UNITED NUCLEAR INDUSTRIES, INC.

PROGRESS REPORT
STEAM GENERATOR CLEANING SOLVENT
SCANNING STUDIES FOR
INDIAN POINT NOS. 1 AND 2

CONSOLIDATED EDISON COMPANY OF NEW YORK

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CONSOLIDATED EDISON COMPANY OF NEW YORK

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STEAM GENERATOR CHEMICAL CLEANING
INDIAN POINT GENERATING STATION UNIT NO. 2

UNI INTERIM REPORT NO. 4

I. INTRODUCTION

United Nuclear Industries (UNI) entered into a subcontract with Consolidated Edison Company of New York (Con Edison) on August 8, 1977, for the purpose of developing methods to chemically clean the secondary side tube to tube support crevices of the steam generators of the Indian Point Nos. 1 and 2 PWR plants.

This report is the fourth compiled for activities performed for Phase I of this effort. The previous report (UNI Interim Report No. 3) presented the first results of the Task 1 laboratory solvent evaluations. The laboratory solvent evaluations are divided into five subtasks as summarized in Table I.

This fourth interim report presents the results of laboratory testing conducted under Subtask IIIA of the UNI Solvent Selection Program (see Table I).

TABLE I

SOLVENT SELECTION PROGRAM

SUBTASK I - INHIBITOR STUDIES

- Beaker tests of candidate inhibitors with selected solvent types
  1) Corrator readings vs. temperature
  2) Corrator readings vs. inhibitor concentrations

SUBTASK II - SOLVENT SCOPING STUDIES

- Initial study of 15 candidate solvents
  1) Magnetite removal and limited corrosion studies
  2) 4-liter reaction flasks @ 85 C without N_2
- Preliminary waste treatment tests

SUBTASK IIIA - SOLVENT SELECTION

- Detailed evaluation of best 10 solvents from Phase II Testing
  1) Removal of magnetite from artificial crevices
  2) Complete corrosion studies
  3) 4-liter reaction flasks @ 85 C with N_2 purging

SUBTASK IIIB - SOLVENT SELECTION

- High temperature testing of best five solvents from Phase IIIA
  1) Magnetite removal from artificial crevices
  2) Additional corrosion studies
  3) Pressure autoclaves @ 121 C with N_2 blanket

SUBTASK IV - SOLVENT OPTIMIZATION

- Additional testing of the best one or two solvents from Phase III
  1) Inhibitors/surfactants
  2) Con Edison autoclave crevice samples
  3) Waste treatment evaluation

SUBTASK V - PILOT SCALE TEST

- Fully evaluate the solvent simulating the designed IP-2 application
  1) Corrosion in liquid and vapor phase
  2) Crevice cleaning

II. SUMMARY AND CONCLUSIONS

Uniform, stress and crevice corrosion tests were performed on coupons of carbon, low alloy, and stainless steel and Inconel 600. Corrosion and pitting measurements were made with a Magna Model 1172 Corrator.

In addition, coupons of reactor-exposed AISI 1010 carbon steel with a radioactive magnetite film were tested with the ten best solvents from initial scanning tests. The solvents were placed in four-liter reaction flasks, heated to 85 C and sparged with nitrogen.

A significant decrease was found in solution corrosiveness after nitrogen sparging for all solvents not containing hydrazine. Test results indicate that nitrogen sparging of non-hydrazine containing solvents should be conducted prior to the introduction of the solvent into the steam generators. This procedure will control corrosion to the lowest possible level.

Based upon the corrosion results and ability of the solvents to remove magnetite films, Citrosolv (ammoniated citric acid) is the leading contender for application in the Indian Point steam generators. Citrosolv and several chelant-base solvents have been selected for the final evaluation program.

III. DISCUSSION OF LABORATORY PROCEDURES

CORROSION COUPONS

Coupons of ASTM A-105, ASTM A-245, ASTM A-285, ASTM A-415, ASTM A-508, ASTM A-516, ASTM A-533 carbon and low alloy steels, Type 304 stainless steel, both sensitized and unsensitized, and Inconel 600 were employed in the corrosion tests. Nominal compositions for these alloys are given in Table II.

The A-105 coupons were machined from flange stock; the A-285 A-516, Type 304 SS and Inconel 600 were machined from sheet stock; the A-508 from round lifting lugs cut from forgings; and the A-533 from plate stock. The latter two alloys were received from the Westinghouse Tampa, Florida steam generator fabrication plant, and the other alloys were from commercial suppliers.

Three types of corrosion measurement configurations were employed: uniform corrosion, stress corrosion, and crevice corrosion. The samples for the uniform corrosion measurements were machined into 1.5x1x0.06, 1.5x0.5x0.06, or 1x0.5x0.06 inch samples with a $\frac{1}{4}$ inch hole drilled through the middle for mounting in the solvent. The ASTM A-415 alloy was welded with Type 308 SS welding rod to Type 304 SS with an alloy surface ratio of about 1:3, respectively. The samples were mounted on a glass rod with tygon spacers to prevent any galvanic coupling.

The samples for the U-bend stress coupons and the crevice corrosion coupons were machined into 4.75x0.5x0.06 inch coupons. The U-bend coupons had a .25 inch hole drilled in each end for applying stress. The coupons were partially bent from a flat configuration to the U-bend configuration, a bolt inserted through the holes, and then the bending was completed by tightening the nuts on the bolts. This manner of stressing placed the outer fiber of the U-bend beyond the yield point and the stress was not allowed to be relaxed after permanent deformation had been obtained. The U-bend coupons were suspended in the solvents on a polymer string to prevent contact with the other coupons present.

TABLE II

CORROSION ALLOY NOMINAL COMPOSITION

ALLOY	COMPOSITION									
	C	Mn	P	S	Si	Ni	Cr	Mo	Other	Heat No.
A-105 Gr II	.30	.70	.010	.037	.11				Tube Turns	60-J
	.29	.73	.018	.022	.17				Tube Turns	71-L
A-245(1)	.25m		.04m	.05m					.2 Cu	
A-285	.22	.90	.035m	.045m						
A-415(2)	.15m	.25-.60	.04m	.05m						
A-508	.27m	.50-.90	.025m	.025m	.15-.35	.50-.90	.25-.45	.55-.70	.05 Va max	
A-516 Gr 70	.27m	.85-1.2	.035m	.04m	.15-.30					
A-533 Gr A	.22	1.42	0.12	0.014	.22			.59	Lukens	B-1375
Class II	.23	1.38	0.14	.013	.25			.58	Lukens	B-1375
Type 304	.08m	2.00m	.040m	.03m	.75m	8-11.0	18-20			
Inconel 600	.15m	1.0m	.015m	.5m	72min	14-17.0			Fe6-10 Cu .5m	

m = maximum

(1) Replaced in 1971 by A-504 and A-611

(2) Replaced by A-569

The crevice samples were also machined into 4.75x0.5x0.06 inch coupons. The coupons were mounted in pairs into a fixture as shown in Figure 1. A 16-mil diameter stainless steel wire was inserted between the coupons at each end to form a crevice. Then the middle of the coupon pair was deflected away from the fixture with a screw which caused this area to be in tight contact between the mating pairs. A resultant variable width crevice was thus formed, ranging from zero width at the center of the coupon length to 16 mils at the ends. The coupon pairs were deflected so that the outer surface of the outer coupon was just at the yield stress. Deflections were calculated from the formula:

$$S = \frac{\pi^2 E h Y}{2L^2} \quad \text{or} \quad Y = \frac{2SL^2}{\pi^2 E h}$$

Where S = stress, psi
Y = deflection, inches
L = coupon length, inches
E = Young's Modulus
h = coupon thickness

Young's modulus and yield stress for each of the alloys is given in Table III. Each fixture contained four coupon pairs. The pairs tested were: Type 304 SS to Type 304 SS, Inconel 600 to Inconel 600, Inconel 600 to ASTM A-516, and ASTM A-516 to ASTM A-508.

Prior to exposure, each coupon was polished with 320 grit emory cloth, degreased in acetone, dessicated, and weighed.

After exposure, each coupon was rinsed in water, lightly scrubbed with a brush and Lava soap to remove adherent films, rinsed in demineralized water, dried in acetone, dessicated for one hour, and reweighed. Photographs were taken of many of the samples to show corrosion and deposition.

One of the Type 304 SS U-bend samples and one of the uniform corrosion samples was exposed in the sensitized condition. The material was sensitized by holding at 1150°F for one hour and air cooling.

TABLE III

PHYSICAL CONSTANTS FOR CREVICE SAMPLES

Alloy	Yield Stress (lbs/in^2)	Young's Modulus	Thickness (inches)
A-508	40×10^3	30×10^6	.062
A-516	40×10^3	30×10^6	.062
304 SS	35×10^3	29×10^6	.060
Inconel 600	35×10^3	32.5×10^6	.050

CORRATOR PROBES

Instantaneous corrosion and pitting rate measurements were periodically taken during the course of the test. The measurements were made with a Magna Model 1172 Corrator and AISI 1010 steel electrodes.

The corrator probes were placed into the cold solvent samples and equilibrated several hours before initial readings were taken. The corrators remained immersed in solvent throughout the complete testing period.

FILMED SAMPLES

Coupons were cut from AISI 1010 carbon steel fuel spacers removed from the Hanford N Reactor. The spacers had been exposed for more than one year to 540°F pressurized, demineralized water adjusted to pH 10 with NH_4OH which formed a tightly adherent magnetite film. The magnetite film contained radioactivity uniformly distributed in the film. Periodic measurement of the residual radioactivity during cleaning provided a rapid method of quantitatively measuring the amount of magnetite removed by the solvent. Visual observations for the presence of magnetite were also made.

Two spacer samples were used to evaluate magnetite removal for each solvent tested. One sample was a plain section of a 1-inch ring identical to that used in the Subtask II testing described in our third interim report. The second sample was fabricated to simulate crevices in the Indian Point 2 steam generators by bolting a 4.5x0.5 inch coupon of Inconel 600 to the ID surface (Figure 2). The resulting crevice was very tight at the area where the Inconel 600 coupon was bolted on, ranging up to 10 mils wide at the ends of the coupon. A tight crevice was also formed on the opposite side under the lockwasher and nut.

A second, tighter crevice was formed on the same sample by applying a 0.5 inch diameter epoxy patch over the magnetite on the OD surface. This crevice was more restrictive to solvent penetration than the actual steam generator crevices since the epoxy partially penetrated into the magnetite surface film. Magnetite film thickness, calculated from weights before and after descaling, and using a density of 2.5 grams/cm^3, was about 0.3 mils.

SOLVENTS

The ten best solvents from the initial scanning tests[1] were selected for this testing. The solvents and their composition are shown in Table IV. The chemical formulas for the chelants are also shown in Table IV. The numbering sequence is that used during the previous tests. Each solvent was made from reagent grade chemicals added to deionized water. Diethylthiourea corrosion inhibitor at a concentration of 0.1% was added to each solvent except Solvent 7, which is a proprietary solvent already containing inhibitors and surfactants. Solvent 6 also is a proprietary solvent containing inhibitors; but additional diethylthiourea was added based on results of the Subtask II scanning tests, which indicated this solvent would likely be one of the most corrosive tested.

TEST SEQUENCE

The ten solvents were tested in two sets of five solvents. The first set consisted of solvents 1,2,6,7 and 10 while the second set consisted of solvents 3,8,9,12 and 15A. Each test set required three days to complete and they were performed in series.

Four liters of each solvent was placed in a reaction flask equipped with heaters, magnetic stirrers, condensors, thermometers, and a nitrogen sparge tube as shown in Figure 3.

In the first test set the corrator probes were placed into the cold, air-saturated solvents and checked periodically until the readings became stable. Nitrogen sparging was then initiated to deoxygenate the solvents and at equilibrium corrator readings were recorded. After the second set of corrator readings, the solvents were heated to 85°C with corrator readings being obtained as the temperature increased. The corrosion coupons and magnetite film samples were placed into each test solution as the temperature approached 85°C. The exposure period was about 40 hours at 85°C with a continuous low volume nitrogen purge. Corrator readings and activity measurements on the spacer samples were taken periodically throughout the test.

The second set of five solvents was tested using the same procedure with the exception that the nitrogen sparging was not initiated until the solvents had reached 65°C.

TABLE IV

SOLVENTS FOR SUBTASK IIIA TESTING*

1. EDTA 10%
   N_2H_4 1%
   NH_4OH to pH7

2. EDTA 4½%
   NH_4OH to pH7

3. CITROSOLV
   CITRIC ACID 3%
   NH_4OH to pH 3.5
   NH_4OH to pH 9
   $NaNO_2$ 1%

6. CITROX 10% AS
   TURCO 4521

7. PHOSPHORIC ACID 10% AS
   TURCO 4512A

8. EDTA 3%
   CITRIC ACID 2%
   N_2H_4 to pH7

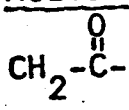
9. OXALIC ACID 4½%
   CITRIC ACID 2%
   NH_4OH to pH4
   H_2O_2 to 1.0M

10. EDTA 10%
    NH_4OH to pH9
    ACETIC ACID to pH7

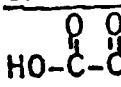
12. DTPA 5%
    CITRIC ACID 2%
    N_2H_4 to pH8

15A. HEEDTA 10%
     NH_4OH to pH4

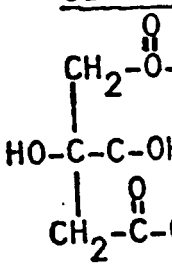
ACETIC ACID



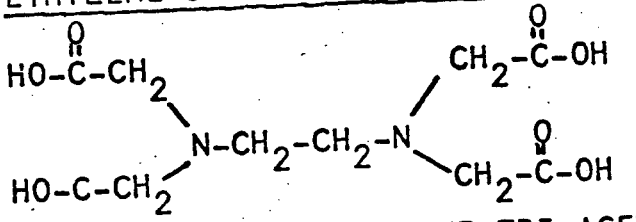
OXALIC ACID



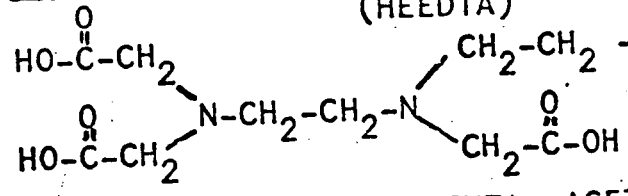
CITRIC ACID



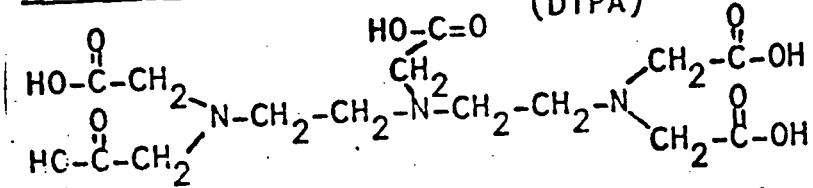
ETHYLENE DIAMINE TETRA ACETIC ACID (EDTA)



HYDROXYETHYLENE DIAMINE TRI ACETATE (HEEDTA)



DIETHYLENE TRIAMINE PENTA ACETIC ACID (DTPA)



*Numbering sequence reflects those assigned in previous tests.

IV. RESULTS

CORRATOR MEASUREMENTS

The effect of oxygen on the corrosiveness of the solvents was measured at the start of each test. Readings were taken in the freshly prepared solvents which were oxygen saturated and again after sparging the solutions with nitorgen. The results, given in Table V, show a significant decrease in solution corrosiveness after nitrogen sparging for all solvents not containing hydrazine. In those solvents containing hydrazine the oxygen was effectively removed; therefore, nitrogen provided no further reduction in corrosion. These data indicate that nitrogen sparging of non-hydrazine containing solvents should be conducted prior to introduction of the solvent into the steam generators in order to control corrosion to the lowest possible level.

Corrator readings taken periodically during the 40-hour exposure period for each solvent are shown in Figures 4-13. Pitting corrosion was low for all solvents except Nos. 12 and 15A; in each of these solvents the pitting corrosion rates increased with time. Uniform corrosion rates were low for Solvents 2,3,6,7 and 10. Uniform corrosion in Solvents 1,9 and 15 slowly increased in time and for 1 and 15 reached a rate off scale (>100 mils/year) of the measuring instrument. Uniform corrosion in Solvents 8 and 12 increased rapidly with time and were greater than 100 mils/year in just a few hours.

MAGNETITE FILM REMOVAL

Visual observation of the amount of film removed and radiation readings were measured on samples filmed with magnetite as a function of time. The radiation measurements results are given in Figures 4-13 (along with the corrator readings) in terms of percent of original activity removed. Starting radiation readings were 75 to 100 mR/hr and ending readings were about 0.5mR/hr. In all cases except one, the amount of radioactivity removed was less on the crevice samples than on the plain samples because of the easier access of the solvent to the plain samples. The visual observations corresponded to the radioactivity measurements but in a much less quantitative manner; i.e., when the radiation readings were less than 90% activity removal, magnetite was still visible but the quantity remaining could not be visually determined. Solvents 6,7 and 9 very rapidly removed the magnetite while Solvents 3,8,12 and 15 were slightly slower. Solvents 1,2 and 10 were very slow in magnetite removal.

TABLE V

CORRATOR MEASUREMENTS FOR OXYGENATED VS. N_2 PURGED SOLVENTS

TEST SET 1	OXYGENATED Temp=30°C mils/year		DEOXYGENATED Temp=30°C mils/year	
Solvent	P	C	P	C
1	2	4	1	2
2	80	50	2	1
6	10	23	1	3
7	35	55	2	4
10	65	45	1	1
TEST SET 2	**Temp=52°C**		**Temp=65°C**	
3	2	75	1	6
8	1	3	1	5
9	8	85	2	8
12	2	6	2	10
15A	90	55	20	15

P = Pitting Corrosion

C = Uniform Corrosion

Solvents 6 and 9, although removing the magnetite very rapidly, caused very extensive iron oxalate precipitation in the crevices, and thus cannot be considered further. Solvent 7, the remaining solvent which rapidly removed magnetite, caused severe corrosion to A-508 steel as discussed below and must also be rejected. Solvents 1,2 and 10 are too slow, comparatively, in removing oxide from exposed surfaces to be considered further for removing magnetite from crevices.

CORROSION COUPON MEASUREMENTS

Coupons of Inconel 600, Type 304 SS, and several types of mild and low alloy steel were exposed to the solvents. Coupon configurations included U-bend stress samples, uniform corrosion samples, and stress crevice pairs. Each type of sample was weighed before and after the exposure and uniform corrosion rates calculated from the weight loss data; the results are given in Table VI. The data show that some solvents were very corrosive to some of the steel alloys, and some were very corrosive to other steel alloys. In general, the unalloyed mild steel such as A-245 was only mildly attacked, but the alloyed steels such as A-508, A-516 and A-533 were rapidly attacked in certain solvents. For example, Solvent 7 completely destroyed the A-508 alloy but caused only mild corrosion on the other alloys. Solvent 1 selectively attacked the A-516 alloy. Solvents 8 and 12 caused excessive corrosion on several of the steel alloys. It should be noted that a corrosion rate of 7 mils/day results in dissolution of about half the coupon thickness in two days.

None of the solvents caused any significant corrosion to the Inconel 600 or Type 304 SS, sensitized or unsensitized. Also, none of the solvents caused stress corrosion cracking in either the U-bend or stress-crevice samples. Solvent 7 did cause pitting of the A-533 alloy at the stress area of the U-bend sample, however. Accelerated crevice corrosion was not observed except in Solvent 7. Solvents exhibiting acceptable corrosion rates (<1 mil/day), in order of least corrosion to highest corrosion, were Nos. 10,2,3 and 6.

TABLE VI

CORROSION IN NITROGEN SPARGED SOLVENTS AT 185°F, MILS/DAY

Coupon Type	Alloy	Solvent 1	2	3	6	7	8	9	10	12	15A
U-Bend	Inconel 600	<.001	.001	<.001	.002	.002	<.001	.001	<.001	.003	<.001
	Type 304SS, Sens.	.010	.01	.01	.004	.004	.01	.010	.006	.011	.004
	Type 304SS	.012	.01	.02	.005	.003	.01	.013	.006	.011	.004
	ASTM A508	.09	.02	.04	.01	Destroyed	2.71	.39	.02	5.20	.04
	ASTM A533	2.52	.07	.06	.02	.02	4.28	.44	.05	3.22	.10
	ASTM A105	1.08	.07	.18	.08	.06	3.70	.49	.05	4.06	.23
	ASTM A516	1.18	.09	.29	.33	.10	3.56	.97	.06	4.11	1.06
Uniform	Inconel 600	.001	.002	.001	.03	.002	<.001	.011	<.001	.002	.002
	Type 304SS, Sens.	.001	.001	.002	.03	.002	<.001	.07	<.001	.001	.001
	Type 304SS	<.001	.002	<.001	.03	.002	<.001	.06	<.001	<.001	.001
	Weld (A415-304SS)	.64	.39	.46	.27	.71	1.68	.92	.37	2.29	1.18
	ASTM A508	.94	.06	.13	.08	4.20	3.14	.44	.05	3.25	.29
	ASTM A533	6.41	.09	.10	.06	1.18	4.82	.37	.08	6.83	.33
	ASTM A105	.49	.06	.18	.13	.07	3.60	.49	.05	3.28	.40
	ASTM A516	.19	.08	.29	.34	.09	4.12	.88	.08	4.47	.99
	ASTM A285	.17	.06	.19	.09	.09	1.68	.33	.05	1.71	.30
	ASTM A245	.53	.06	.72	.05	.07	.93	.25	.06	.83	.28
Stress-Crevice Pairs	[ASTM A516*	1.85	.51	.95	1.10	.48	4.42	2.00	.45	5.79	3.05
	ASTM A508]	.09	.87	.06	.05	Destroyed	1.76	.10	.04	2.96	.06
	[ASTM A516	.33	.50	.97	1.14	.02	3.98	2.13	.44	4.62	2.95
	Inconel 600]	.002	.001	.001	.002	.002	.001	.02	<.001	.004	.001
	[Type 304	.02	.012	.06	.007	.001	.004	.02	.02	<.001	.01
	Type 304]	.02	.011	.05	.005	.002	.002	.02	.02	.002	.01
	[Inconel 600	.003	<.001	.002	.003	.003	.001	.003	<.001	.004	.002
	Inconel 600]	.003	.001	.002	.003	.002	.001	.003	<.001	.004	.002

*Brackets indicate coupon pairs.

Even more significant than the uniform corrosion rates calculated from the weight loss data were the results of the microscopic examinations to determine the extent of pitting attack. These results are summarized in Table VII. The least amount of pitting occurred in Solvent 6 but this solvent caused extensive oxalate deposition. Solvent 2 also caused very little pitting, closely followed by Solvents 3 and 10. All the other solvents caused pitting.

DISCUSSION

A summary of the test results for all solvents comparing their relative corrosiveness as measured by corrator probes, uniform corrosion calculated from coupon weight loss data, the relative intensity of pitting attack, and their effectiveness in removing magnetite is given in Table VIII. For all measurement criteria, Solvent 6, Turco 4521 Citrox, caused the least corrosion and was the most effective in removing magnetite. However, this solvent caused excessive amounts of iron oxalate deposits in the crevice areas, which completely eliminates it for further consideration in cleaning steam generator tube-to-tube support plate crevices. For any other application without crevices, this solvent would be the logical choice. The other solvent in the test series containing oxalate, Solvent 9, likewise caused excessive iron oxalate deposits; therefore, it is concluded that oxalate containing formulations should not be further considered. The oxalate deposits were found primarily on the mild steel and low alloy steel samples and with only slight deposits in crevice areas on either the Inconel 600 or the Type 304 SS. This indicates that the deposits form only at rapidly corroding surfaces and are not dependent on the iron content of the bulk solvent.

Based on an overall evaluation of the parameters, Solvent 3, ammoniated citric acid (Citrosolv) is clearly the optimum solvent for use in the steam generator tube support plate crevice cleaning. This solvent is a fairly effective magnetite solvent and causes very little corrosion. Second and third choices would be Solvent 15A, which is an effective magnetite solvent but causes some pitting corrosion on the steel alloys; and either Solvent 2 or Solvent 10, each of which very slowly removes the magnetite but causes very little corrosion.

TABLE VII

MICROSCOPIC EXAMINATIONS OF CORROSION COUPONS

SOLVENT COMPOSITION

ALLOY	1. NH_4OH to pH7 1% N_2H_4 10% EDTA	2. 4½% EDTA NH_4OH to pH7	3. 3% CITRIC ACID NH_4OH to pH3.5	6. 10% T-4521 (CITROX)	7. 10% T-4512A (PHOSPHORIC ACID)	8. 3% EDTA 2% CITRIC N_2H_4 to pH7	9. H_2O_2 to 0.8M 4½% OXALIC 2% CITRIC NH_4OH to pH4	10. 10% EDTA NH_4OH to pH9 ACETIC ACID to pH7	12. 5% DTPA 2% CITRIC N_2H_4 to pH8	18A. 10% HEEDTA NH_4OH to pH4
Type 304SS, Unsensitized	Excellent	Excellent	Excellent	Excellent, deposit in crevice	Excellent	Excellent	Excellent (dull)	Excellent	Excellent	Excellent
Type 304SS, Sensitized	Excellent	Excellent	Excellent	Excellent, deposit in crevice	Excellent	Excellent	Excellent (dull)	Excellent	Excellent	Excellent
Inconel 600	Excellent	Excellent	Excellent	Excellent, deposit in crevice	Excellent	Excellent	Excellent (shiny)	Excellent	Excellent	Excellent
A245 Carbon Steel	Good	Good	Etched slightly few <1 mil pits	Excellent, oxalate ppt	Some surface etching	Etched	Slight etch, deposition	Gray, excellent	Mild etching	Mild etching
ASTM A508 Uniform U-Bend Crevice	Lots of pits 2-5Wx10-40L Few pits 1-2Wx2-5L No pits	None to a few <1 mil pits on uniform sample	Occasional 1x4 No pits No pits	Excellent, oxalate ppt	Chunks gone Dissolved,	Heavy uniform corrosion, long shallow pits on U-bend coupon	Etched with shallow elongated pits, deposition	Gray, excellent	Heavy uniform corrosion, surface etching, few very small pits	Excellent condition
ASTM A533	Severe, overlapping pitting, very deep 5-25 mil dia	Occasional <1 mil pit	Excellent	Excellent, oxalate ppt	Severe pitting 3/16" dia, 40 mils deep, crevice & stress areas attacked	Severe etching, number gone	Slightly etched, deposits of oxalate	Gray, excellent	Heavy uniform corrosion, very shallow pits	Thousands of <1 mil pits
ASTM A516	Covered with 2-5Wx10-40L pits, severe	Shallow 2-3Wx10L pits, all over	Frequent pits, 2-4Wx5-10L	Scattered <1 mil pits, ppt	Crevice attack deposit in crevice	Heavy uniform corrosion	Severe etching (sugaring) deposition	2-5Wx10-20L pits, wire groove	Heavy surface etching with shallow, elongated pits	Severe surface etching 3-6Wx10-50Lx 10D pits
ASTM A105	Covered with 2-5Wx40L pits	No pits	No pits, slight etching	Excellent, oxalate deposit	Crevice attack	Severe etching	Severe but smooth etching	Etched	Severe surface etching	Etched, 5 mil dia pits
ASTM A285	Covered with ¼Wx1-4L pits	Gray, no pits	Excellent	Excellent, oxalate ppt	Good condition	Severe etching	Etching, lots of <1 mil pits	Excellent	Surface etching with shallow pitting	Etched 5 mil dia pits

NOTE: Numbers following pit identification indicate pit size in mils.
W = width
L = length
D = Deep

TABLE VIII
SUMMARY OF TEST RESULTS
RELATIVE COMPARISONS

SELECTION PARAMETER	No. 1	No. 2	No. 3	No. 6	No. 7	No. 8	No. 9	No.10	No. 12	No.15 A
Solvent Composition	10% EDTA 1% N_2H_4 pH7 NH_4OH	4½% EDTA pH7 NH_4OH	3% Citric Acid pH 3.5 NH_4OH (plus Passivation)	10% Turco 4521 Citrox	10% Turco 4521 H_3PO_4	3% EDTA 2% Citric Acid pH7, N_2H_4	4½% Oxalic Acid 2% Citric Acid pH4 NH_4OH 1M H_2O_2 (Passivation)	10% EDTA pH9 NH_4OH pH7 Acetic Acid	5% DTPA 2% Citric Acid pH8, N_2H_4	10% HEEDTA pH4 NH_4OH
Corrosion Readings										
a) Pitting	Low	Low	Low	Very low	Low	Low	Increased to 10	Low	High	Increased to >100
b) Corrosion	Increased to >100	Steady at 30	Increased to 55	Steady at 10	Decreased to 10	Rapidly increased to >100	Increased to >100	Steady at 20	Rapidly to >100	Increased to >100
Coupon Data										
Relative Corrosion	High	Low	Low	Moderate	Very high	High	Moderate	Lowest	High	Moderate
Pitting Severity	Severe	Very low	Low	None	Severe	Severe	High	Low	High	High
Magnetite Removal										
a) in crevice	78%	47%	94%	99%	98%	83%	98%	44%	91%	90%
b) non crevice	95%	94%	95%	99%	99%	88%	99%	94%	94%	95%
Other				Heavy Oxalate deposits			Heavy Oxalate deposits			

The three formulations containing hydrazine--Solvents 1, 8 and 12--all started out with low corrosion rates as measured by the Corrator probes, but after a few hours the Corrator readings were off scale (>100 mils/year). These observations are borne out by the high uniform corrosion rates and pitting observed on the coupons. Apparently, the nitrogen bubbling accelerates the depletion rate of the hydrazine.

Several interesting observations can be made in comparing the effects of the various additives amongst the solvents. When comparing Solvents 2 and 10, both with EDTA and final adjustment to pH7 with NH_4OH, it appears that the acetic acid in Solvent 10 provides no useful purpose: both solvents had low corrosion rates and neither one removed magnetite very rapidly.

A comparison of Solvent 1 and Solvent 2 (both adjusted to pH7 with NH_4OH but requiring much less NH_4OH in Solvent 1 because of the hydrazine present) shows that Solvent 1 was both more corrosive and faster in removing magnetite. The increased magnetite dissolution (measured at $\frac{1}{2}$ hour exposure) is probably a combination of the higher EDTA concentration and the presence of the hydrazine to promote ferrous ion formation, which is more readily chelated than the ferric ion.

A comparison of the effectiveness of EDTA versus HEEDTA is obtained by comparing the results for Solvents 2 and 15A. Solvent 15A is much more effective in removing magnetite but is much more corrosive. This increased corrosiveness is probably because the pH for Solvent 15A was only pH4 as compared to pH7 for Solvent 2. It is possible that the use of additional corrosion inhibitor (0.1% diethylthiourea was used in these tests) or increasing the pH would reduce the corrosion of the HEEDTA solution.

A comparison of EDTA versus DTPA is obtained by comparing the results for Solvents 8 and 12. Unfortunately, each of these solvents contained hydrazine, and they rapidly became corrosive after a few hours of nitrogen sparging. In retrospect, it appears that if nitrogen sparging is to be employed, a better comparison for these solvents would have been made had the pH been adjusted to pH7 with NH_4OH instead of N_2H_4. This would also have provided a direct comparison of the effect of citrate ion by comparing with Solvent 2.

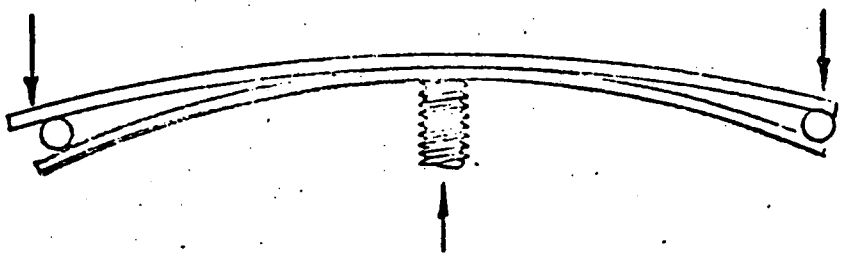
While nitrogen sparging adversely affected the hydrazine containing formulations, it definitely lowered the corrosiveness of all the remaining formulations as shown in Table V.

When nitrogen was sparged through Solvent 3, uniform corrosion was much lower and pitting corrosion was much less (Figure 5). Without sparging Solvent 3 exhibited a much higher uniform corrosion and pitting corrosion was greater than 100 mils/year (Figure 14).

At this point in testing, Solvent 3 is clearly superior to the other solvents; however, for the IIIB the best remaining solvents will be tested along with Solvent 3 for application at higher temperatures.

V. REFERENCES

1. UNI Interim Report No. 3, Steam Generator Chemical Cleaning for Indian Point Generating Station Unit No. 2, September 14, 1977.



DETAIL A

CREVICE COUPONS SHOWING
VARIABLE CREVICE

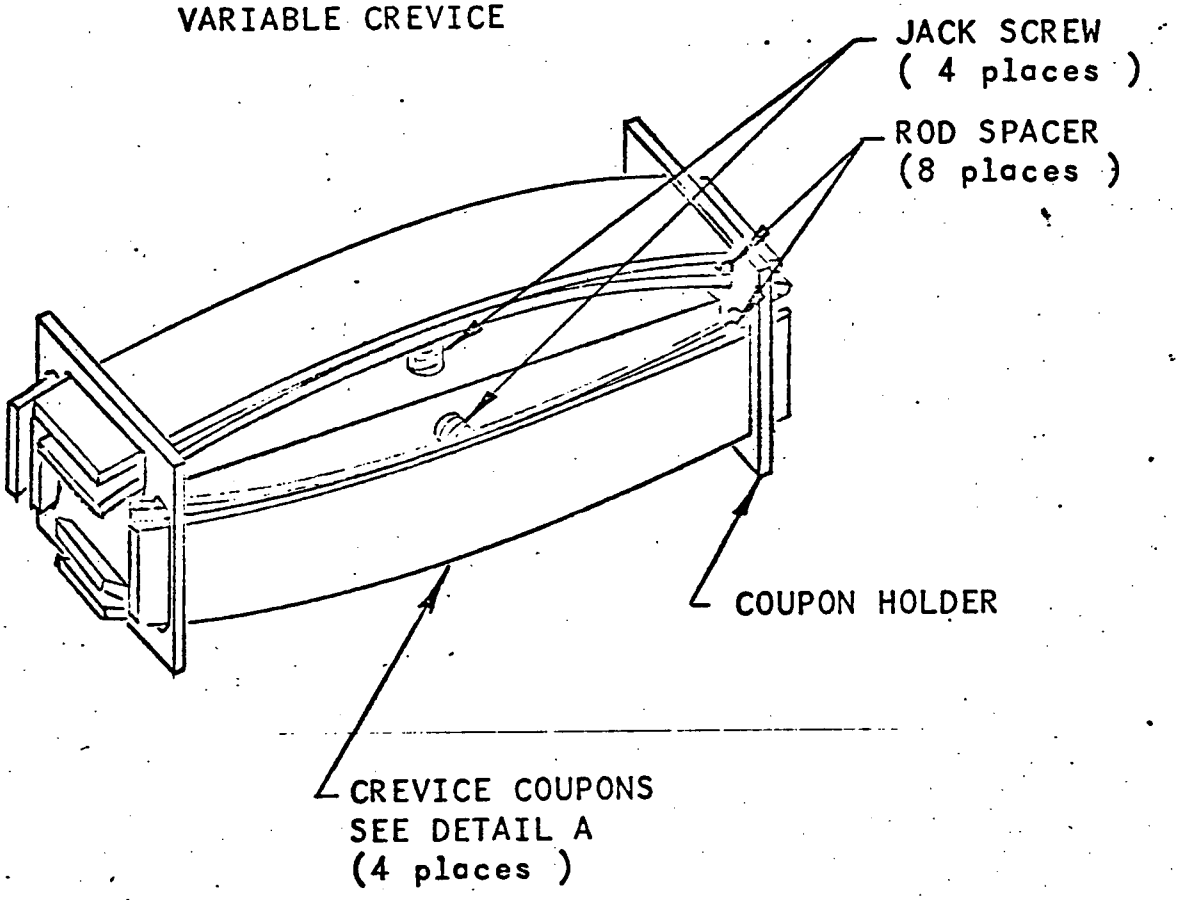


FIGURE 1

CREVICE STRESS COUPON ASSEMBLY

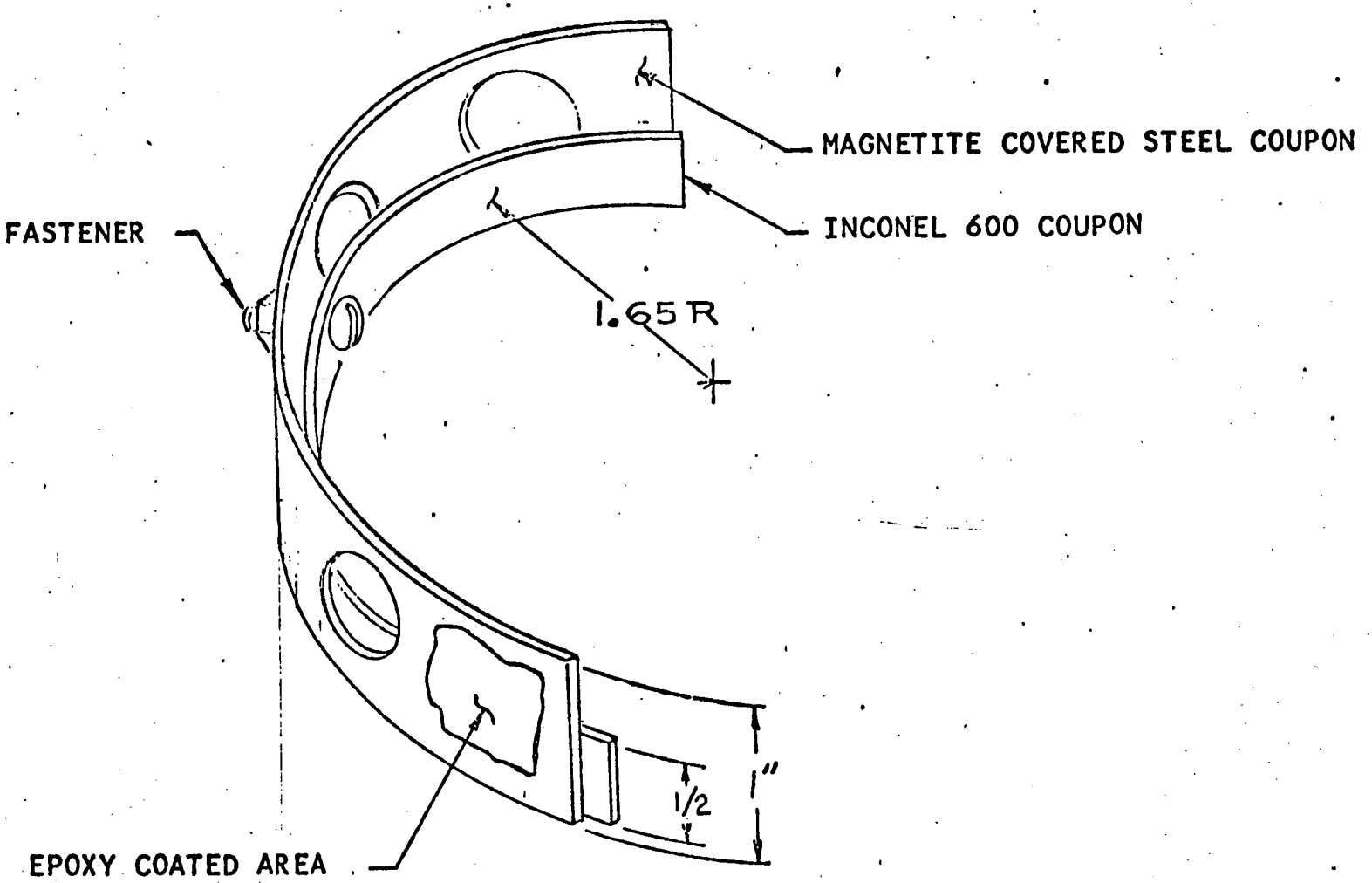


FIGURE 2

ARTIFICIAL CREVICE COUPON ASSEMBLY

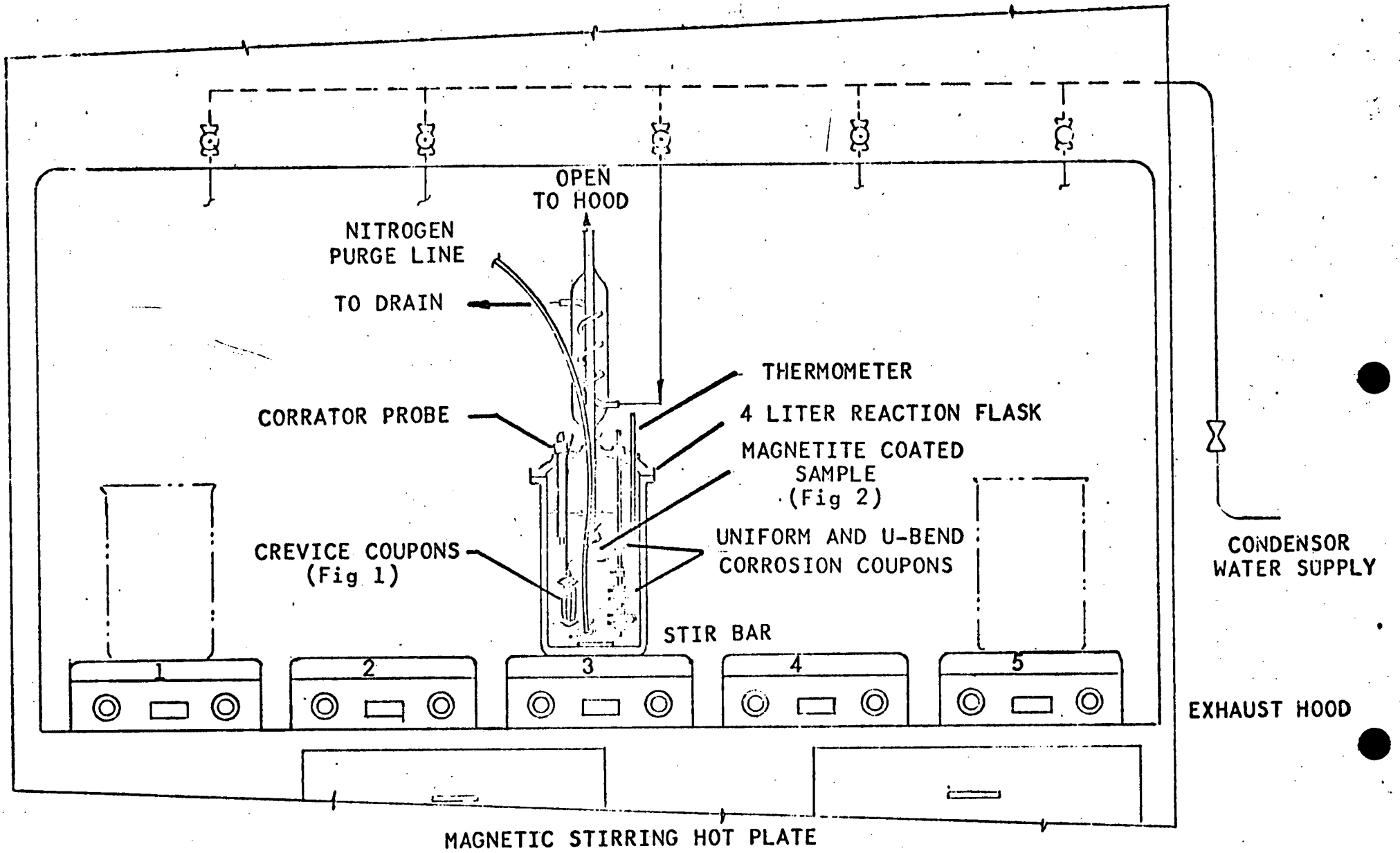
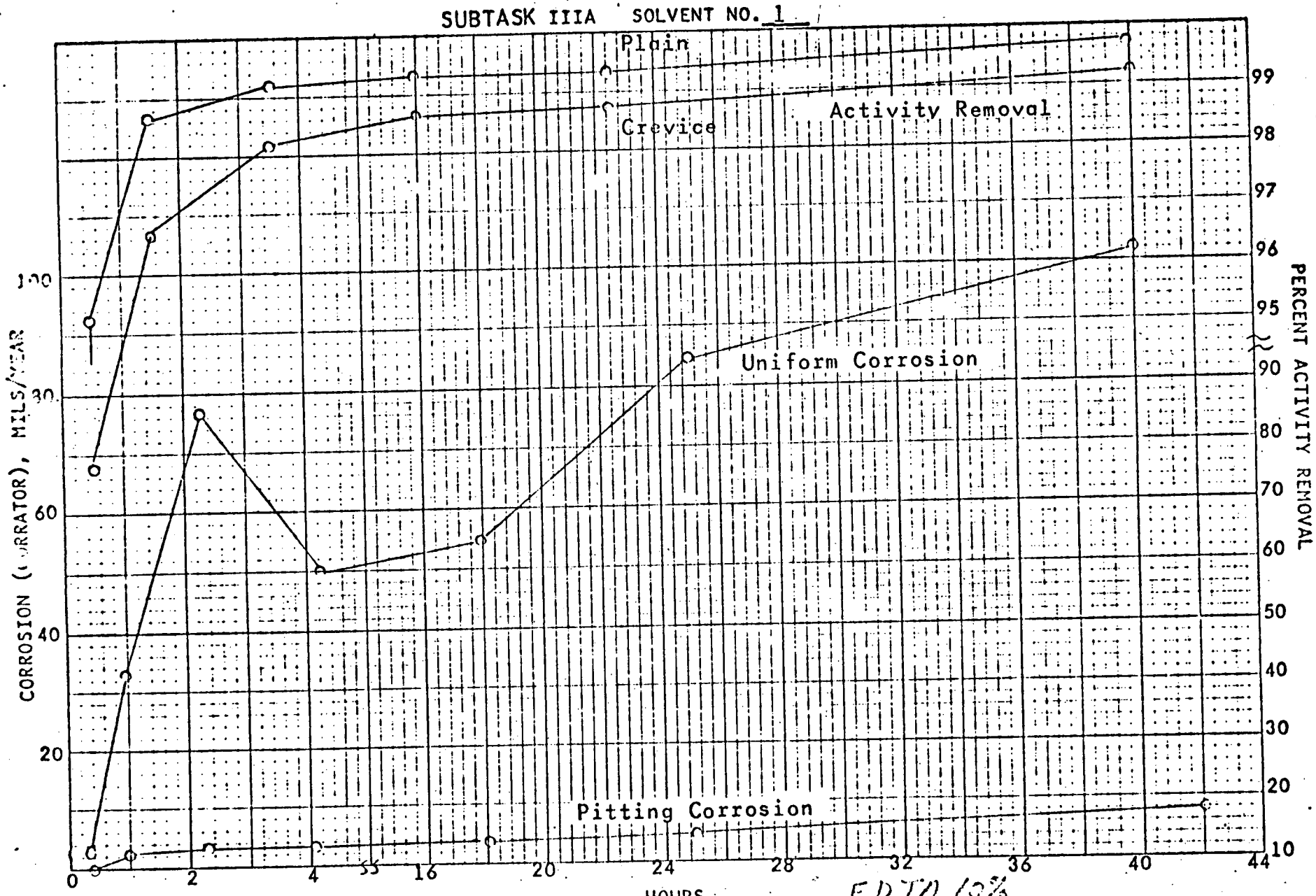


FIGURE 3

REACTION FLASK ASSEMBLY FOR SUBTASK IIIA SOLVENT TESTING

FIGURE 4

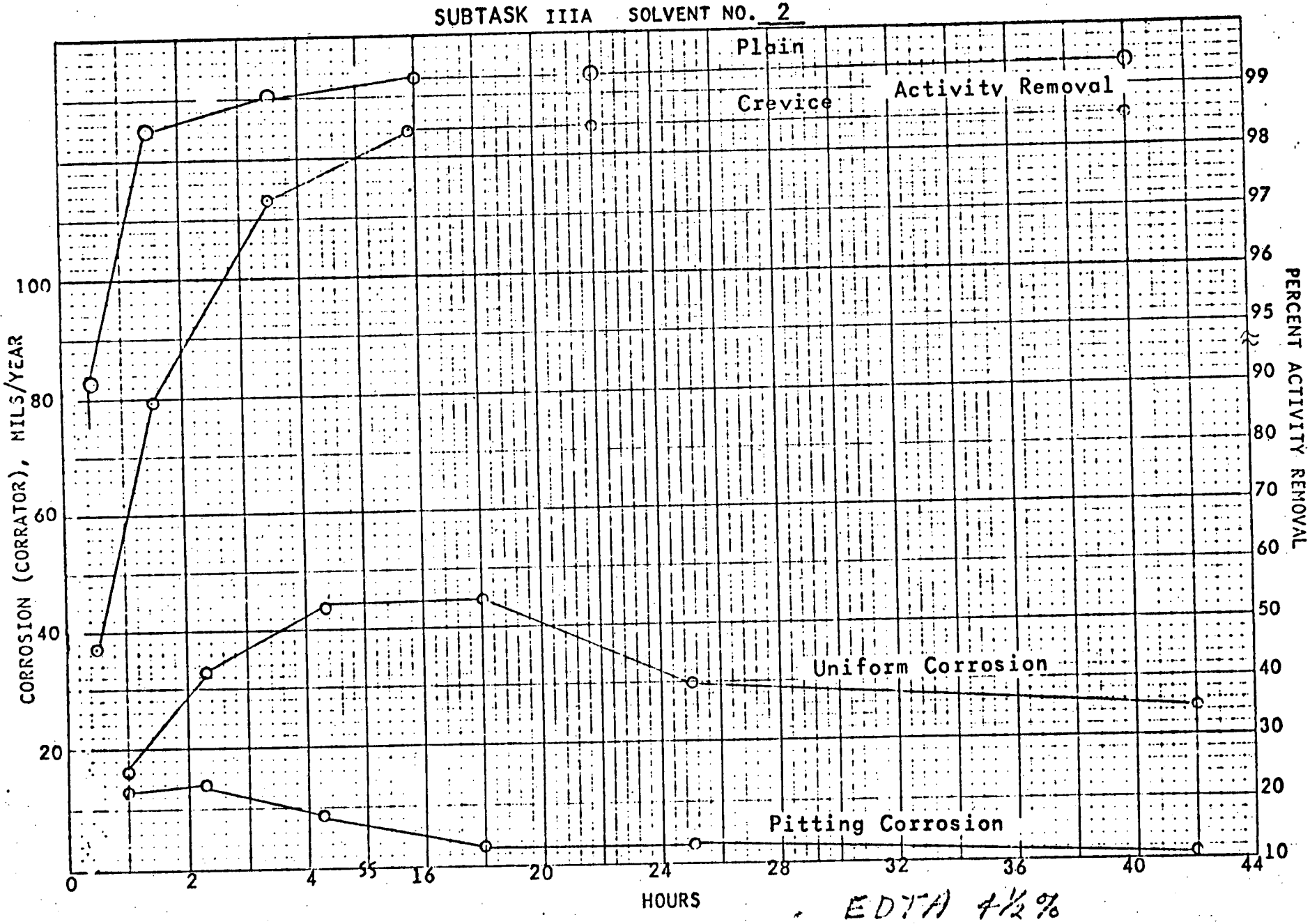
SUBTASK IIIA SOLVENT NO. 1



EDTA 10%
N_2H_4 1%
NH_4OH to pH7

FIGURE 5

SUBTASK IIIA SOLVENT NO. 2



EDTA 4½%
NH_4OH to pH7

FIGURE 6

SUBTASK IIIA SOLVENT NO. 3

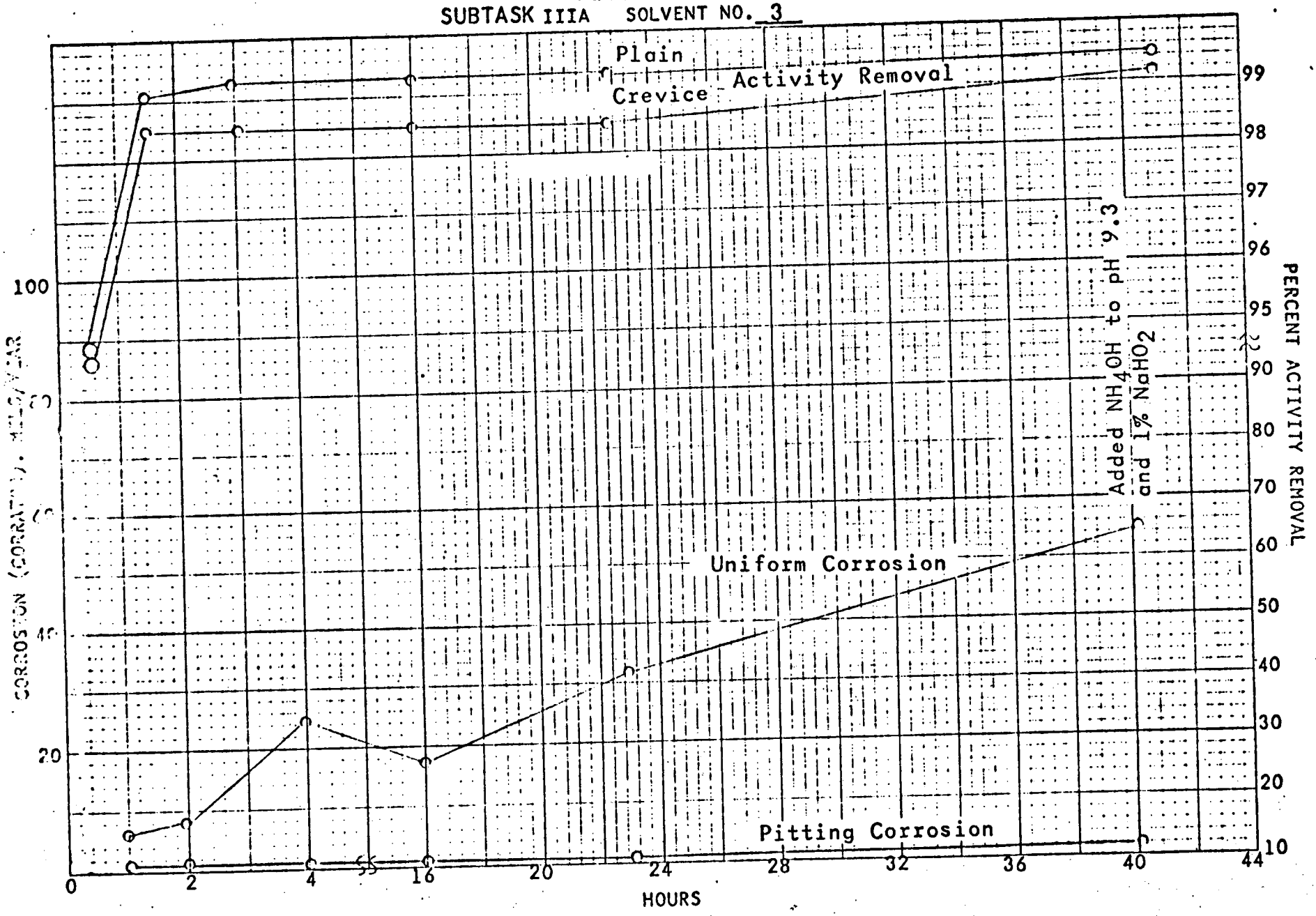


FIGURE 7

SUBTASK IIIA SOLVENT NO. 6

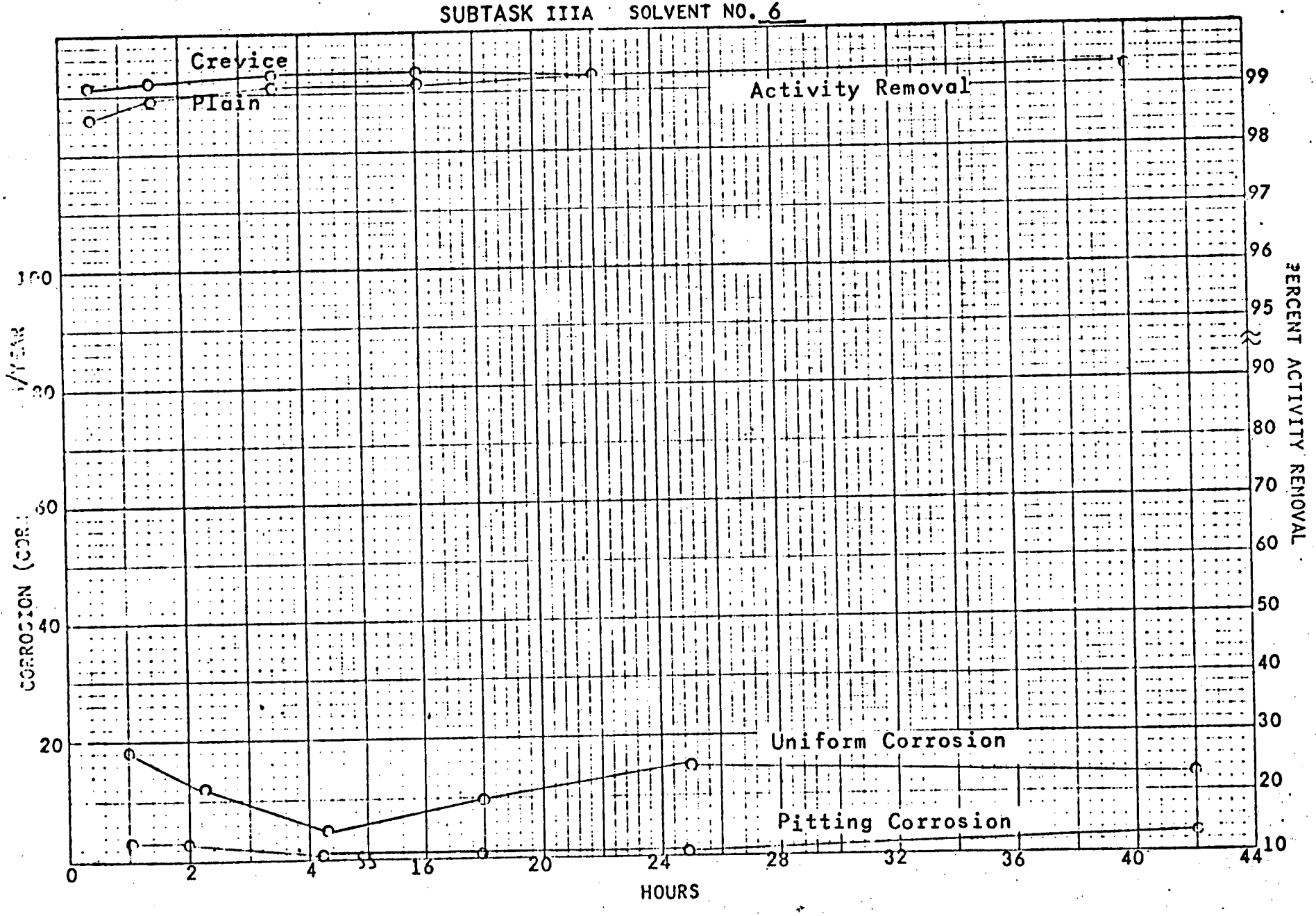


FIGURE 8

SUBTASK IIIA SOLVENT NO. 7

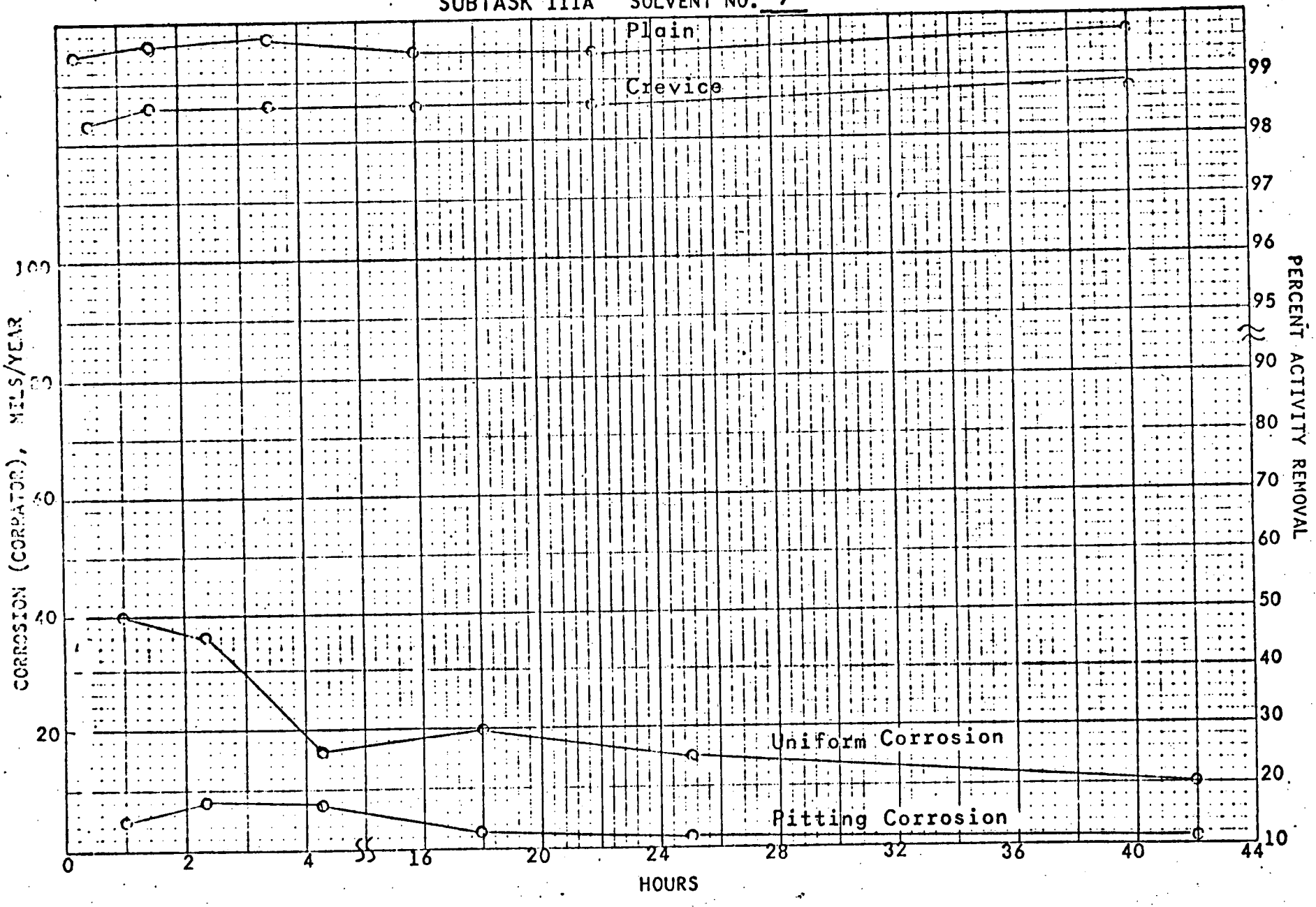


FIGURE 9

SUBTASK IIIA SOLVENT NO. 8

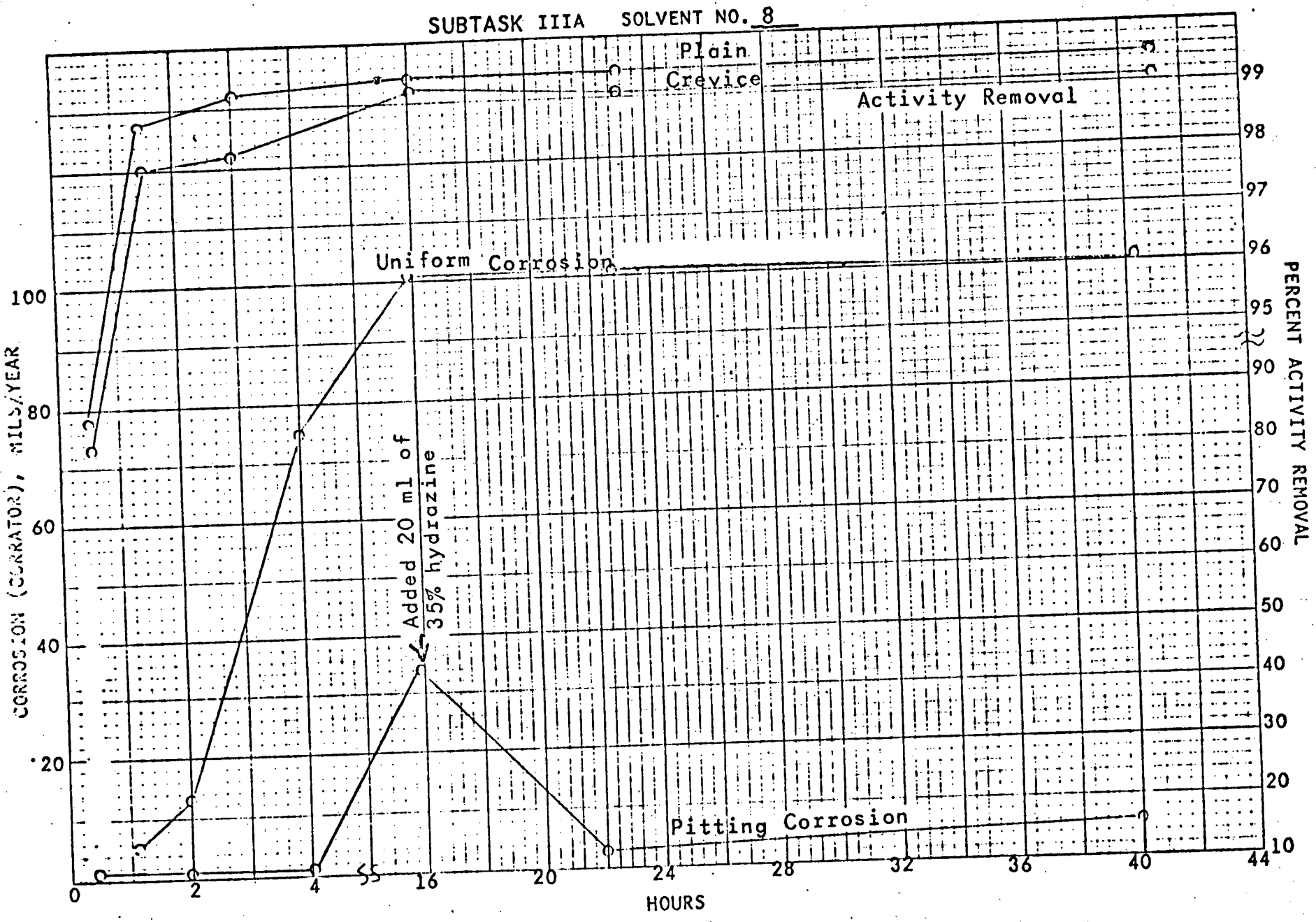


FIGURE 10

SUBTASK IIIA SOLVENT NO. 9

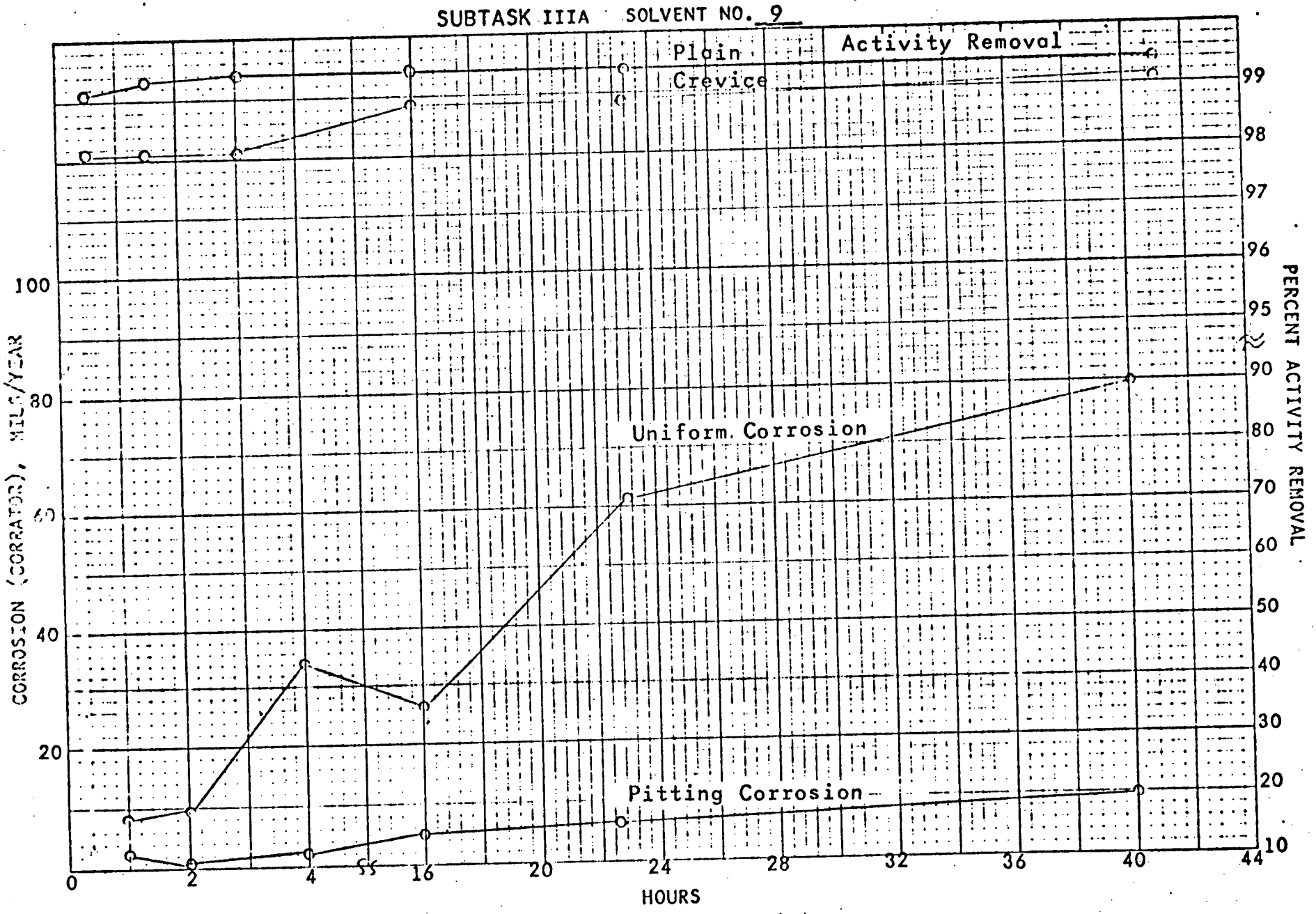


FIGURE 11

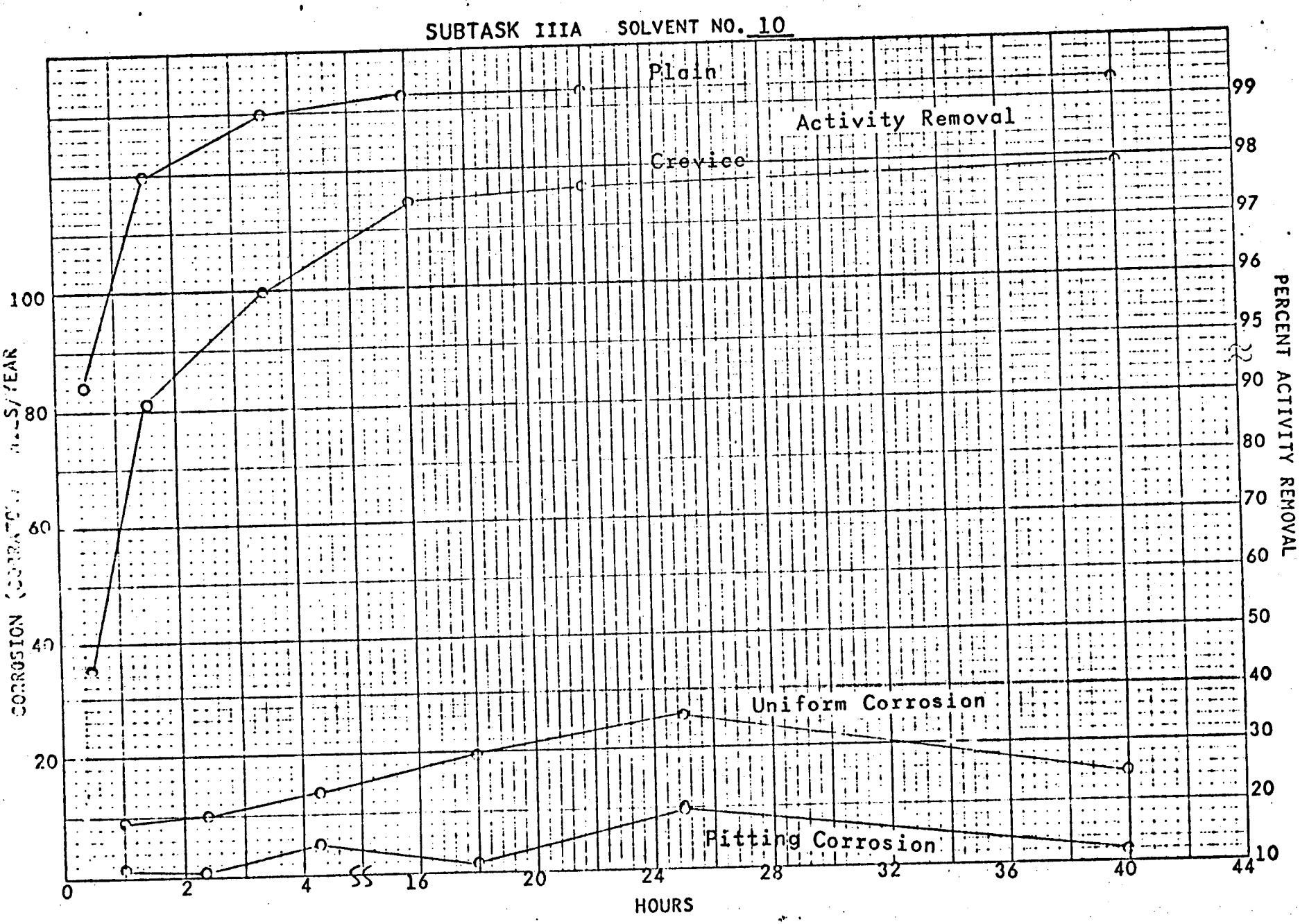

SUBTASK IIIA SOLVENT NO. 10
Plain
Activity Removal
Crevice
Uniform Corrosion
Pitting Corrosion
100
80
60
40
20
0
2
4
16
20
24
28
32
36
40
44
HOURS
99
98
97
96
95
90
80
70
60
50
40
30
20
10
PERCENT ACTIVITY REMOVAL

FIGURE 12

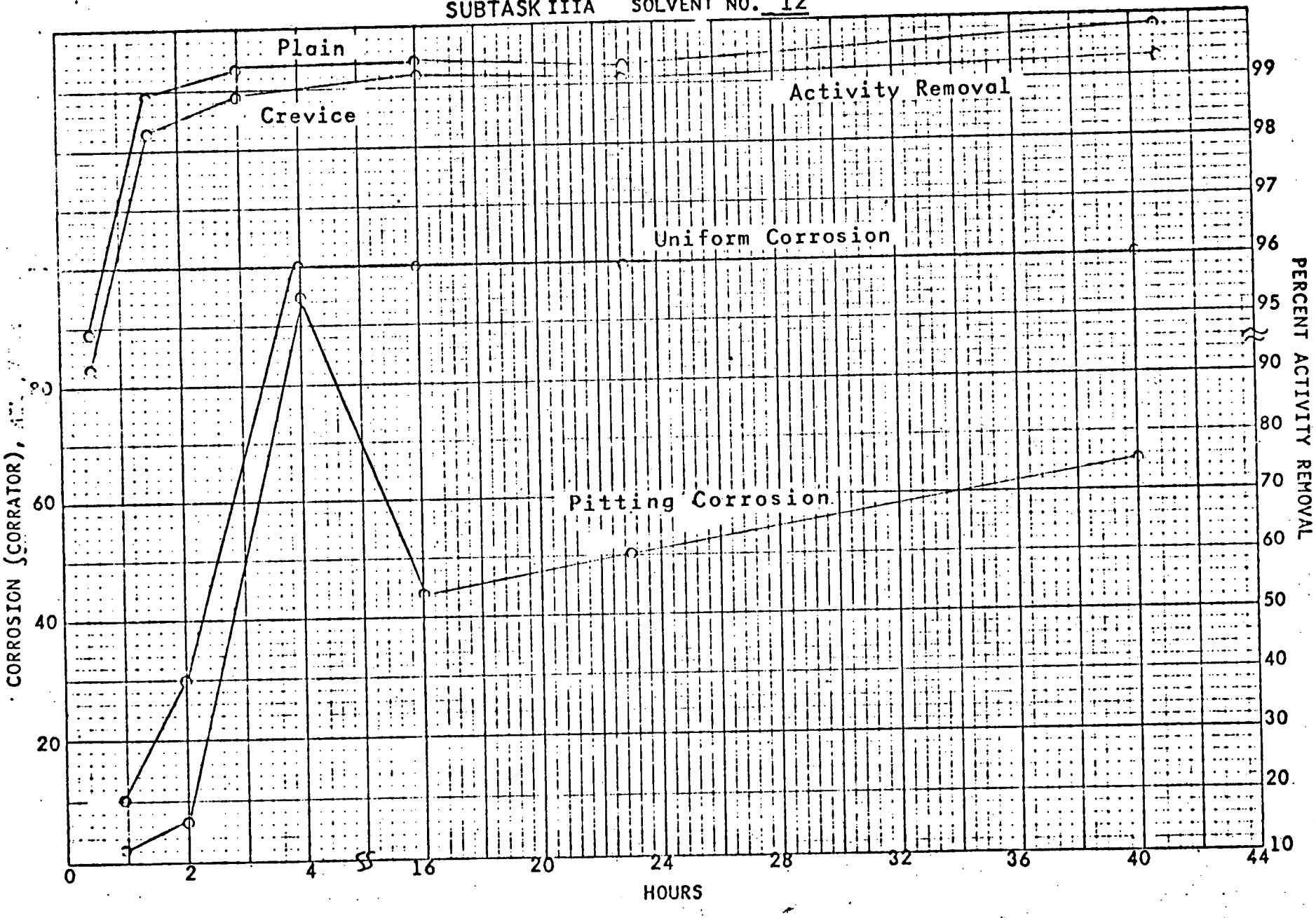
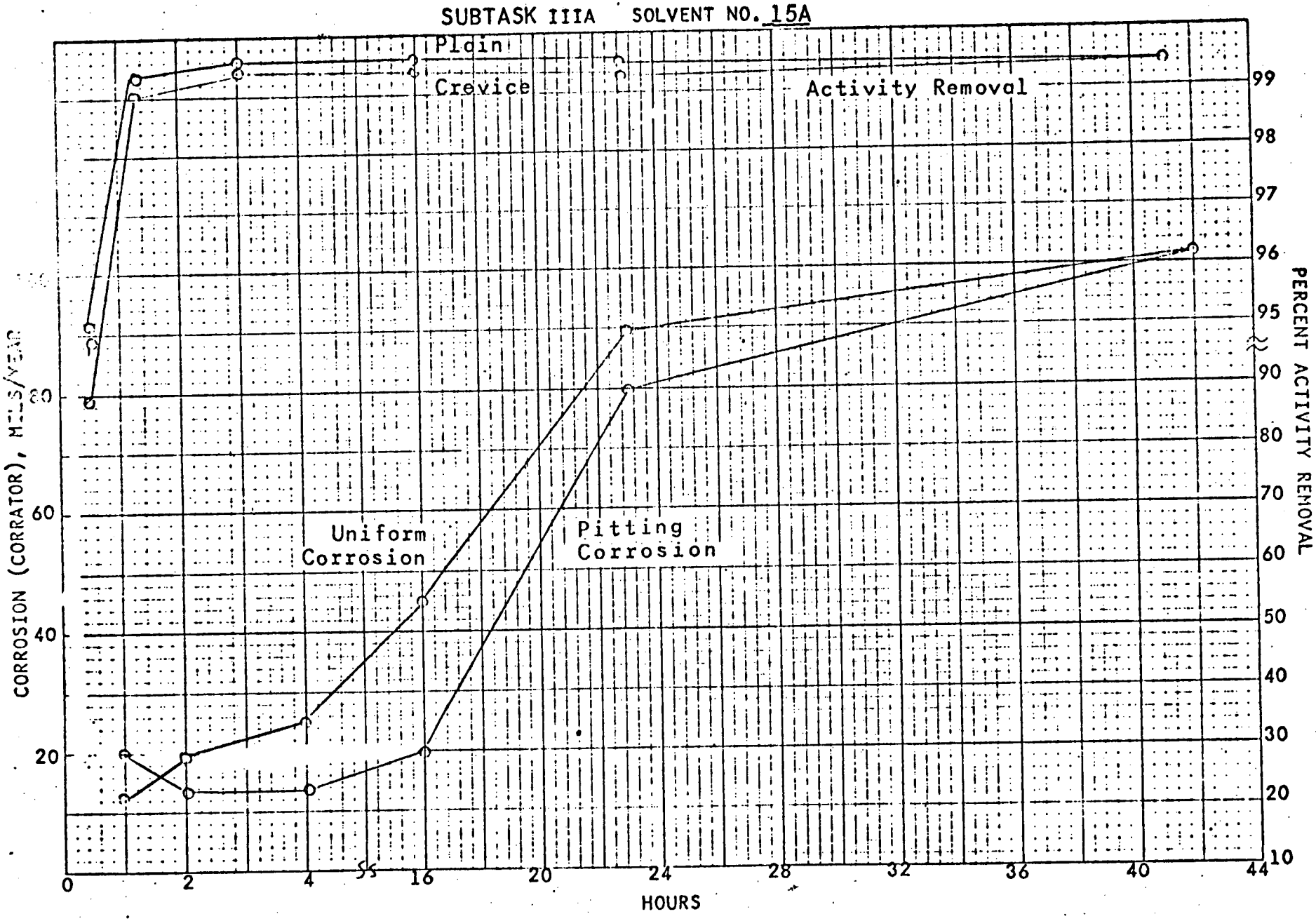

SUBTASK IIIA SOLVENT NO. 12
Plain
Crevice
Activity Removal
Uniform Corrosion
Pitting Corrosion
CORROSION (CORRATOR),
PERCENT ACTIVITY REMOVAL
HOURS
0
2
4
16
20
24
28
32
36
40
44
20
40
60
90
10
30
50
70
80
95
96
97
98
99

FIGURE 13


SUBTASK IIIA SOLVENT NO. 15A
Plain
Crevice
Activity Removal
Uniform Corrosion
Pitting Corrosion
CORROSION (CORRATOR), MILS/YEAR
PERCENT ACTIVITY REMOVAL
HOURS
0
2
4
16
20
24
28
32
36
40
44
20
40
60
80
10
30
50
70
90
95
96
97
98
99

UNITED NUCLEAR INDUSTRIES, INC.
A SUBSIDIARY OF UNITED NUCLEAR CORPORATION

COMMERCIAL DIVISION

1201 JADWIN AVENUE RICHLAND, WASHINGTON 99352 (509) 946-7661

September 14, 1977

Consolidated Edison Company of New York
4 Irving Place
New York, New York 10003

Attention: Mr. Paul F. McTigue

Dear Mr. McTigue:

Enclosed are three copies of the first reporting of results from our laboratory evaluation program for selecting a solvent to clean the secondary sides of the Indian Point steam generators. These first tests consisted of inhibitor scanning tests to select an inhibitor for use in the magnetite dissolution tests and the results of the magnetite dissolution tests.

Of the fifteen solvents employed in the dissolution tests, thirteen exhibited excellent magnetite dissolution capability by completely cleaning in one-half to one hour a magnetite film that had been formed on carbon steel during long-term, in-reactor exposure to high temperature, pressurized water. These results show that the initial selection of candidate solvents was skillfully made. The problem now is not one of finding a solvent that will remove magnetite but of eliminating most of the candidates.

The subsequent work (Subtask IIIA and IIIB of Table I) following the initial scanning and corrosion tests described in this report, have been completed and the data are being evaluated. As soon as the evaluation is completed, we will send you a progress report with the results. Some of the results available now show that the Citrox-type solvents and the chelant-oxalate solvents, while very effective in most cases in removing magnetite, should not be used in the steam generator application because very extensive iron oxalate

deposition occurs in crevices. Also, several of the solvents caused extensive pitting corrosion of the ASTM A508 and A533 alloys not apparent on the alloys employed during the initial scanning tests; these results will eliminate several other potential solvents.

We are now in the process of preparing for the higher temperature autoclave tests, and these will be completed in a few days.

Procedure writing progress includes completion of approximately 50 per cent of the Indian Point 1 procedures. We had hoped to have to you, at this time, some more extensive conceptual designs for the jumpers and temporary lines, but we have not yet received the prints required for this final effort. We may transmit the required information by phone to assure coordination of both our efforts.

In discussions with Al White on September 13, we agreed to fabricate a combined liquid phase coupon rack, coupon rack exposure chamber, sampling system, and liquid level monitoring station as one skid-mounted assembly. The coupon exposure chamber will contain corrator probes and thermocouples. The assembly includes a pump for recirculating the liquid and a recorder for recording the signal outputs. We will test the assembly here with one of our recorders, and when it arrives at Indian Point will install a rental recorder. A schematic for your comments is attached. As we discussed, it will be much easier and require less exposure to cut the low-level liquid line and tie the system in there than to tie into one of the lower handholes on SG No. 12.

With regards to our telephone conversation of September 14, where we discussed tying into the check valves near the Boron Storage Tank for the temporary jumpers, I see no problem cutting the pipelines and installing tees as alternatives for NSG-7 and BA-33. However, for BA-43 it will be necessary to open this check valve anyway to remove the check so that return flow from the steam generator can be obtained. Unfortunately, this is the hardest of the three to adapt. In regards to the other check valve in the main flow path, SD-223, we are assuming that it can be placed in the open position with the piston operator. If not, please indicate what action must be taken.

Also during our telephone conversation of September 14, you indicated there is a possibility that you may want to conduct the IP-1 demonstration in November in order to have more time to make equipment and piping modifications or purchases. This is good news because of the tight schedule. However, we are making every effort to concur with our contractual agreement to complete Phase I work in October 1977. Pursuant to that effort, we are proposing the attached schedule for your comment.

Very truly yours,

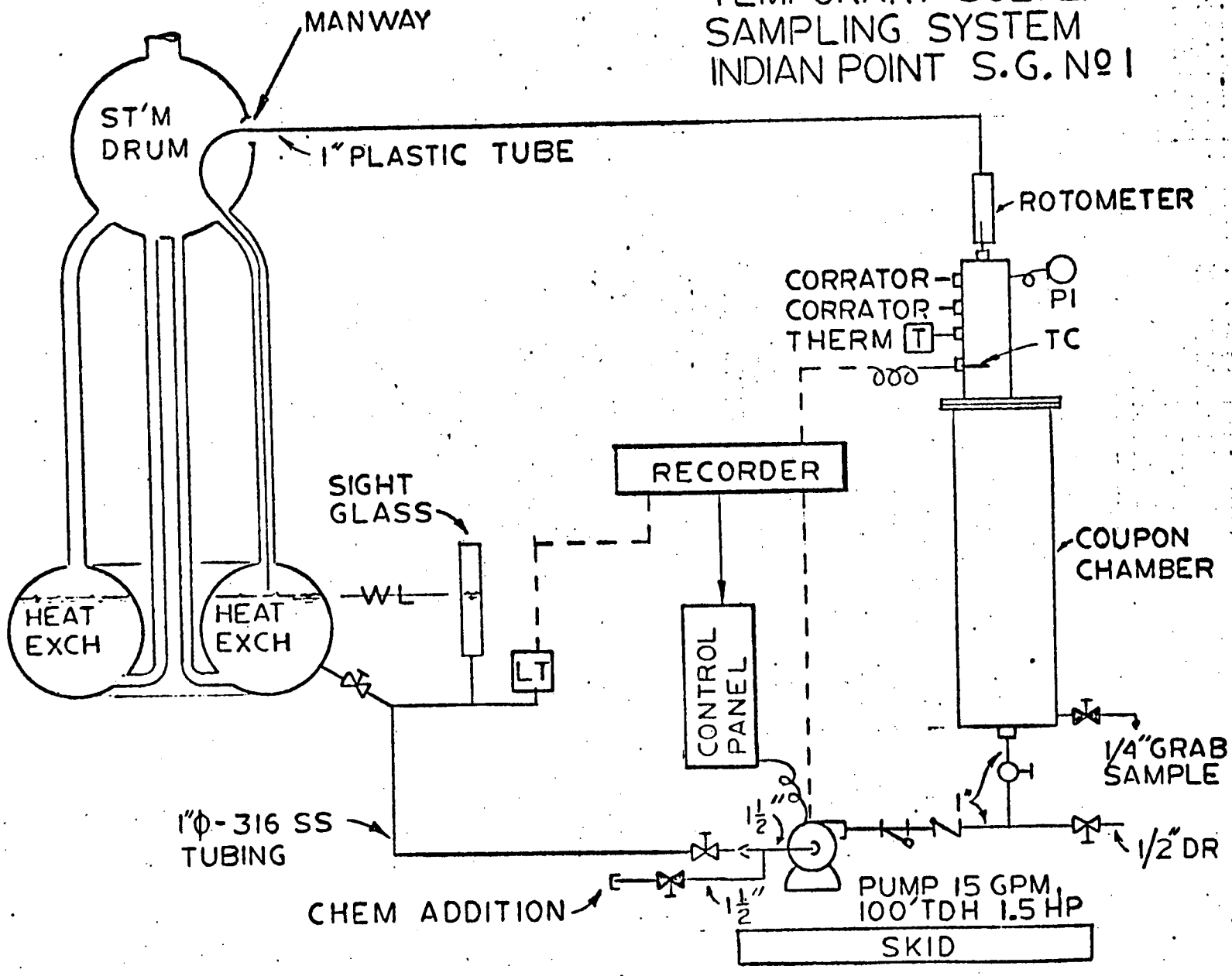
Alvin P. Larrick

Alvin P. Larrick
Project Manager

Enclosure

cc: Sam Rothstein
Paul L. Silliman
John P. Dusch

FLOW DIAGRAM TEMPORARY SOLVENT SAMPLING SYSTEM INDIAN POINT S.G. Nº 1



LINE	SYSTEM	ACTIVITY SCHEDULE AND SEQUENCE FOR PROCESS - IP-1	PRIORITY	OCTOBER 1977
				WA
1		Materials and Solvents At Site		
2		Temporary Modifications Completed		
3		Installation of Equipment Completed		
4		Prerequisites Completed		
5		Preparation Checkout Completed		
6		Approval To Start Demonstration Received		
7		Procedure:		
8		1 Preoperational Checkout		
9		Initial Line Flush		
10		Complete Checkout		
11		2 Cleaning Demonstration		
12		Mixing Chemical Solvent		
13		Line Flush with Chemical Solvent		
14		Transfer Chemical Solvent to S.G. No. 12		
15		Cleaning Demonstration and Sampling		
16		Return Chemical Solution to Storage Tank		
17		3 Demonstration System Rinsing		
18		First Rinse with Hydrazine Addition		
19		Second Rinse		
20		4 Return Demonstration System to normal		
21		5 Process Spent Chemical Solution		
22		6 Evaluation of Demonstration and Reporting		
23				
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42				
43				

T	W	T	F	S	S	M	T	W	T	F	S	S	M
18	19	20	21	22	23	24	25	26	27	28	29	30	31
G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S	G D S