. The HAZ condition in Unit 5 specimens is attributed to the longer solvent exposure of 132 hr compared to a Unit 6 exposure of 60 hr.

Analysis of Ion-Exchange Samples

During the dilute chemical cleaning of Units 5 and 6, ion-exchange beds were used to regenerate the dilute solvent, control pH, and remove iron and copper from solution. These ion-exchange columns were changed periodically, in accordance with the following criteria.

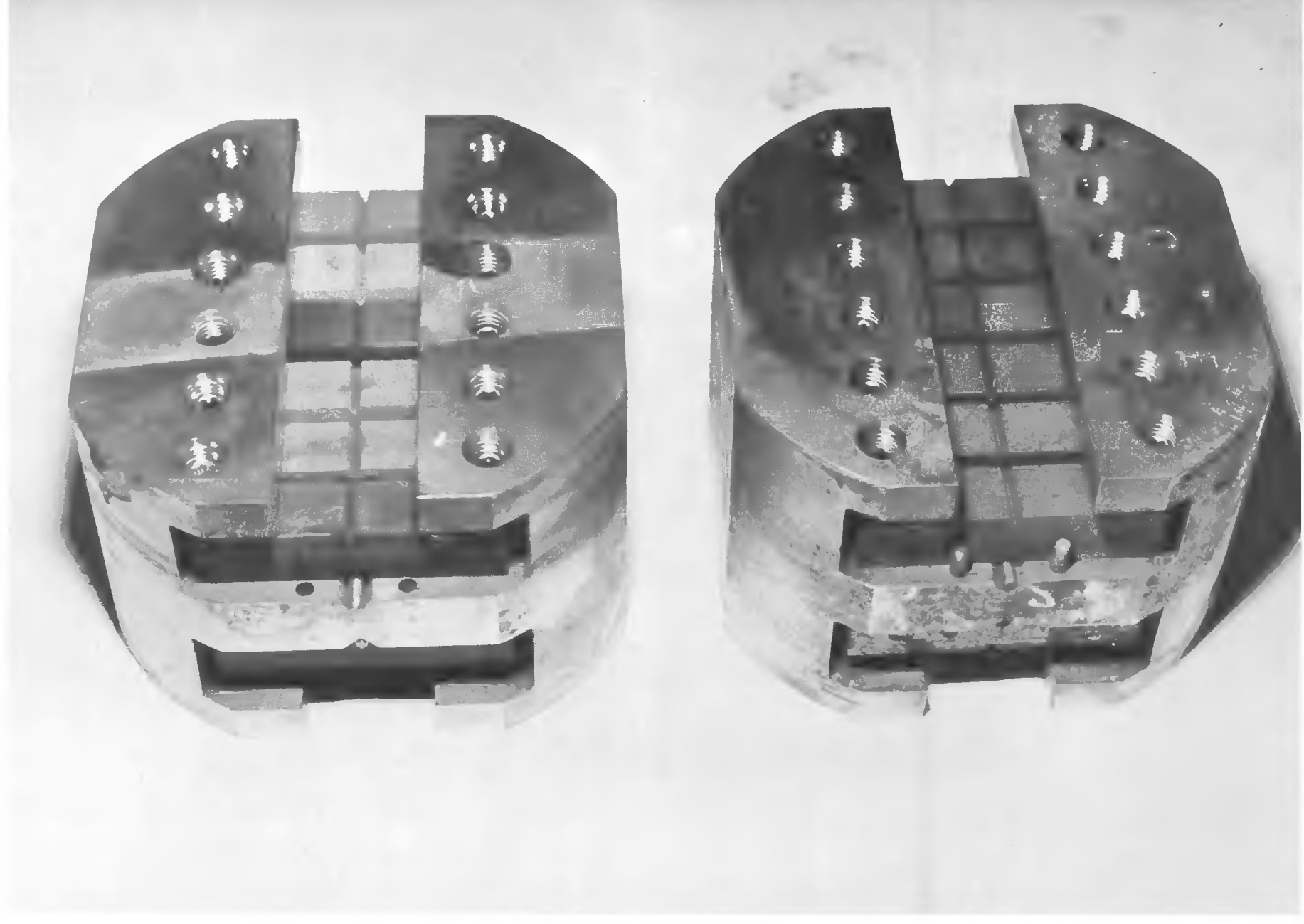


FIGURE 4-24. Top View of 3 Point Stressed, Pre-cracked Specimens and Holders After Unit 5 Cleaning.

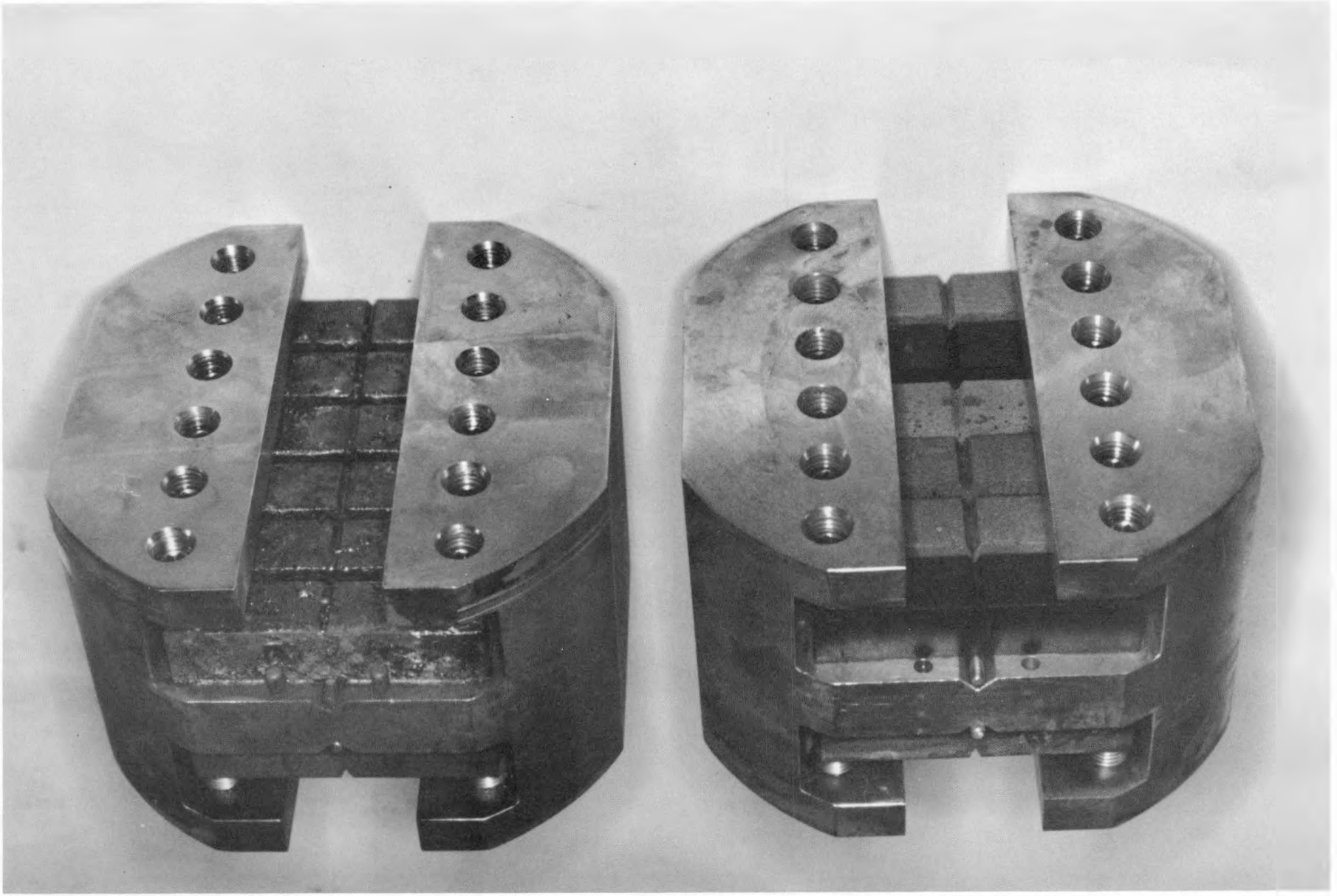


FIGURE 4-25. Top View of 3 Point Stressed, Pre-cracked Specimens and Holders Prior to Unit 5 Cleaning.

Table 4-21

Average Corrosion Rates Observed for Unit 5
Dilute Chemical Cleaning

ASME No.	Coupon Type	Corrosion Rate (mils/day) Vapor Phase	Corrosion Rate (mils/day) Liquid Phase
SA285C	Welded	0.01	0.29
	Welded U-Bend	--	0.29
	Nonwelded	--	0.28
SA533A	Welded	0.02	0.75
	Welded U-Bend	--	0.66
	Nonwelded	--	0.84
	Nonwelded U-Bend	--	0.95
SA508	Welded	0.01	0.35
	Nonwelded	--	0.37
SA106	Welded	--	0.39
	Nonwelded	--	0.62
SA333	Welded	--	0.17
SA234WPB	Welded	--	0.28
	Nonwelded	--	0.28
SA516	Welded	--	0.47
	Nonwelded	--	0.56
IN600	Welded	--	0.002
	Welded U-Bend	--	0.001
	Nonwelded	--	0.001

1. The hydrogen from cation exchanger was changed when a solvent pH increase indicated that the column was depleted.

2. The ammonium form cation exchanger was changed out when iron was detected in the effluent samples.

Analytical data indicated that the H^+ form cation exchanger was depleted with NH_4^+ rather than dissolved iron when the above criteria were used to define the change-out time. In order to improve efficiency of ion-exchange usage during the cleaning of Unit 5, the change-out criteria were changed to the following:

1. When a pH rise indicated that the H^+ form ion-exchanger was exhausted with NH_4^+, it was removed and reserved to replace an iron-depleted NH_4^+ form column. The column was then used until it was fully depleted with iron.

2. The depleted NH_4^+ form ion-exchange columns were changed out as they become depleted with iron and were recharged with fresh H^+ form ion-exchange material for subsequent use in the pH control cycle. Iron-depleted resins were reserved for later analysis.

With the modified criteria, all the ion-exchange material used was kept on-line until analytical data indicated exhaustion with respect to iron.

After the dilute chemical cleaning was completed, the reserved ion-exchange materials from each column were mixed, sampled and analyzed for iron content. The analyses were performed by eluting small samples of resin with hot 10% HCL and colorimetrically determining the amount of eluted iron. Earlier analysis of fresh resin samples depleted with $FeSO_4$ indicated that the recovery of iron using this technique was better than 90%. The measured capacity values, expressed as meq Fe^{+3}/ml, for each ion-exchange column are shown in Table 4-22. As the data

Table 4-22

Ion-Exchange Performance During
Dilute Chemical Cleaning

Unit No.	Column No.	Capacity (meq/mL)[a] H^+ form	Capacity (meq/mL)[a] NH_4^+ form
6	1	0.43	1.95
	2	0.29	1.39
	3	0.41	1.77
5	4	0.65	1.47
	5	0.57	1.28
	6	0.48	1.50
	7	0.27	2.15
	8	1.80[b]	--
	9	1.46[b]	--
	10	1.84[b]	--
	11	1.57[b]	--
	12	2.00[b]	--

[a] Based on exchange of iron as Fe III

[b] H^+ column converted on-line to NH_4^+ and continued in service to Fe breakthrough.

indicate, cation-exchange resins which were continued in service to exhaustion for iron, averaged 1.68 meq/cc, which is equal to 85% of the original capacity (2.0 meq/cc) of the exchange material.

It is assummed that after removal of the bulk sludge pile by water lancing, the steam generator will have only surface film and filled crevices in the following approximate amounts (Table 4-1):

212 lb	remaining on tubesheet
278 lb	on Inconel tube surfaces (0.2 mil film)
306 lb	on C/S surfaces (2.0 mil film)
98 lb	in packed crevices
894 lb	Total Deposits to be Removed

Assuming a total sludge loading of 894 lb Fe_3O_4 and only a negligible quantity of iron introduced by corrosion, the amount of strong acid cation exchange material required for solvent regeneration and pH control is estimated to be 300 ft^3 based on the following equation:

$$\frac{900 \text{ lbs} \times 453.6 \frac{g}{lb} \times 1000 \frac{mg}{g} \times \frac{3 \times 55.85 \text{ (3Fe)}}{231.6 \text{ } (Fe_3O_4)}}{2.0 \frac{meq}{cm^3} \times 0.85 \times \frac{55.85}{3} \frac{mg}{meq \text{ } Fe^{+3}} \times 28300 \frac{cm^3}{ft^3}} = 330 \text{ ft}^3$$

4.3 TASK 3 - PROCESS SCALE-UP FOR STEAM GENERATOR CLEANING

Laboratory and pilot-scale tests completed in the DOE/CRC Steam Generator Cleaning Program have demonstrated that the dilute chemical cleaning process is feasible for use in cleaning PWR steam generators which are not heavily fouled or fully dented. Where possible, the process parameters have been used to estimate scale-up requirements for a full-size SG cleaning application. The scale-up values are given in Table 4-23.

Based on the pilot-scale recirculation tests, it is estimated that 500 ft^3 of H^+ form cation resin, 1500 ft^3 of NH_4^+ form cation resin, and 800 ft^3 of mixed-bed resin would be required to clean a full-scale steam generator. These resin quantities include sufficient capacity for removal of iron introduced by corrosion of SG carbon steel surfaces and are based on the following assumptions:

Table 4-23

Process Comparison and Scale-Up
To Full Size Steam Generator

Description	Laboratory Scale	Pilot Scale	Full Scale
Generator Volume (Test Vessel)	4	8.9	22,140 gal
Auxiliary Volume	1.5	2.1	2,214 gal
Total System Volume	5.5	11	24,354 gal
Dilute Solvent Quantities:			
Citric Acid	5.4 g	11 g	182 lb
Gluconic Acid	10.8 g	22 g	374 lb
Ascorbic Acid	5.4 g	11 g	182 lb
Cinnamonitrile	16.2 g	44 g	628 lb
Temperature: ^{o}C	79-81	79-81	79-81
^{o}F	175-178	175-178	175-178
Flowrate	250ml/min	500 ml/min	1,000 gpm
Purification Period	21.6 min/sys vol	22 min/sys vol	23.6 min/sys vol
Gas Sparge Rate	200 cm^3/min	1,500 cm^3/min	16.4 ft^3/min (b)
Ion-Exchange (H^+):			
Column Volume	210 ml	1,135 ml	500 ft^3
Process Volume	330 l/bed	1,780 l/bed	11,800 gal/ft^3
Units Required (c)	1	1	1
Total Volume	2.0 ml	1,135 ml	500 ft^3
(NH_4^+):			
Column Volume	210 ml	1,135 ml	500 ft^3
Process Volume	330 l/bed	1,780 l/bed	11,800 gal/ft^3
Units Required	4	4	3
Total Volume	840 ml	4,540 ml	1,500 ft^3
Mixed Bed:			
Column Volume	420 ml	1,135 ml	400 ft^3
Units Required	2	2	2
Total Volume	840 ml	2,270 ml	800 ft^3

(a) N_2 gas to be recycled to minimize consumption.
(b) Based on an operating period of 100 hours.

1. The total quantity of sludge and surface deposits will result in a solvent loading of 6 g/L as magnetite (Reference 1).

2. The H^+ form cation columns are rebedded when they become exhausted by NH_4^+ and are no longer effective for pH control.

Based on this operating mode the estimated resin costs would be $369,500 as shown in Table 4-24.

Table 4-24

Initial Ion-Exchange Operating Mode

Form	Vol (ft^3)	Cost/ft^3	Total Cost
NH_4^+	1500	$168	$252,000
H^+	500	$ 75	$ 37,500
Mixed-Bed	800	$100	$ 80,000
	Estimated Resin Cost:		$369,500

However, several different operating modes can be used to reduce the ion-exchange requirements for solvent regeneration. The most practical approach is to use several smaller cation resin columns (100 ft^3 each) and appropriate valving to rotate the operating units to take advantage of the conversion of H^+ form resin to the NH_4^+ form during solvent regeneration. This operating mode is shown schematically in Figure 4-26. Assuming the same 100-hr resin costs as shown in Table 4-25, the projected cost is about 43% of the previous estimate. Since all resin containing radionuclides will require disposal by an approved encapsulation system, disposal costs will also be dependent upon resin volumes.

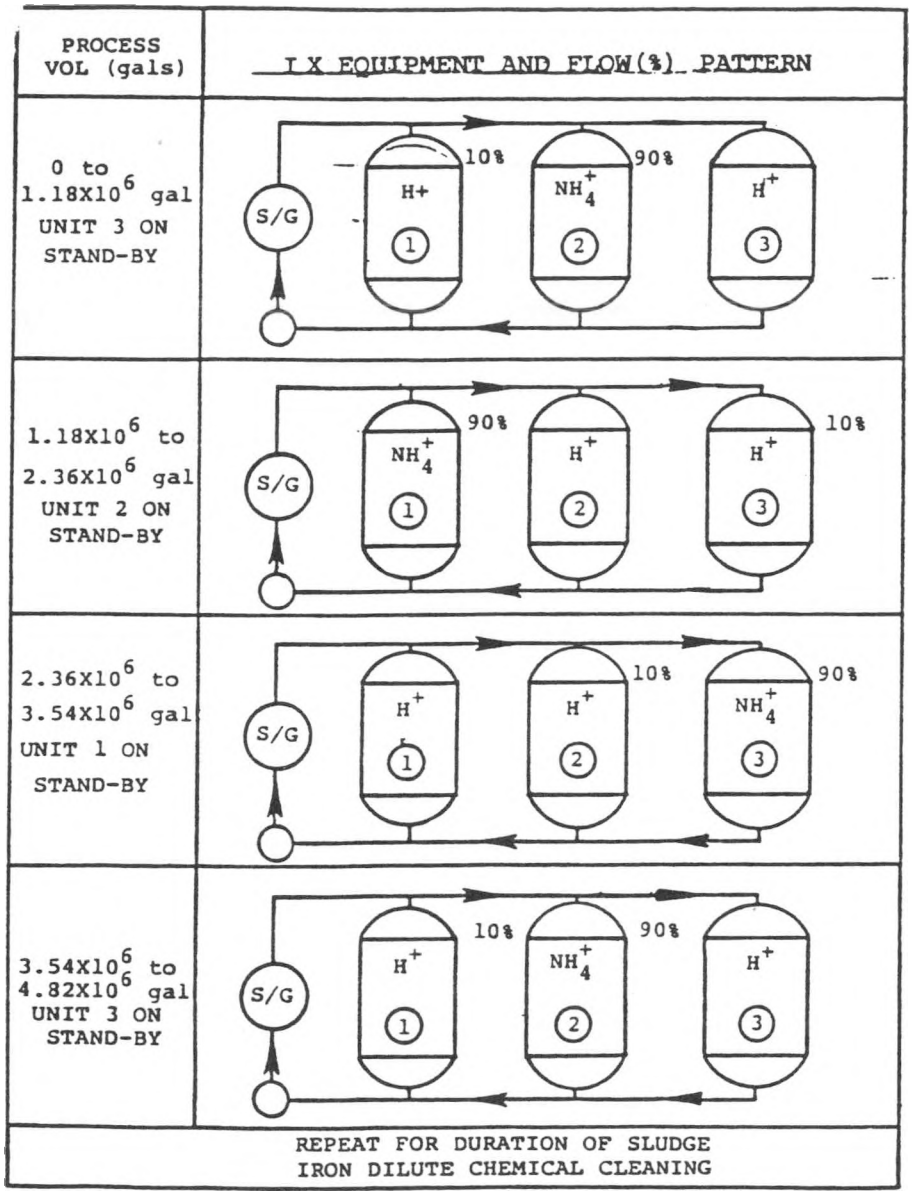


FIGURE 4-26. Modified Ion-Exchange Operation.

Table 4-25

Modified Ion-Exchange Operating Mode

Form	Vol (ft^3)	Cost/ft^3	Total Cost
NH_4^+	100	$168	$ 16,800
H^+	1500	$ 75	112,500
Mixed-Bed	800	$100	80,000
	Estimated Resin Cost:		$209,300
	Projected Savings:		$160,200

If the steam generator to be cleaned contains no significant radioactive contamination on the secondary side, additional cost reduction can be realized by regenerating the ion-exchange beds with sulfuric acid when they become exhausted with iron rather than discarding them. The estimated cost for an operation of this type is shown in Table 4-26.

Table 4-26

Operating Mode With Regeneration

	Form	Vol (ft^3)	Cost/ft^3	Total Cost
	NH_4^+	100	$168	$ 16,800
Resin	H^+	200	$ 75	$ 15,000
	Mixed-Bed	800	$100	$ 80,000
H_2SO_4	lbs/ft^3	lbs	Cost/lb	Total Cost
	10	10,000	$ 0.13	$ 1,300
		Estimated Total Cost:		$113,100
		Projected Savings:		$256,400

This saving is about 69% of the cost estimate for the initial ion-exchange operating mode of discarding the resin when exhausted and replacing it with fresh ion-exchange material.

There is clearly a strong economic incentive to apply the dilute chemical cleaning process before the secondary system becomes radioactive contaminated and before the total quantity of deposits exceeds the solvent loading assumed in this project for "moderately" fouled steam generators (6 g/L).

4.4 CONCLUSIONS

The objective of this project was to determine the feasibility of using a dilute chemical cleaning process to maintain the secondary side of PWR steam generators in a clean condition. The process is intended to be applied during short unit shutdowns and repeated as necessary to prevent denting and to maintain the steam generator in a clean condition.

A low-concentration, inhibited solvent was developed and operating parameters were defined to provide continuous regeneration of the solvent during the cleaning operation. The process was successfully demonstrated by cleaning two DOE/CRC model steam generators which had been fouled under prototypical steam generator operating conditions at the Commonwealth Edison Company State Line Facility.

The dilute process was shown to be effective for sludge dissolution and also compatible with ion-exchange resins for solvent regeneration and clean-up. The solvent formulations are:

Iron Oxide & Crevice Cleaning	Copper/Passivation
0.1 wt% citric acid	Demineralized water at pH 9.2 with
0.1 wt% ascorbic acid	ammonium hydroxide
0.1 wt% gluconic acid	pH 10 with ethylenediamine
pH 3.5 with ammonium hydroxide	3 wt% hydrogen peroxide
0.3 wt% Cinnamonitrile	

Application temperature is 80°C for the iron solvent and 40°C for the copper solvent. After completion of the copper step, excess hydrogen peroxide is destroyed by increasing temperature to 80°C.

Solvent pH is maintained in the desired range during cleaning by controlling flow through parallel H^+ and NH_4^+ cation resin beds. The cation resin removes complexed iron and copper by ion-exchange and regenerates the spent solvents. Chelate-based solvents were tested early in the program, but were not regenerable. However, they were effectively removed by mixed-bed ion-exchange resin.

Solvent clean-up after application of either step of the dilute chemical cleaning process is accomplished by mixed-bed ion-exchange. The solvents, dissolved iron, dissolved copper, and inhibitor are removed by the mixed-bed ion-exchange resins.

Cinnamonitrile, a sulfur-free inhibitor, reduced corrosion rates for carbon and low alloy steels to an average of 0.16 to 0.96 mils/day. The greatest uniform corrosion occurred on the SA533A and SA516 carbon steel. The least corroded alloys were the SA333 and SA234WPB piping alloys and SA285C, the steam generator support plate and wrapper alloy. Weld specimens in the bench type tests showed high HAZ corrosion, but the HAZ area of identical weld specimens was not selectively attacked in the model steam generator cleaning demonstrations. Further investigation of HAZ corrosion is needed. No crack propagation was observed for any of the stressed, precracked specimens.

The dilute process removed surface deposits very effectively. The equilibrium iron level in the solvents peaked, then returned to constant levels within 20 hr and 35 hr for Units No. 6 and 5, respectively. The peak in equilibrium iron concentrations was concluded to represent removal of the surface deposits that were most accessible to the solvent. Unit No. 5 was more heavily fouled than Unit No. 6, and thus the surface deposits took longer to dissolve.

The tube-to-support plate crevices of Unit No. 6, which were estimated as initially 60 to 75% blocked, were cleaned less effectively than the crevices in Unit No. 5, which were estimated initially 80 to 90% blocked. Crevice cleaning effectiveness of the dilute process was concluded to be

a function of the application time of the solvent. The iron solvent application time was 60 hr for Unit No. 6, as compared to 132 hr for Unit No. 5. The dilute process was consistently shown to be effective for cleaning partially blocked crevices. However, crevices which were either dented or fully impacted, leaving no access for solvent penetration, were not effectively cleaned by the dilute process.

5.0 CONCLUSIONS

Although additional work will be required to qualify or improve the effectiveness of both the On-Line Chelant Addition and Dilute Chemical Cleaning Processes, the feasibility of both processes has been demonstrated. Sections 5.1 and 5.2 summarize the significant conclusions of each project. Section 5.3 suggests additional work that will be required prior to application in an operating PWR steam generator.

5.1 ON-LINE CHELANT ADDITION

The feasibility of using an on-line chelant for treatment of PWR steam generator water has been demonstrated by this project. Additional study will be required of some aspects of this treatment process prior to a full scale demonstration.

Results obtained in this project support the following conclusions:

1) Metal complexes of EDTA and HEDTA are sufficiently stable to allow transport of typical metal ions (Fe, Ca, Mg, Cu) from the steam generator prior to deposition. Results of the thermostability testing indicate that HEDTA complexes are more stable than EDTA complexes.

2) On-Line addition of EDTA can prevent packing of crevices in a fresh water fouled MSG. One MSG operated successfully for 169 days with accelerated lake water fouling/EDTA water chemistry with no signs of crevice packing and no signs of corrosion. An identical MSG, unit 2, had packed crevices after 80 days of operation with lake water fouling alone. This suggests that EDTA will prevent crevice packing and related corrosion from occurring in lake water cooled PWR steam generators. EDTA failed to stop crevice packing with accelerated sea water fouling conditions.

3) Chelants have the ability to remove sludge deposits containing iron and copper from MSG's. EDTA cleaned existing sludge and prevented sludge formation from all MSG's, but crevices packed with corrosion deposits were not cleaned during the test period.

4) Chelants may play a role in the pitting of Inconel 600 tubing under severe sea water fouling conditions.

5) Corrosion rates were low and no localized corrosion problems were identified with the following exceptions:

   a. No conclusions can be drawn regarding the behavior of stressed SA533 because of problems with the specimens of this material.

   b. The relationship of EDTA to the pitting observed in the severely fouled sea water must be determined.

   Notched-precracked-stressed specimens of SA508 and SA285C exposed to 0.1% EDTA + AVT water chemistry showed no environmentally-induced-stress-corrosion. No pitting or general corrosion was observed when galvanic pairs or copper plated coupons were exposed to 0.1% EDTA + AVT water chemistry.

6) A more protective film was apparently formed when using EDTA + AVT water chemistry than was formed using AVT alone. All coupons tested were passivated in less than 80 days when exposed to 0.1% solutions of either EDTA or HEDTA in AVT water chemistry. AVT showed greater passivation rates than either EDTA or HEDTA. However, sludge formation was observed with AVT, whereas, the EDTA and HEDTA treated systems had no sludge.

7) Trace amounts of iron were shown to significantly increase the rate of passivation with EDTA or HEDTA treatment.

8) Chelant metal complexes can be removed from solution using anion demineralizer resin.

5.2 DILUTE CHEMICAL CLEANING

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

1. DETU and cinnamonitrile are inhibitors of choice for dilute solvent cleaning formulations containing combinations of chelants and citric acid.

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

3. 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.

4. 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. The dilute solvent formulation of choice is:

   0.1 wt% citric acid
   0.1 wt% gluconic acid
   0.1 wt% ascorbic acid
   0.3 wt% cinnamonitrile

   Adjusted to pH 3.4 to 3.8 with NH_4OH and applied at $80^{o}C$.

6. Regeneration of the spent complexing acid solvent can be achieved with strong acid cation exchange resin in either the H^+ form or the NH_4^+ form.

7. Corrosion rates of most materials of construction can be controlled to about 1 mil/day in a recirculating system by using 0.3 wt% cinnamonitrile. A more effective inhibitor should be identified before any demonstration of the process in an operating steam generator.

5.3 FUTURE WORK

Both chemical cleaning processes evaluated were shown to be feasible cleaning techniques, however, additional qualification work will be required prior to full size application. The following areas must be addressed.

1) Define operating parameters for chelant addition that will eliminate pitting of Inconel 600. This must address both operating and shutdown modes.

2) Qualify chelant addition with turbine materials.

3) Qualify chelant addition with stressed SA533.

4) Improve inhibitor performance with the Dilute Chemical Cleaning Process.

6.0 REFERENCES

1. Tvedt, T. J. and Dawson, J. Jr., American Power Conference, Chicago, Illinois, April, 1978.

2. Margulova, T. Kh., et.al., Teploenergetika, 18(5), 89-91, 1971.

3. Margulova, T. Kh., and V. D. Filintseva, Teploenergetika, 22(11), 72-74, 1975.

4. Monakhov, A. S., Teploenergetika, 23(3), 11-13, (1976).

5. Margulova, T. Kh. and L. M. Burauk, Teploenergetika, 16(3), 84-86, 1969.

6. D. Schneidmiller, Steam Generator Dilute Chemical Cleaning Program, Annual Report, Program Start through 1980, DOE Report #DOE/ET/34015-1, March 1982.

7. D. Schneidmiller, Steam Generator Dilute Chemical Cleaning Program, Annual Report for 1981, DOE Report #DOE/ET/34015-3 September, 1982.

8. Private Communication with A. E. Martell.

9. Ramunas, J. Motekaitis, X. B. Cox III, et. al, Can. J. Chem. 60 1207-1213, (1982).

10. Swan, F. E., PWR Steam Generator Chemical Cleaning Process Testing in Model Steam Generators, Topical Report, DOE/ET/34015-5, April, 1984.

11. King, P. J. and Dautovich, D. P., Nuclear Technology, 55, 196-206, October, 1981.

12. TVEDT, T. J., Wallace, G. L. and Griffin, F., Evaluation of On-Line Chelant Addition to PWR Steam Generators, Topical Report, DOE Report #DOE/ET/34015-7, September, 1983.

13. Schneidmiller, D., Simon, G. P. and Smoot, D. E., Dilute Chemical Cleaning of PWR Steam Generators Off-Line Cleaning Process Evaluation, Topical Report, DOE Report #DOE/ET/34015-6, July, 1983.

14. D. J. Stiteler, D. Schneidmiller, and C. A. Richardson, A Chemical Cleaning Process to Remove Deposits from Nuclear Steam Generators, NACE No. 32, paper presented at International Corrosion Forum, National Association of Corrosion Engineers (NACE), Houston, Texas, March 1982.

15. D. Schneidmiller, D. J. Stiteler, Steam Generator Chemical Cleaning Process Development, Final Report for EPRI Contract S150-1, December, 1982.

LISTING OF PUBLISHED REPORTS

DOE/ET/34015-1, Steam Generator Dilute Chemical Cleaning Program, Annual Report, Program Start through 1980, March, 1982.

DOE/ET/34015-2, Investigation of On-Line Chelant Addition to PWR Steam Generators, Annual Report, Program Start through 1980, October, 1982.

DOE/ET/34015-3, PWR Steam Generator Dilute Chemical Cleaning Program, Annual Report for 1981, December, 1982.

DOE/ET/34015-4, Investigation of On-Line Chelant Addition to PWR Steam Generators, Annual Report - 1981, November, 1982.

DOE/ET/34015-5, PWR Steam Generator Chemical Cleaning Process Testing in Model Steam Generators, Topical Report, April, 1984.

DOE/ET/34015-6, Dilute Chemical Cleaning of PWR Steam Generators Off-Line Cleaning Process Evaluation, Topical Report, July, 1983.

DOE/ET/34015-7, Evaluation of On-Line Chelant Addition to PWR Steam Generators, Topical Report, September, 1983.

DOE/ET/34015-8, Steam Generator Chemical Cleaning Project, On-Line Chelant Addition - Dilute Chemical Cleaning, Final Report, December, 1983.

APPENDIX A

TEST EQUIPMENT DESCRIPTIONS

A.1 THERMOSTABILITY TESTING EQUIPMENT (CHELANT ADDITION)

All experiments were conducted in a two-liter titanium autoclave. Titanium was selected because it had been shown to be an inert material by other researchers (ref. 8). In addition to the autoclave, the reactor also included a two-element heating mantel and a temperature controller. This equipment is shown in Figure A-1. A typical experiment consisted of the following steps:

1. Preparation of the test solution in glass breaker.
2. Transfer of solution to the autoclave.
3. Assembly of the reactor.
4. Purge of the test solution of oxygen with a nitrogen sparge.
5. Heat-up of the solution.
6. Sampling.
7. Analyze samples.

Appendix A.2 describes the experimental procedure in more detail. As soon as the reactor reached the desired temperature, sampling was initiated on a predetermined time schedule. The first sample was arbitrarily designated as t(0) and all other samples were reported relative to this time. To quickly halt the decomposition reaction at the proper time, all samples were cooled by passing the sample collection line through a heat exchanger.

The primary analytic procedure employed was paired-ion liquid chromotography. In addition to determining the concentration of EDTA in all samples, this technique was also used to determine major decomposition products. In addition, pH and hydrazine were determined using standard methods.

A.2 MATERIALS COMPATABILITY TESTING EQUIPMENT (CHELANT ADDITION)

The corrosion coupons were arranged on the coupon rack as shown in Figure A-2. One specimen of each alloy was placed on each row of the rack. The position of each specimen was carefully noted. After each examination,

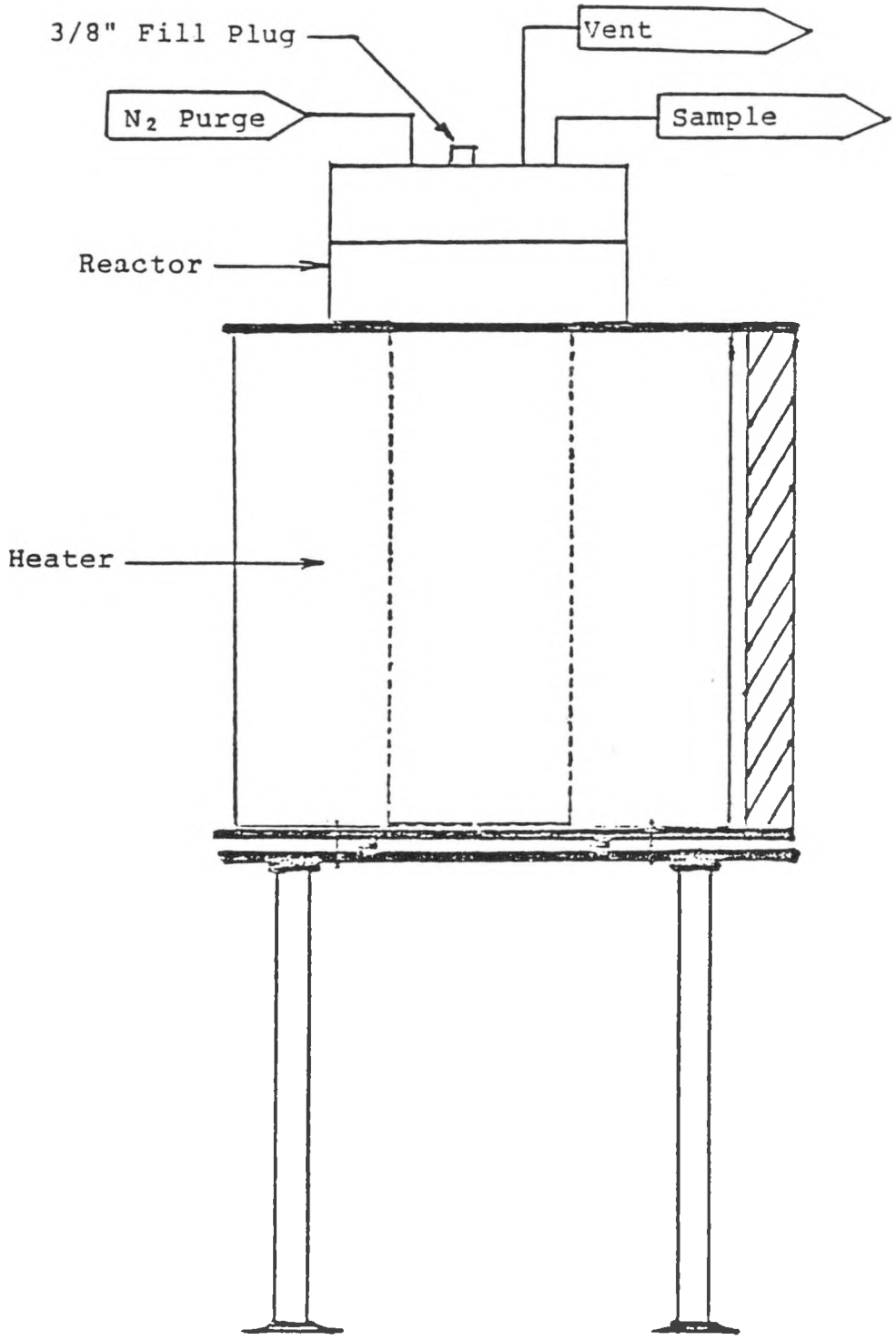


FIGURE A-1. Reactor for Kinetic Study.

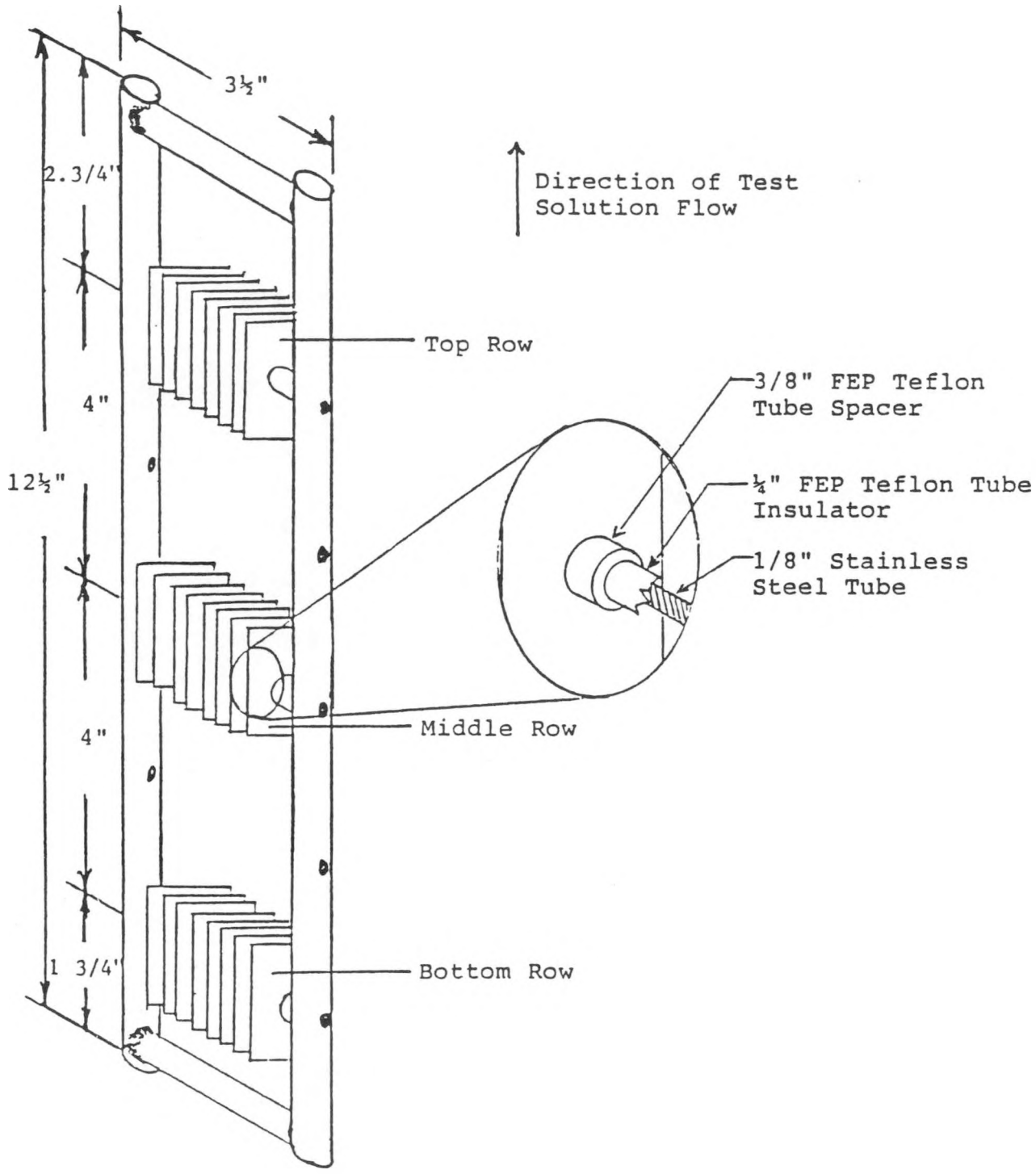


FIGURE A-2. Corrosion Coupon Rack.

the coupon was returned to its original position. This procedure allowed the position of the coupon within the reactor to be evaluated. It should be noted that the coupons were electrically isolated from both the coupon rack and other coupons by Teflon insulators.

Figure A-3 shows the test reactor. The inlet tube extends to the bottom of the reactor while the outlet tube is situated at the top of the reactor. Therefore, the flow of solution is from bottom to top. The flow rate was designed to simulate the residence time of a typical PWR steam generator. At that flow rate, plug flow was attained within the reactor. Since the chelant will thermally decompose at a finite rate, it was decided to construct a dynamic test loop so that fresh solvent could be continuously added to the reactor and the corrosivity of chelants could be evaluated.

Prior to the initial exposure, all coupons were scoured using hydrochloric acid and pumice. This procedure removed all oxides from the surface of the coupons, leaving the surface active to corrosion. Following this procedure, the coupons were carefully stored in a desiccator to prevent rusting. After exposure to the test solution, the coupons were washed with Ivory Soap so that only loosely adhearing deposits were removed. The passive film was not removed using the milder procedure.

Test Solution Preparation

Water was prepared by condensing 200 psig steam and passing the condensate through a mixed-ion-exchange resin. The Water was collected in a 50 gallon stainless steel mixing tank. Chemicals were added to the mixing tank by pulling a vacuum on the tank and sucking them in. Mixing was accomplished by recirculating the tank contents with the transfer pump. After adjusting the composition, the solution was then transferred to the feed tank. All tanks were continuously purged with nitrogen.

The feed solution had the following composition.

EDTA $0.1 \pm 0.01\%$

N_2H_4 100 ± 20 ppb

pH 9.5 ± 0.1

Dissolved O_2 < 20 ppb

Water conductivity < 0.5 mho (before chemical adjustment)

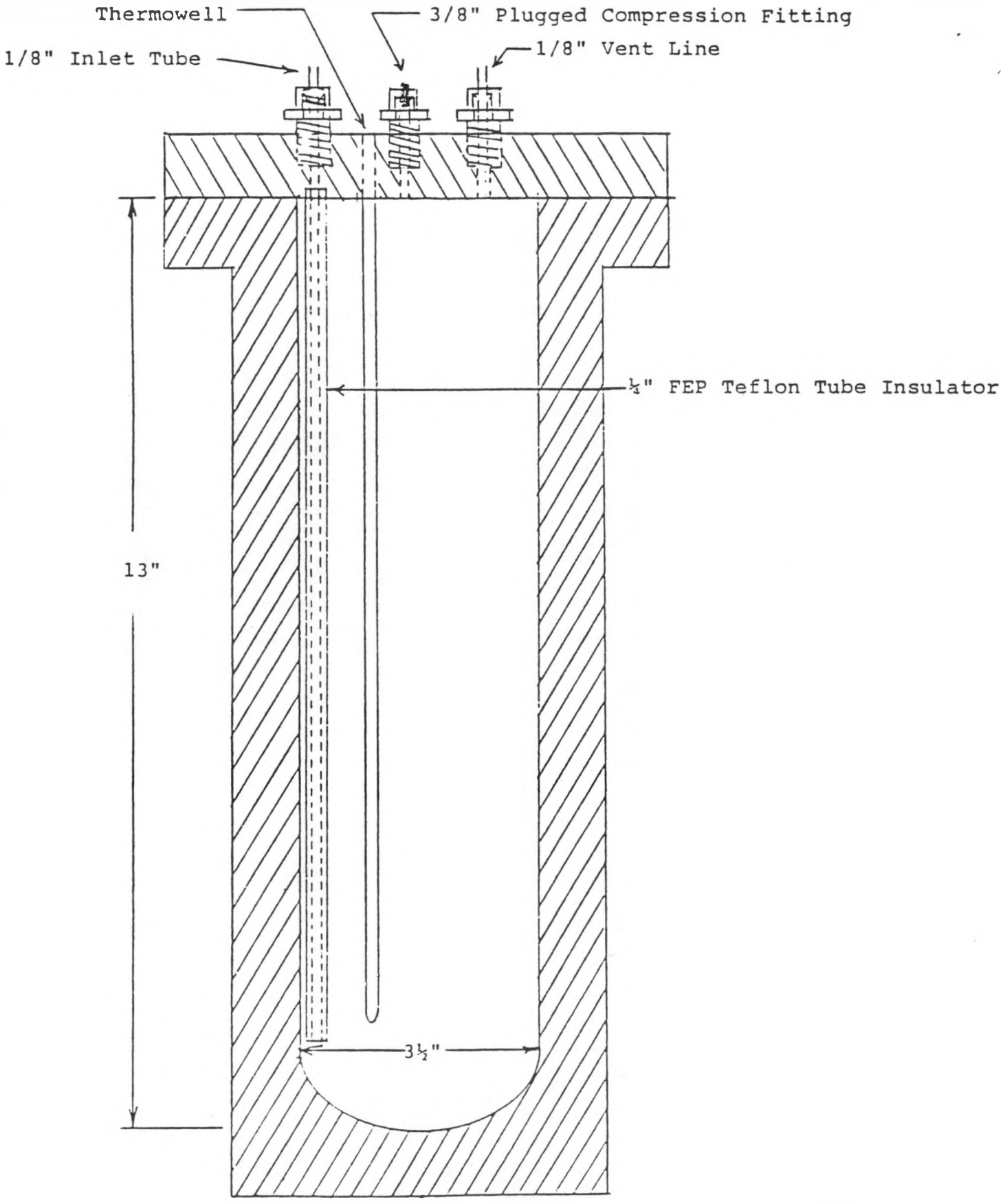


FIGURE A-3. Corrosion Test Reactor.

Specimen Preparation

Flat metal coupons were suspended on a sample rack as illustrated in Figure A-2. The sample rack constructed from 304 stainless steel rod. The rack ends were 3/8" rod, and the sides 1/2" rod. Holes, 9/64" in diameter, were drilled at 1-1/2", 5-1/2", and 9-1/2" from the bottom of the sample rack on both sides to allow one-eighth O.D. stainless tubing to support the test coupons. The stainless steel tubing was covered with 1/4" O.D. x 1/8" I.D. FEP TEFLON tubing in order to electrically isolate the coupons from the rack. Coupon separators were constructed from 3/8" O.D., FEP TEFLON tubing in order to electrically isolate the coupons from each other.

One coupon of each test metal was placed on each row. The coupons were 1" wide, 1-1/2" long and 0.060" thick (except for Inconel 600 which was 0.050" thick).

Prior to the initial exposure, all coupons were prepared in the following manner:

1. Dipped in 1:1 HCl.
2. Rinsed with tap water.
3. Scrubbed with pumice soap.
4. Rinsed with tap water
5. Rinsed with acetone.
6. Air dried.
7. Stored in a desiccator.

After the initial exposure, the following procedure was used:

1. Rinsed with acetone immediately to dry coupon.
2. Weighed coupon.
3. Photographed coupon.
4. Scrubbed with IVORY bar soap.
5. Rinsed with tap water.
6. Air dried.
7. Reweighed coupon.
8. Loaded coupons on rack and started reactor.

(Note: When not involved in above operations, all test coupons were stored in a dessiccator).

Operation of Corrosion Test Loop

After loading the coupons on the rack, it was then placed in a 2-liter reactor. The following start-up and operating procedure was used:

1. Pressurized with high purity nitrogen.
2. Leak tested.
3. Test solution was pumped into the bottom of the reactor, allowed to flow over the coupons, and out the top of the reactor for 16 to 20 hours. During this period, the pressure in the reactor was maintained at 1200-1250 psig.
4. The reactor was then heated to 292°C for the duration of the run.
5. Operating conditions which were maintained.

Pressure:	1200-1250 psig
Temperature:	290° - 294°C
Flow Rate:	8.5-8.9 ml/min
Calculated Residence Time:	4 hrs

Fresh solution was continuously pumped through the reactor during the exposure.

At the completion of each portion of a test, the following shutdown procedure was used:

1. The heaters were turned off.
2. The corrosion reactor was allowed to cool to below 175°C.
3. The pump was stopped.
4. The pressure was released.
5. The coupons were treated as described in the Specimen Preparation section.

Corrosion Data

Weight losses were determined after each exposure interval by subtracting the coupon weight (after scrubbing with IVORY soap) from its weight prior to the exposure. The corrosion rate was calculated from the original measured coupon dimensions and the weight loss during an interval. All weighings were on an analytical balance. Care was exercised so that each coupon was reloaded onto the test rack in the exact position it had occupied during the previous run.

A.3 ENVIRONMENTALLY ASSISTED CRACKING TEST EQUIPMENT

In order to verify that various cleaning processes do not induce stress corrosion cracking on the materials of steam generator construction, a materials test program was incorporated into the chemical cleaning test program in the model boilers. Precracked, three point bend specimens were used to study crack growth during exposure to the proposed chelant and acid solutions. The materials tested were ASME SA508 Class 2, SA533 Grade B, SA285 Grade C, and turbine disc material.

Encompassed in this appendix is a detailed review of the specimen holder design. In addition, a brief review is presented outlining the necessary parameters required to initiate and propagate intergranular stress corrosion cracks (IGSCC).

A.3.1 FACTORS IN MEASURING ENVIRONMENTALLY ASSISTED CRACKING

The appearance of environmentally assisted cracking (EAC) in a material requires two service conditions; a steady state tensile load (i.e., tensile stress) and an aggressive environment. The minimum values of stress and the rate at which a crack grows during exposure, depends on both the material and the environment. At very low stresses, even a susceptible material will not show crack extension. At higher values of stress, the crack growth rate may vary over many orders of magnitude, depending on the interaction potential of the environment. Thus, the first step in an evaluation of EAC is the selection of a specimen where

a relatively high level of stress can be produced in an area that will be exposed to the environment. This is most easily and reproducibly done with a standard fracture toughness specimen configuration (ASTM E399-78) containing a fatigue precrack. The precrack serves to localize the high stress area to a well characterized region that can readily be examined before and after exposure. The examination serves two purposes: first, it can define whether or not EAC has occurred and, second, it can be used to obtain an estimate of cracking rates should crack growth occur.

Several specimen configurations are suitable for EAC evaluation, notably the commonly used compact tension specimen (CS) which is easily self-stress loaded. Due to space limitations in the available steam generators, the three point bend specimen was selected for EAC evaluation. Since fixture dimensions and specimen size were limited to a relatively small volume, a specimen cross section of 0.5 by 0.5 inch (12.7 x 12.7 mm) and 2.25 inch (57.2 mm) long was selected as the standard for this evaluation.

The ASTM E399-78 measurement capacity of such a specimen can be calculated from the following:

$$K = (B/2.5)\sigma_{ys} \qquad (1)$$

where: K = the applied stress intensity factor
B = specimen thickness
σ_{ys} = material yield strength
2.5 = a constant used in ASTM E399-78 and developed empirically on high strength steels

For σ_{ys} of 50 ksi and B of 0.5 inch, the maximum value of K_I is 22 ksi. While this value of K would not be adequate to obtain plane-strain toughness on this material, it is adequate to determine the extent of EAC susceptibility. In addition, recent work indicates that the constant in equation (1) may be as low as 1.0 permitting a plane-strain measurement capacity, K_{IC} of 35 ksi.

This study, being concerned with EAC susceptibility alone, was carried out at K levels both above and below the ASTM E399-78 specification. The design of the fixtures and the specimen pre-cracking matrix was such that a range of stress intensities adequate to define a EAC susceptibility was produced.

A.3.2 SPECIMEN AND FIXTURE DESIGN

Conventional environmentally assisted cracking (EAC) studies generally make use of constant-load fixturing and measure time-to-failure for a range of loads in order to determine the degree of susceptibility to a given environment. This test technique most often makes use of precracked compact tension or three point bend precracked specimens. These tests enable determination of the threshold level of stress intensity (K_{IEAC} or K_{ISCC}) as well as an estimation of crack growth rates during exposure. The values of these characteristic EAC parameters determined from constant displacement ("self-stress") specimens compare closely with those determined using constant load and constant-K tests as a result of the normally rate limited behavior of most metals. The limiting rate over a broad range of applied K_I is denoted by the plateau rate, a_p. The EAC "threshold-plateau" behavior allows the quantitative use of specimens that show increasing or decreasing values of K for either constant load or constant displacement.

Constant displacement loading has been used extensively for compact specimen (CS) geometries exposed to environments essentially at room temperature and atmospheric pressure. Consequently, the specimens have been K calibrated both numerically and experimentally for this loading mode. However, the space requirement for elevated temperature and pressure made the less well-characterized, displacement loaded, three point bend specimen more attractive for this program.

Thus, one of the first requirements in the program was to characterize this specimen for constant displacement loading. A determination of the relationship between displacement, crack length (a) and applied K was made prior to the building of any self-stressed fixtures. The value of

stress intensity calculated at given crack lengths was then verified using experimental methods. The technique used involved preparation of fifteen specimens, fatigue precracked so as to cover the range of crack lengths to be evaluated. These specimens were then strain gauged and load calibrated in a three point bend fixture using a standard tensile machine (e.g., Tinius Olsen). Each numbered fixture was then evaluated over the range of K to be applied and the calibration values obtained used for determination of the actual loads. In the event a fixture was substantially out of range, the displacement limit (i.e. the fulcrum) was modified before use. Since the calibrations were to be done at room temperature, thermal expansion effects were found to be of second order importance.

$S = X\ L\Delta T$

X = coefficient of thermal expansion
L = length
ΔT = increase in temperature

The model steam generators had a working area 4.75 inches diameter by 7 inches tall. Figure A-4 shows the 4.5 inch diameter device capable of holding 12 specimens, 6 per side. Loading was accomplished with (rounded) bolts. In this case, the total displacement was fixed by the pin diameter selected for the fulcrum. Specimen location, separation and gaging during the exposure were provided by 28, 6-32 NC stainless steel cap screws.

A.3.3 SPECIMEN PREPARATION

Machined and notched, numbered specimens were fatigue precracked to depths determined from the matrix of values selected to give the desired applied stress intensity levels. An additional lot of specimens (e.g., 15) were fatigue precracked to selected depths and strain gauged for calibration purposes. All specimens had scribe marks placed at the end of the fatigue precrack to permit evaluation of EAC extension.

Four tests fixtures were manufactured and each of these were calibrated using gauged specimens prior to use.

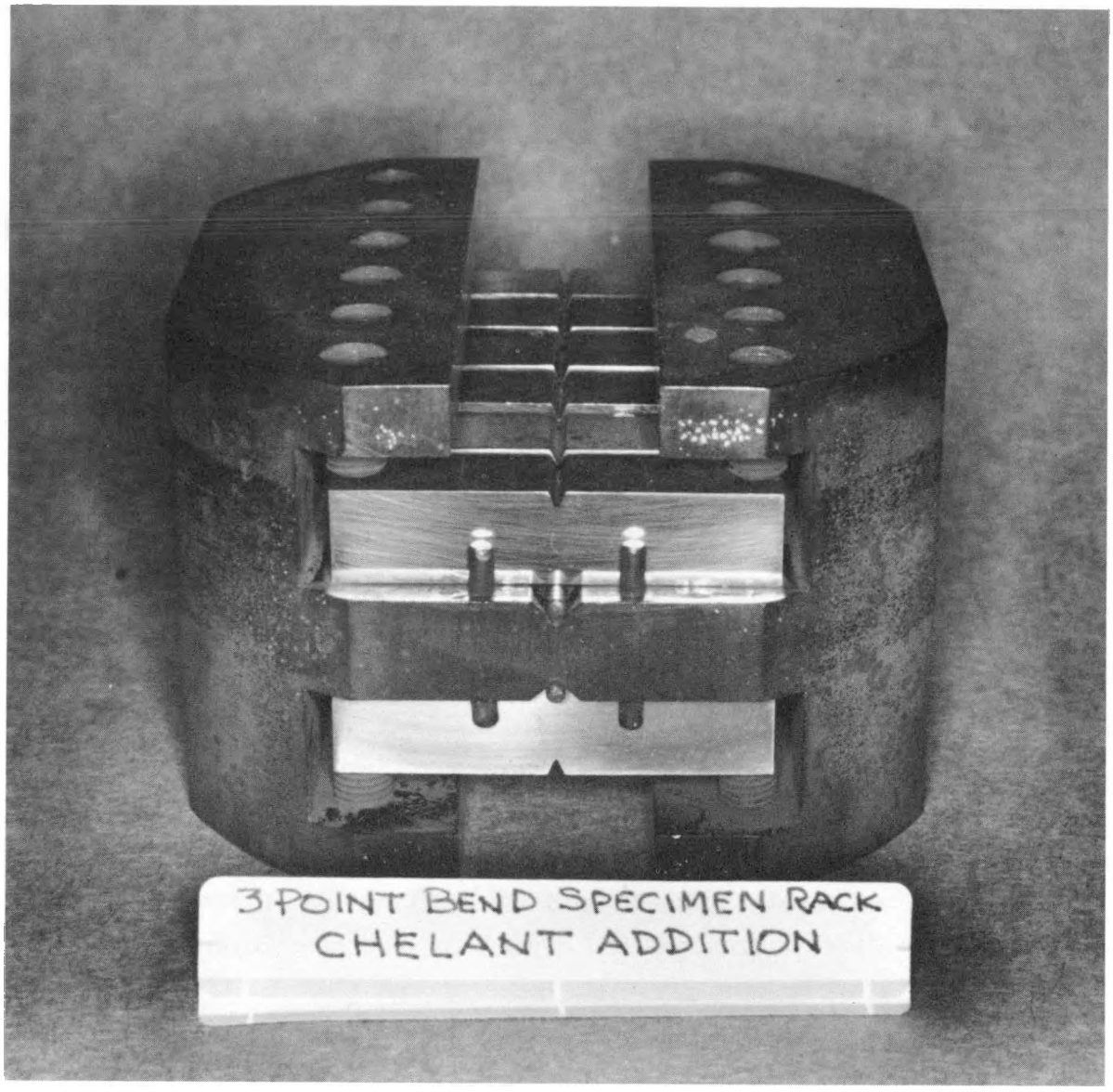


FIGURE A-4. Specimen Test Fixture.

Due to the fact that the fixture design uses a center fulcrum, the loading was done incrementally on both sides to avoid fixture damage and non-uniform displacements. Visual inspection was all that was required to insure that the given displacement had been applied uniformly, although, as stated above, the fixtures were calibrated prior to loading with precharacterized specimens.

After load application, the fixtures were placed into the environment and exposed for the required time period.

A.3.4 METALLURGICAL EVALUATION OF TEST SPECIMEN

Upon completion of the cleaning solution tests, the "self-stressed" fixtures were removed from the model boiler and disassembled. Table A.3-1 lists the specimen test parameters such as materials, stress intensity (K) factor, and hardness (i.e. heat treatment).

After the three point bend specimens were removed from the test fixtures, both sides of the specimen (normal to the notch) were polished. The polished specimens were metallographically examined to determine if the fatigue precrack had grown due to EAC.

Once metallography had been completed, each three point bend specimen as chilled in liquid nitrogen and broken open. The fractured specimens were then allowed to warm up in a bath of alcohol to avoid oxidation of the fracture face. Evaluation of the fracture faces was performed with the aid of an optical microscope and a scanning electron microscope (SEM).

Table A.3-1

Test Specimen Parameters

Material Specification	Stress Intensity (K) Range, ksi inch	Average Rockwell Hardness Number
SA 508 Class 2	17 - 36	86 R_b
SA 533 Grade B	14 - 40	96 R_b
SA 285 Grade C	18 - 38	78 R_b
Turbine Disc (Ni,Cr,Mo,V)	27 - 31	29 R_b

A.4 MODEL STEAM GENERATOR UNITS

Six model steam generators were designed and built by NUS Corporation to test the cleaning processes. The basic design and operation is described in this appendix. Further details as to the design, operating characteristics and unit qualification can be found in Reference 10.

The model was designed as a four tube model with the same secondary side materials as a typical steam generator. The tube bundle was designed with two support plates, each drilled for different crevice dimensions between the Inconel tubes and the support plate. The upper support plate creates a 7 mil radial crevice and the lower support plate makes a 14 mil crevice. Heat is supplied to the tube to obtain a thermal flux from a higher pressure steam supply through smaller diameter steam tubes. The steam flows into the capped off Inconel tubes, down the inside wall giving up heat and condensing into the bottom pot (see figure A-5).

A diagram of the system are shown in Figure A-6. The steam produced in the secondary side travels up the autoclave, is transported to the air cooled condenser and is condensed. This condensate is collected in a condensate receiver which is physically positioned higher than the autoclave. Gravity forces the condensate back into the autoclave along with any makeup water and the cycle is repeated.

Makeup water is added to the system through a preheater to avoid thermal shock. The makeup water replaces volume lost in sampling and blowdown. A continuous sample of the autoclave condensate is sent to a process hydrogen analyzer used to monitor corrosion. Chemicals are mixed with deaerated water in the storage tanks in order to control the autoclave chemistry. The water level in the autoclave is maintained between 4 inches and 15 inches above the upper support plate and is controlled by varying the blowdown flow to compensate for changes in pump rate or hydrogen analyzer flow.

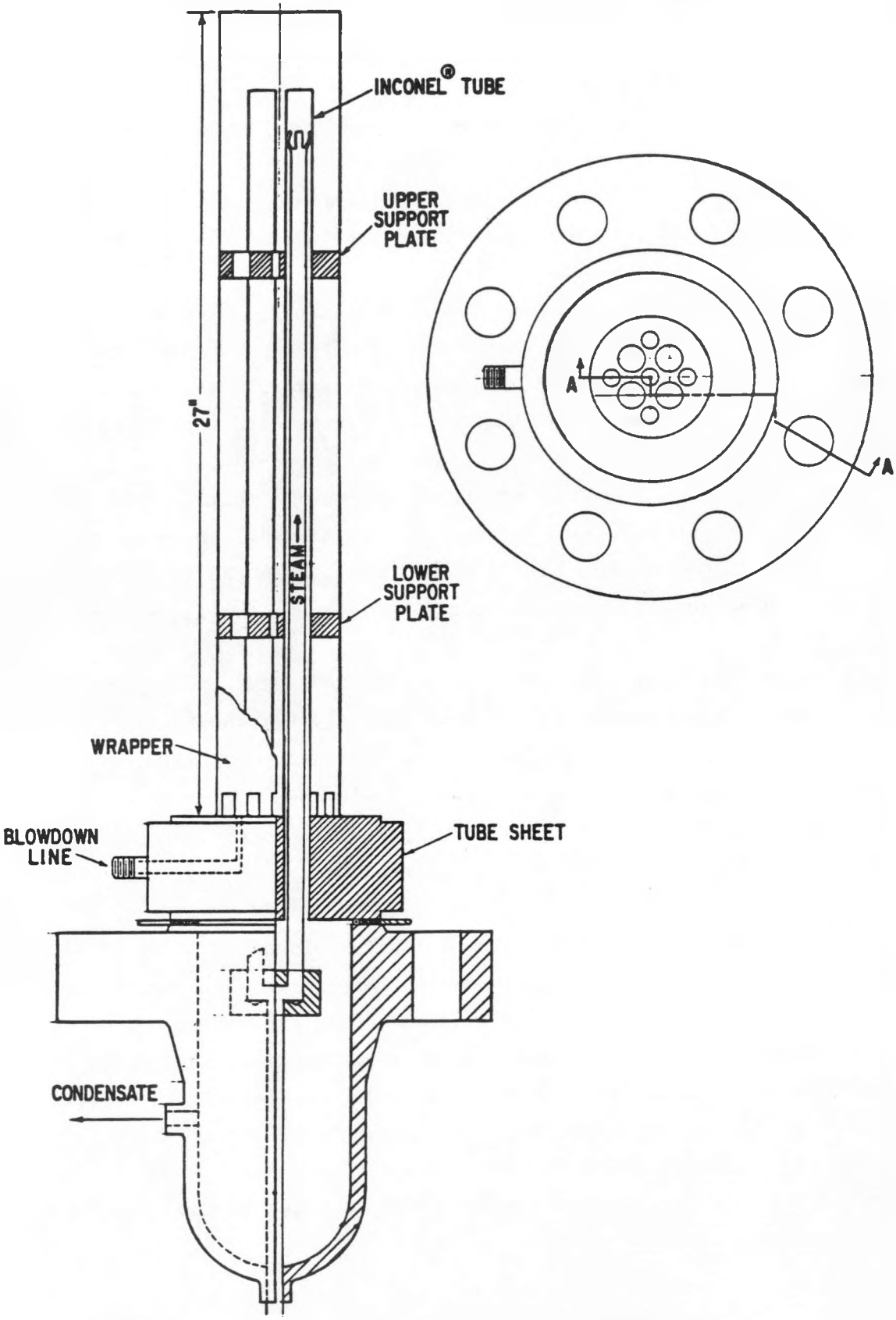


FIGURE A-5. Autoclave Tube Bundle

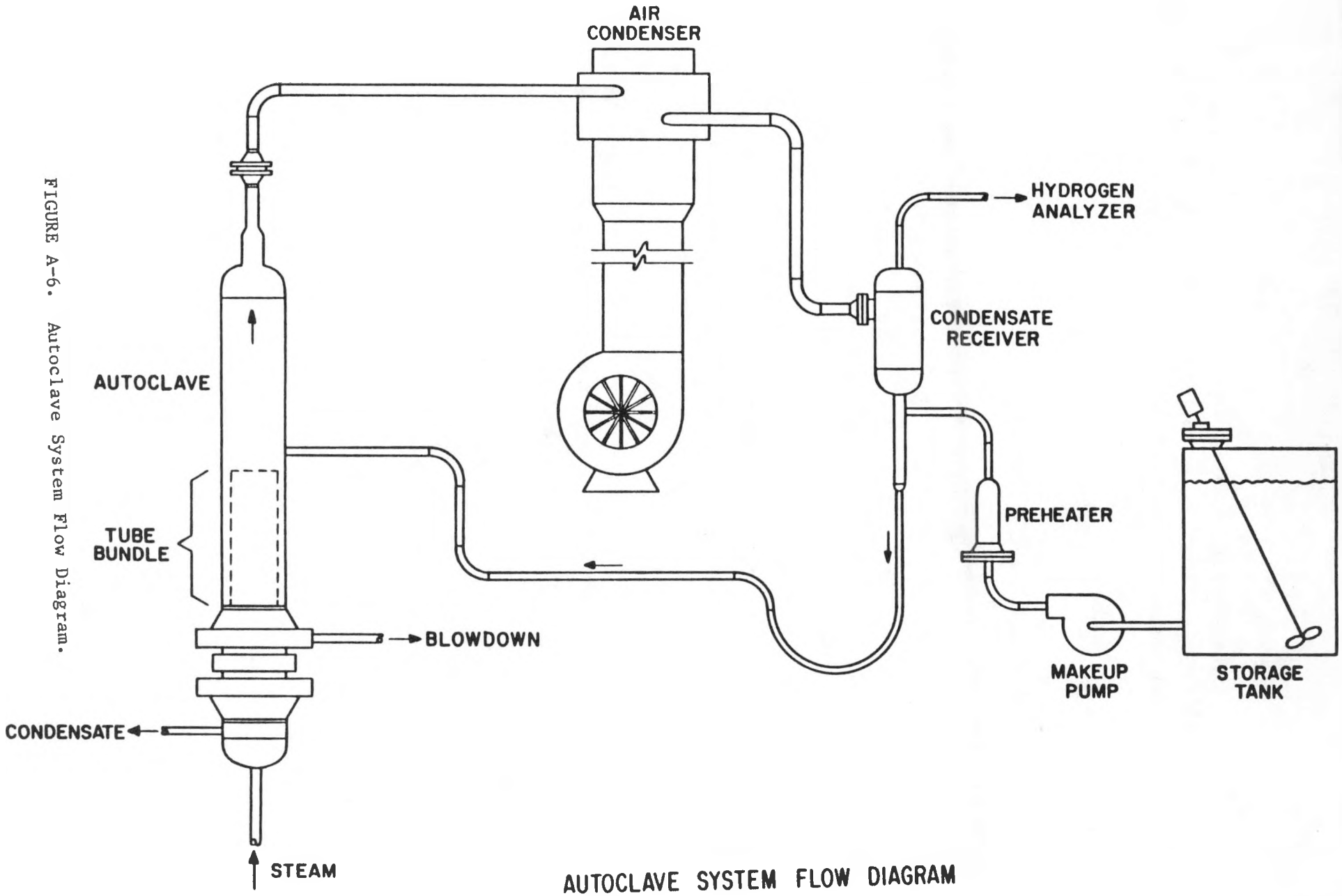


FIGURE A-6. Autoclave System Flow Diagram.

The temperature of the secondary side is dependent on the saturated steam pressure. Pressure is controlled by varying condensation rate in the air cooled condenser.

A.5 PILOT-SCALE CLEANING UNIT (DILUTE PROCESS)

A.5.1 PILOT-SCALE SYSTEM

A transportable recirculation system was designed, fabricated, and tested at UNC, then shipped to the CECo State Line Facility for the demonstration cleaning tests on the MSG's. The design was patterned after the recirculating bench-top system used to develop the dilute solvent cleaning process, and was sized to handle the additional volume of the model steam generators.

Figure A-7, a schematic of the recirculation system, shows the relationship to the model generator to be cleaned and the specific valving and connections between the major components. The cleaning system components were typical of the types that would be used in a full-scale system. For example, the pump for solvent circulation was a stainless steel, centrifugal pump and the ion-exchange columns were welded steel columns with steel resin retention screens.

Five components were not available commercially and were specially fabricated: liquid-gas separator, instrument manifold, in-line heater, ion-exchange columns, and solvent makeup tank. Design drawings for these components are shown in Reference 13. The rotameters, filters, solvent recirculation pump, and recirculating gas compressor were obtained commercially.

Process Flow

During operation of the system, solvent exits the model generator at a penetration located above the level of the SG tubes, and passes through a heat traced line to the gas-liquid separator, which provides feed to the recirculation pump. Solvent is pumped through the filter and can then be diverted either through a mixed-bed ion-exchange column or through the cation exchange columns. The cation columns are operated in parallel,

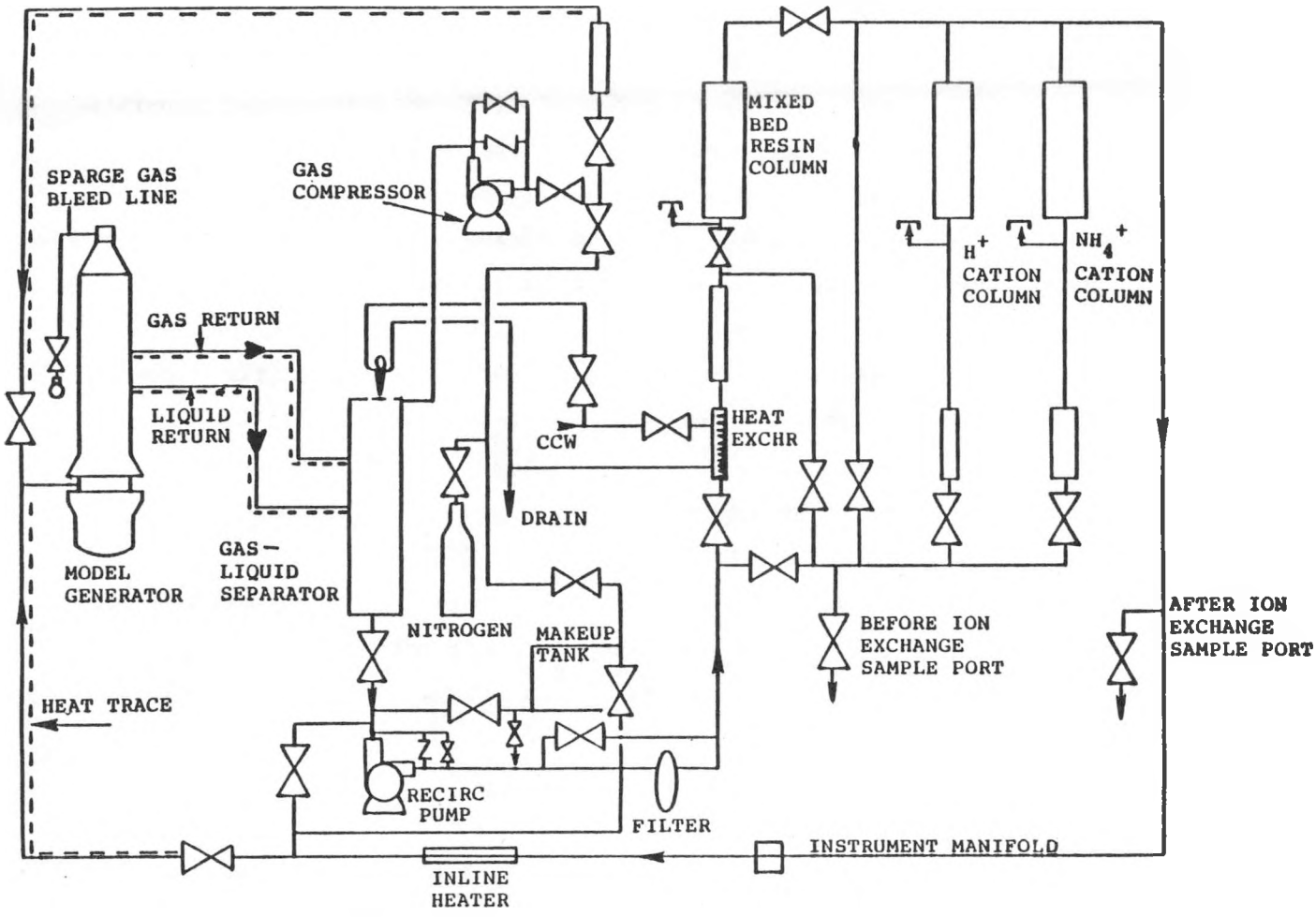


FIGURE A-7. Dilute Chemical Cleaning System.

with flow being divided as necessary to control solvent pH. The cation column effluents are combined and flow through the instrument manifold. Solvent then flows through the in-line heater and back to the model generator, via a heat traced line to the tubesheet blowdown port. At the model generator blowdown port, nitrogen sparge gas is introduced into the solvent through a mixing tee before it enters the model generator.

The nitrogen sparge gas provides solvent agitation and keeps the solvent free of dissolved oxygen. A heat traced line exits the model generator above the nominal liquid level to return sparge gas to the gas-liquid separator. Fresh nitrogen is continuously added to the recirculating sparge gas at the compressor outlet at a slow rate matched to the bleed rate of sparge gas vented from the top of the model generator.

Variations of general process flow were used for the specific cleaning steps, as shown in Figures A-8, A-9, and A-10. The major steps requiring variation of process flow are: the cleanup step, the sludge iron step, and the copper (passivation) step.

The entire system is mounted on a 3 ft by 6 ft caster-supported frame to permit shipment as a single unit and to permit mobility for connecting minimum lengths of the heat traced piping between the model generators and the cleaning system.

Operational Design Verification

The pilot-scale unit was operationally tested at UNC to determine that it had the design capability to establish the flow patterns required for each of the process steps. Tests were conducted to verify the capability to meet initial heatup requirements and to maintain sparge gas recirculation.

Initial heatup capability was determined by using a UNC steam generator model that had a structure and metal mass similar to the DOE model generators.

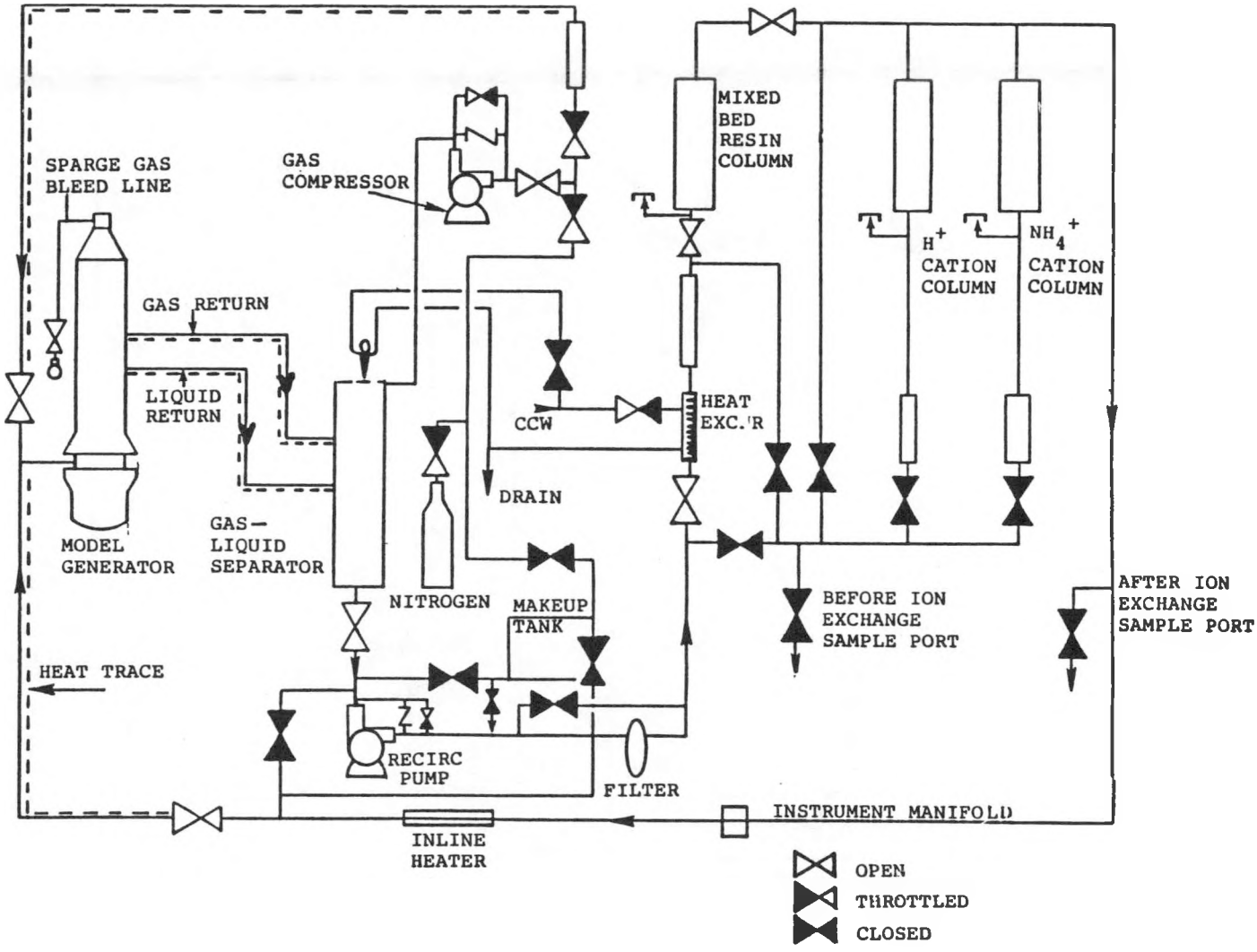


FIGURE A-8. Initial and Final Cleanup.

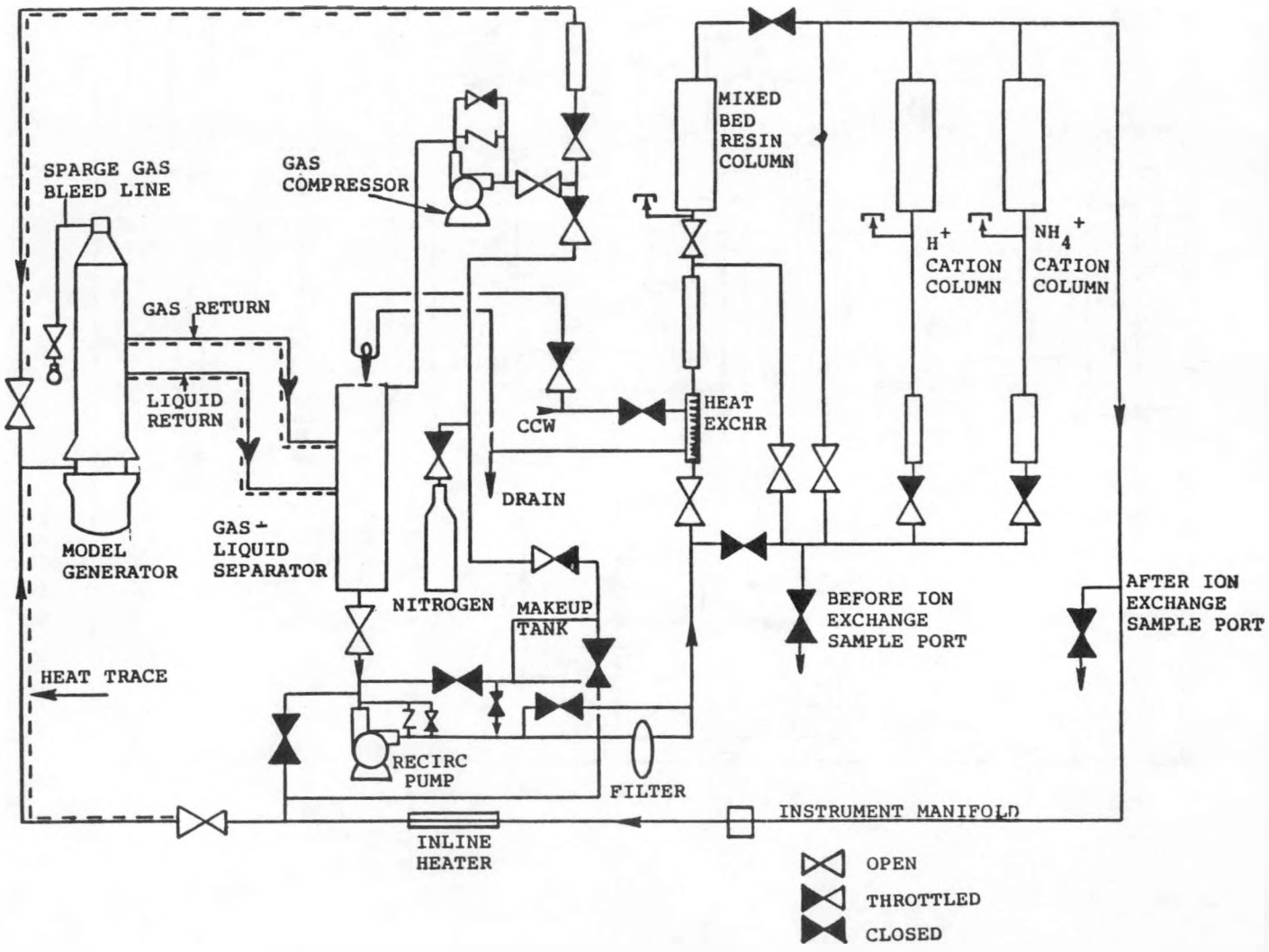


FIGURE A-9. Sludge Iron Step.

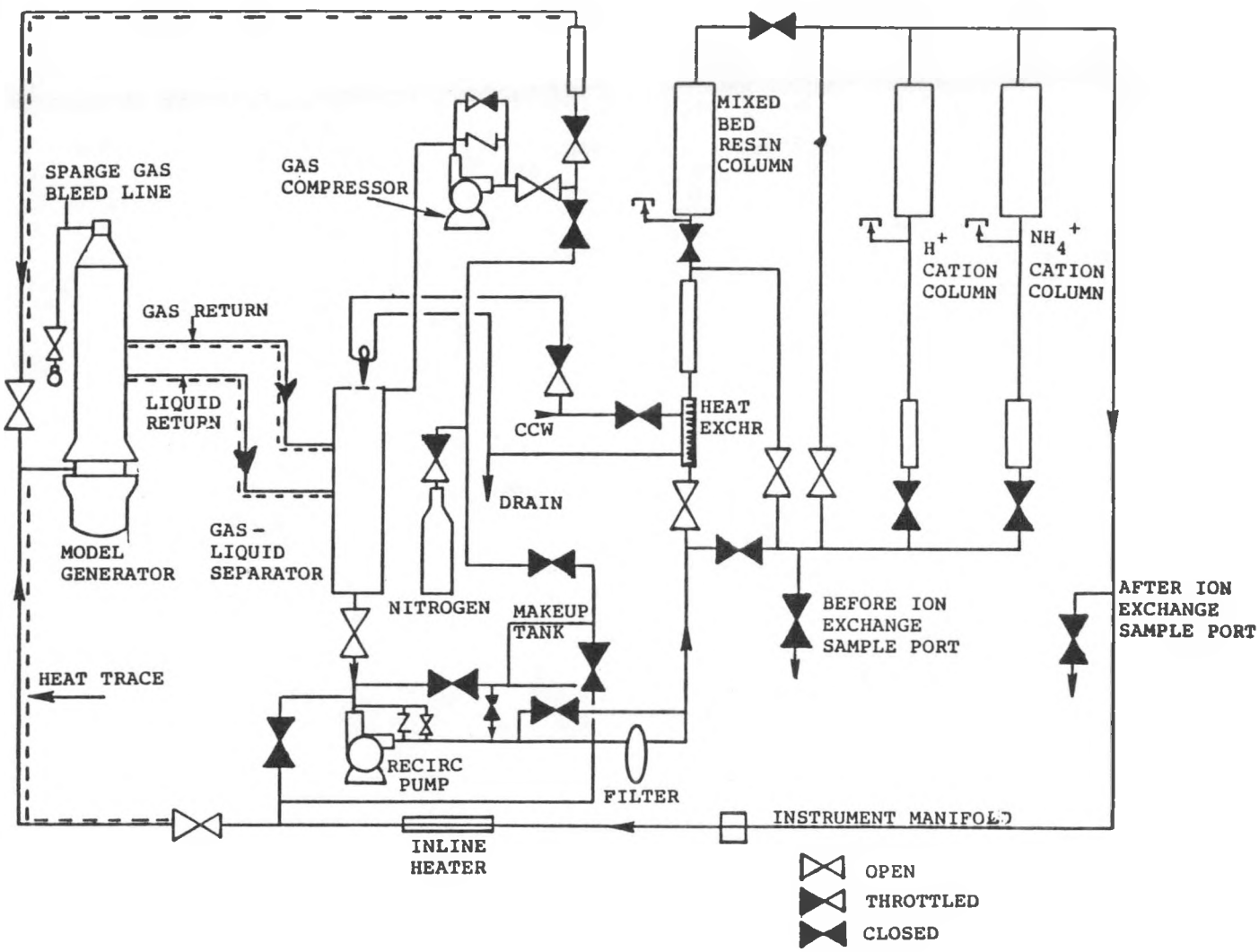


FIGURE A-10. Copper Step (Passivation).

The model shell and the heavy tubesheet flange were the heat sinks requiring the greatest initial heat input by recirculating solvent. Initial heatup of the secondary side by solvent heating required two hours. The capability of the system to establish and maintain operating temperature by solvent heating was demonstrated.

Operation of the compressor for sparge gas recirculation was sensitive to liquid carryover. Liquid flooding was found to damage the compressor. A liquid trap and filter were installed for the cleaning demonstration to prevent flooding. A different compressor design is needed for full-size scaleup.