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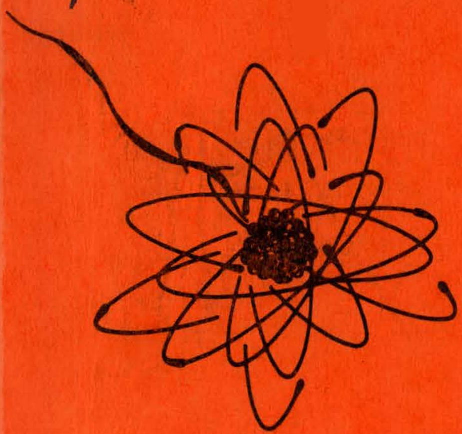

YAEC-68

MASTER

YANKEE ATOMIC ELECTRIC COMPANY
RESEARCH AND DEVELOPMENT PROGRAM

CORROSION OF AISI TYPE 304 STAINLESS STEEL IN HIGH TEMPERATURE BORATED WATER

R & D SUBCONTRACT NO. I under
USAEC-YAEC CONTRACT AT(30-3)-222

DECEMBER, 1958

WESTINGHOUSE ELECTRIC CORPORATION
ATOMIC POWER DEPARTMENT
PITTSBURGH,30 P. O. BOX 355 PENNSYLVANIA

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YAEC-68

Yankee Atomic Electric Company

Research And Development Program

CORROSION OF AISI TYPE 304 STAINLESS STEEL IN HIGH TEMPERATURE BORATED WATER

by

A. Krieg
S. J. Cytron
Nuclear Core Engineering

**For The Yankee Atomic Electric Company
Under Research and Development Subcontract
No. 1 of USAEC-YAEC Contract AT(30-3)-222**

December, 1958

APPROVED:
J. F. Chalupa, Manager
Nuclear Core Engineering

Westinghouse
ELECTRIC CORPORATION
ATOMIC POWER DEPARTMENT
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PITTSBURGH 30, PA.

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I. ABSTRACT

The corrosion of type 304 stainless steel in water containing boric acid at 600°F, 2000 psig and at a flow velocity of seven feet per second was investigated as a function of boron concentration and of alkalinity. At a boron concentration of 39 parts per million and at a pH value of 10, controlled with lithium hydroxide, no trend of corrosive attack with time was found after the first two days. At a concentration of 41 parts per million boron with no pH control (pH = 6.9), a regression type equation of the form $Y = A + B \log (t)$, was found to express the relationship between corrosive attack and exposure time. A similar relationship was found at 1600 parts per million boron with the pH value maintained at 10 using lithium hydroxide. No evidence of microstructural attack was observed on coupon specimens under any of the conditions tested. The effects of surface finish and of position were studied. The effect of orientation of the rolling direction of coupon specimens with respect to the direction of fluid flow was also investigated.

II. INTRODUCTION

The Yankee reactor is of the pressurized water type. A soluble chemical neutron absorber will be used for supplementary control of the reactor for cold shut-down and will be present at start-up. Boric acid has been selected for this purpose on the basis of work performed at several AEC installations[1,2]. Deposition of transport corrosion product (crud) in the presence of boric acid under Van de Graaff radiation has been found to exceed crud deposition in pure water[2]. An alkaline medium appears to be effective in inhibiting crud deposition in stainless steel and Zircaloy isothermal, out-of-pile systems. Lithium hydroxide appears to be more effective than ammonium hydroxide in reduction of crud deposition[2]. Either sodium hydroxide or potassium hydroxide would probably be as effective as lithium hydroxide for pH control but would lead to more severe radiochemical problems.

The major material of construction of the Yankee reactor is type 304 stainless steel. This material is to be used for cladding of fuel and the reactor vessel, for coolant piping and for the steam generator.

A series of out-of-pile tests were performed to evaluate the corrosion behavior of type 304 stainless steel at 600°F in aqueous media containing boric acid with pH adjustment to a value of 10 using lithium hydroxide. Two levels of boric acid concentration were selected for study. A boric acid concentration equivalent to 1600 parts per million boron (0.92% boric acid) was chosen to represent an upper limit for chemical shut-down concentration. A boric acid concentration equivalent to 40 parts per million boron (0.023% boric acid) was chosen to represent a nominal upper limit for steady state operation. In actual operation, the Yankee reactor will probably function with essentially boron-free coolant. However, tests involving a low boron concentration were considered desirable to establish corrosion behavior of the material at the nominal upper limit of boron for steady-state operation. In addition, a test was made at the low boron concentration (40 ppm B) with no pH adjustment to evaluate the effect of pH level on corrosion behavior. The following tests were, therefore, conducted under this program:

A. 40 ppm boron at pH = 10
B. 1600 ppm boron at pH = 10
C. 40 ppm boron at pH = 6.9

It is well known that the rate of corrosive attack on stainless steel in high temperature water is greatest during the initial period of exposure[3]. The Yankee primary coolant system will function at a high boric acid concentration for a limited period only (probably less than 500 hours). Therefore, study of corrosive attack within this period was emphasized in the investigation.

Two dynamic loops were used to carry out the test program. These were designed and built under the auspices of the Westinghouse Materials Engineering Departments and were operated by Materials Engineering Departments personnel under conditions specified by the Westinghouse Atomic Power Department.

The experiments were designed by the Experimental Design and Statistical Analysis Department of the Westinghouse Materials Engineering Departments. The tests were designed to provide information concerning the overall corrosion behavior of type 304 stainless steel and its behavior as a function of surface finish and orientation. The susceptibility of the material to stress corrosion under test conditions was also evaluated.

III. CONCLUSIONS

1. Corrosion Rate

Type 304 stainless steel corrodes to the extent of about 9 milligrams per square decimeter within two days in water containing 40 parts per million boron (present as boric acid) at a pH value of 9.8 obtained with lithium hydroxide. No further corrosion appears to occur thereafter. In water containing 40 parts per million boron with no pH adjustment (pH = 6.9), and in water containing approximately 1600 parts per million boron at a pH value of 9.8 obtained with lithium hydroxide, the corrosion rate is expressed by the relationship, $dY/dt = B/t$, after the first two days of exposure. The corrosion rate at pH = 9.8 increases with increasing boron concentration. However, the corrosion rate at 1600 parts per million boron at pH = 9.8 is less after the first two days than the corrosion rate at 40 parts per million boron with no pH control (pH = 6.9).

2. Stress Corrosion

No tendency towards stress corrosion was exhibited by stainless steel type 304 under any of the conditions tested.

3. Surface Finish and Roughness

A significant effect of surface finish on the extent of corrosion exists but is not consistent from test to test. An increase in surface roughness is found after initial exposure.

4. Rolling Direction Orientation

Exposure of metal to the fluid stream with the metal rolling direction parallel to the direction of flow of the stream increases the extent of corrosion.

5. Position

The upstream end of the test section is a more corrosive environment than the downstream end in all cases except at 40 parts per million boron with pH maintained at 9.8.

IV. EXPERIMENTAL PROCEDURE

A. Equipment

Two similar test loops (one-inch diameter schedule 40 - 347 stainless steel piping) with a volumetric capacity of 26 liters each were used for these investigations. These loops were designated as MED Loop A and MED Loop B.

Partially completed MED Loop A is shown in Figure 1 without insulation for details of assembly. Completed MED Loop A (without the pressurizer) is shown in Figure 2. Figure 3 shows the purification, sampling and chemical injection system, the control panel and the pressurizer. Figure 4 shows the pressurizer, the canned-motor pump and the make-up pump. The loops were designed for operation at temperatures up to 600°F and at pressures up to 2000 psig at a maximum flow velocity of seven feet per second (10.9 gpm) in each of two parallel test sections. All portions of the main loops were constructed of type 347 stainless steel except for certain minor parts in which type 304 ELC stainless steel was used.

A schematic diagram of the MED loops is shown in Figure 5. The test fluid was circulated by a Westinghouse Model A-11-B-2 canned-motor centrifugal pump through a heater section which consisted of a length of three-inch pipe with a one-inch thick aluminum cylinder cast around it. Strip heaters were mounted on the outside of the aluminum cylinder. A thermocouple, in a thermo-well a few inches upstream from the heaters, acted in conjunction with a standard temperature controller to activate the heaters to maintain the required loop temperature within ± 10°F. Downstream from the heater section, the flow entered a by-pass line arranged in parallel with two horizontal test section lines. The by-pass line was equipped with a throttling valve for flow control. Each test section line was equipped with a "fore" valve, a three-foot long three-inch flanged test section, orifice flanges and an "aft" valve, in that order. The test section line valves and the by-pass line permitted removal of a test section for specimen inspection without interruption of operation of the remainder of the loop. Orifice plates were available in each test section line for flow measurement. The test section lines and the by-pass line rejoined downstream from the aft test section valves and returned to the suction side of the canned-motor pump. Loop flow and temperature were continuously recorded.

Removable specimen holders were provided to fit into the test sections (Figure 6). Each holder was designed to contain seven coupon specimens.* The coupons were placed so that the flat surfaces were parallel to the direction of flow with the 1-1/8" edge perpendicular to the direction of flow. Fourteen holders were bolted together to form a specimen holder assembly with capacity for 98 specimens (Figure 7). In the tests to be described, some of the holders were used to contain U-bend specimens rather than coupon specimens. U-bend specimens were inserted with the bend facing upstream. Individual holders were

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* (2" x 1-1/8" x 1/16")

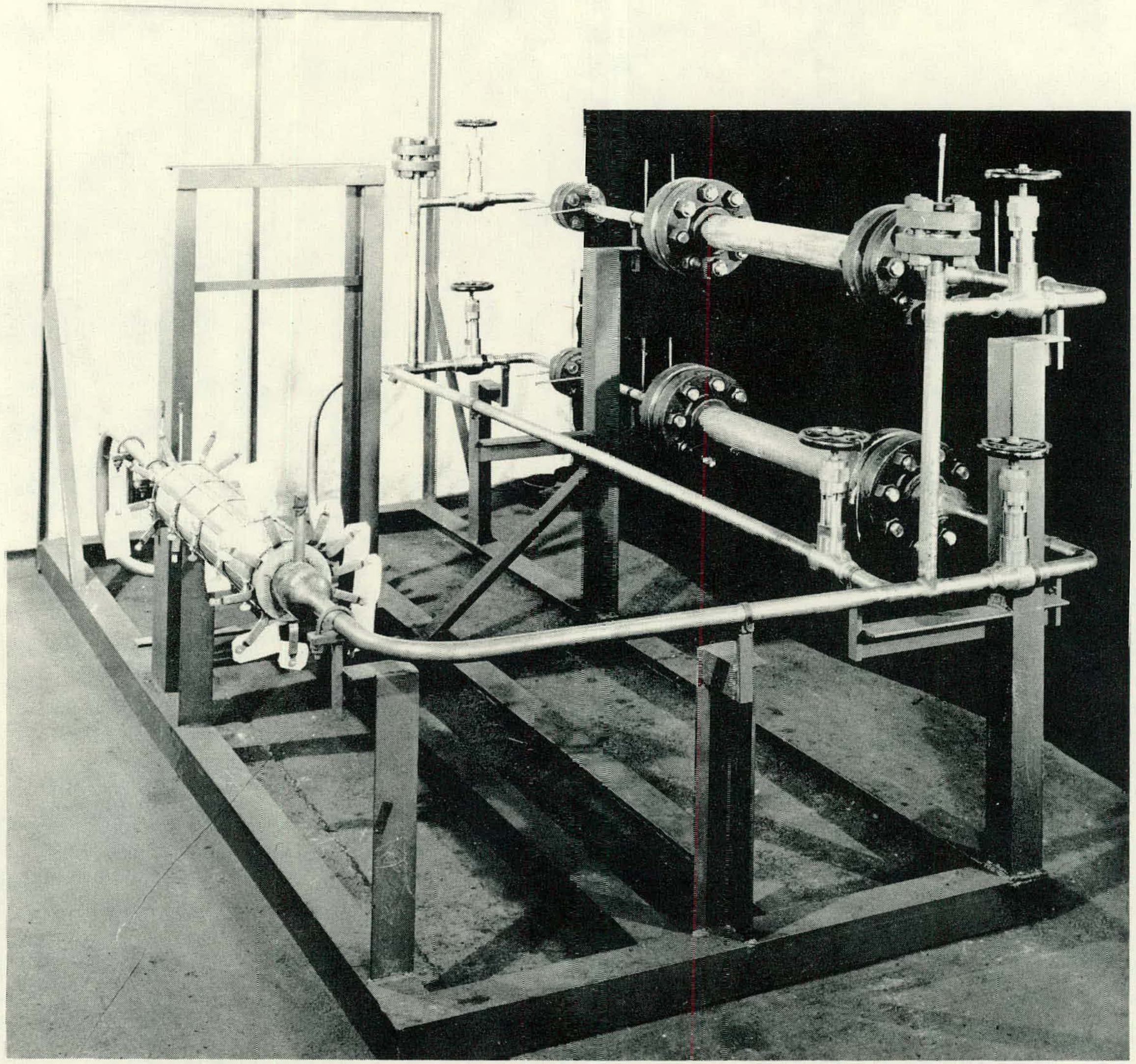


Figure 1 - Partially Completed MED Loop A

The MED Loop A is shown as fabricated by vendor, without insulation, to reveal details of assembly.

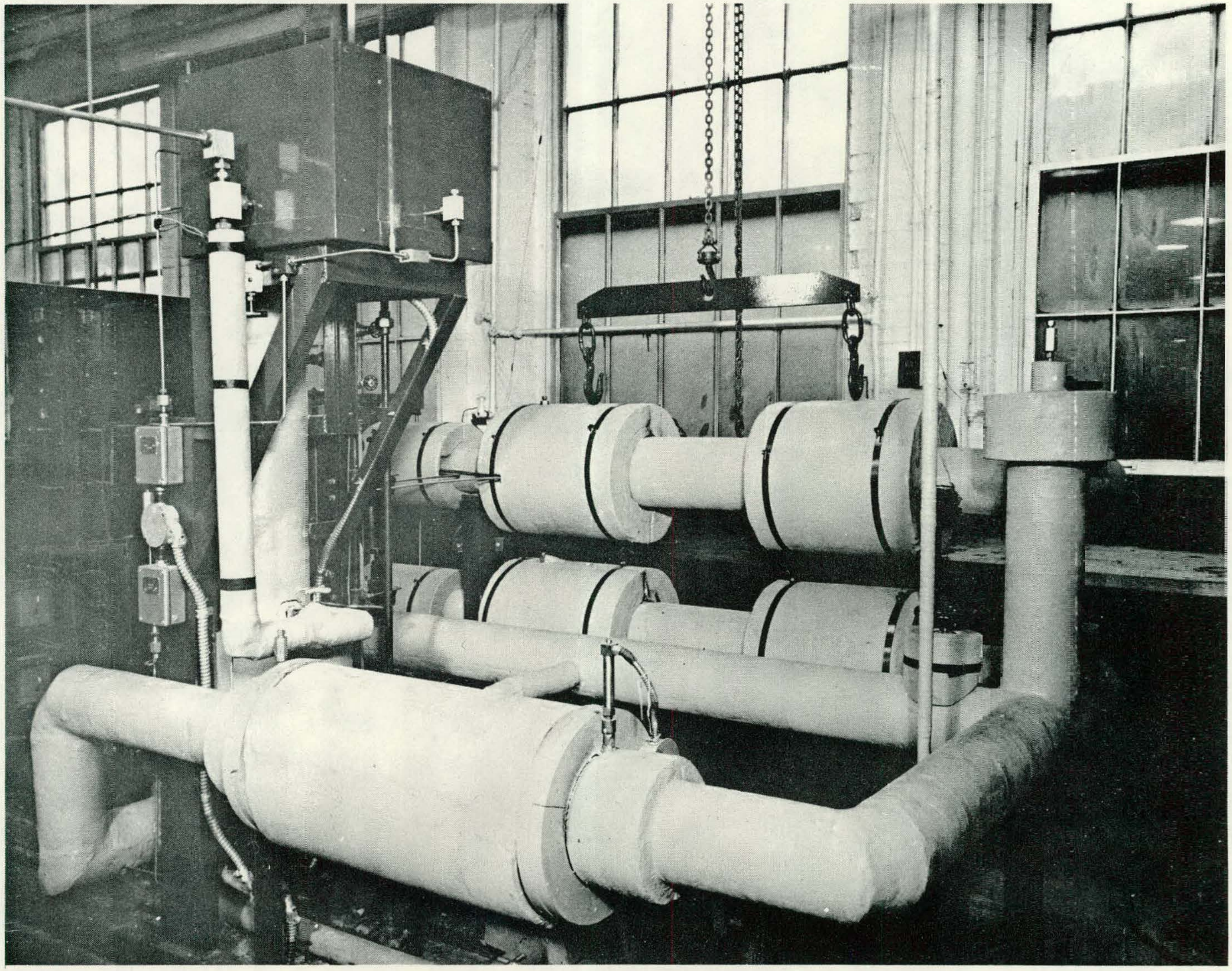


Figure 2 - Corrosion Test Loop Assembled

The assembled MED Loop A is shown, without the pressurizer, tc illustrate the general lay-out of the equipment.

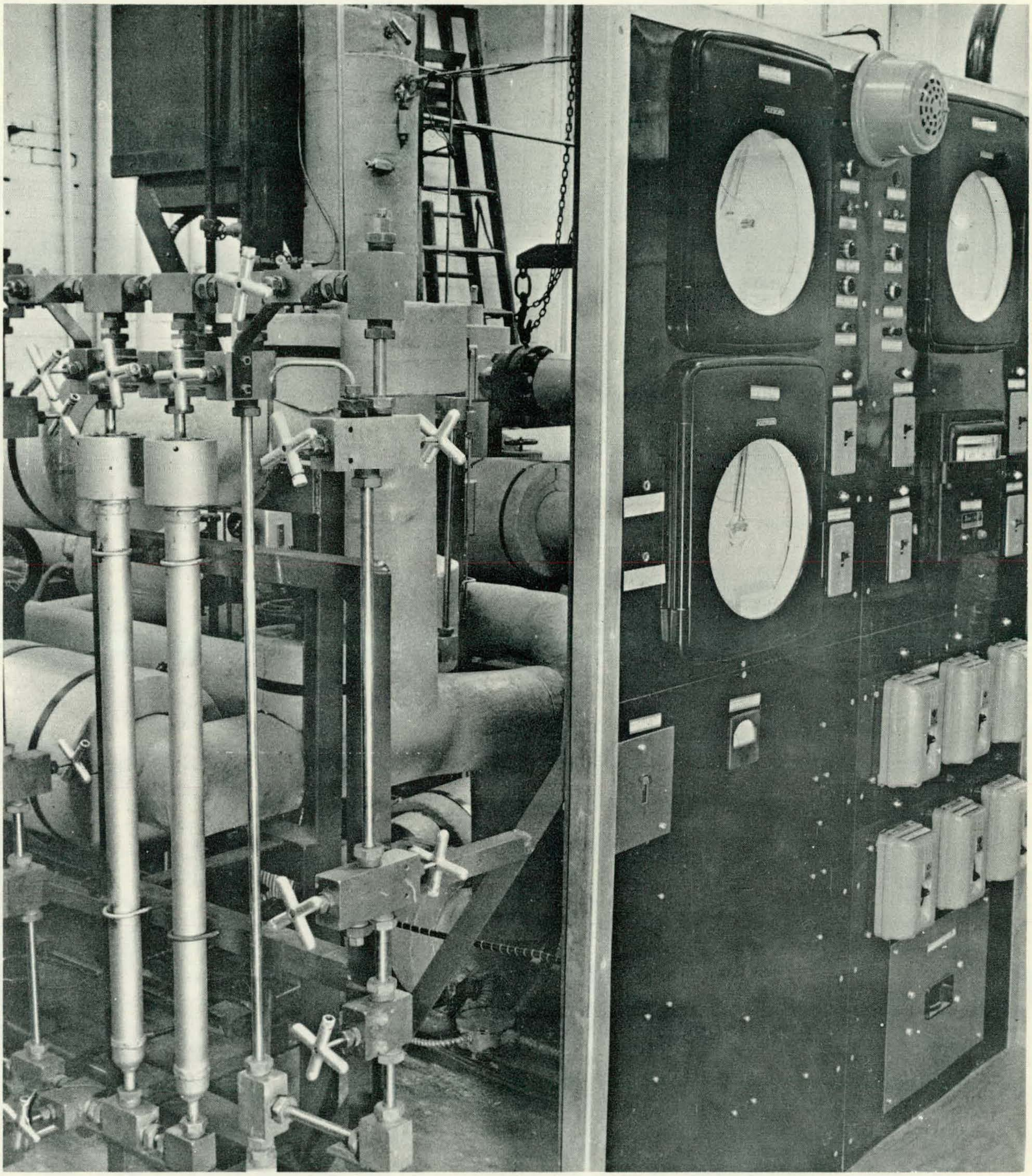


Figure 3

Close-up showing de-ionizing loop on the left, panel on the right, and de-gasser and pressurizer in upper left background.

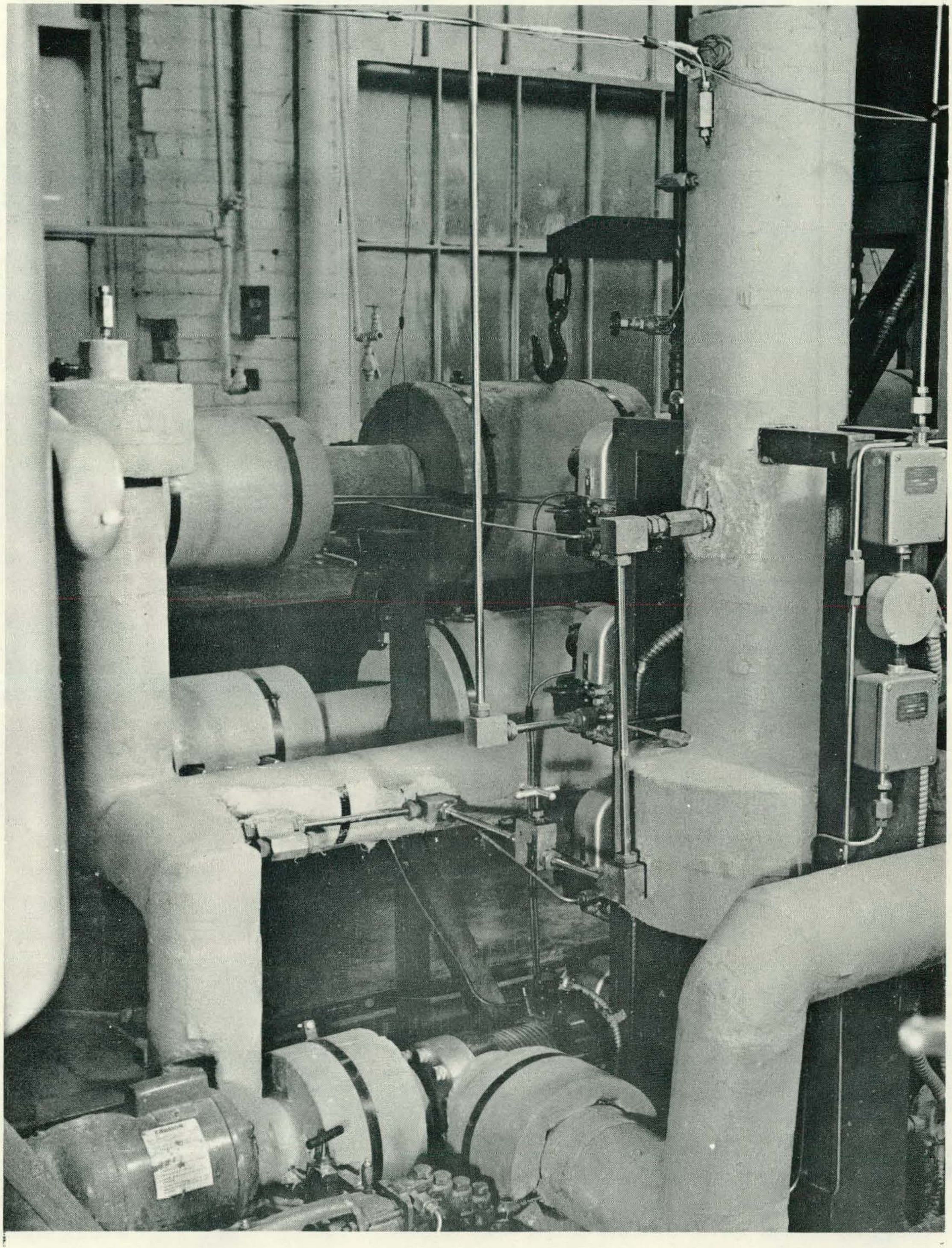


Figure 4

Closeup showing pressurizer on the right, make-up pump in lower left corner, and canned pump in lower center.

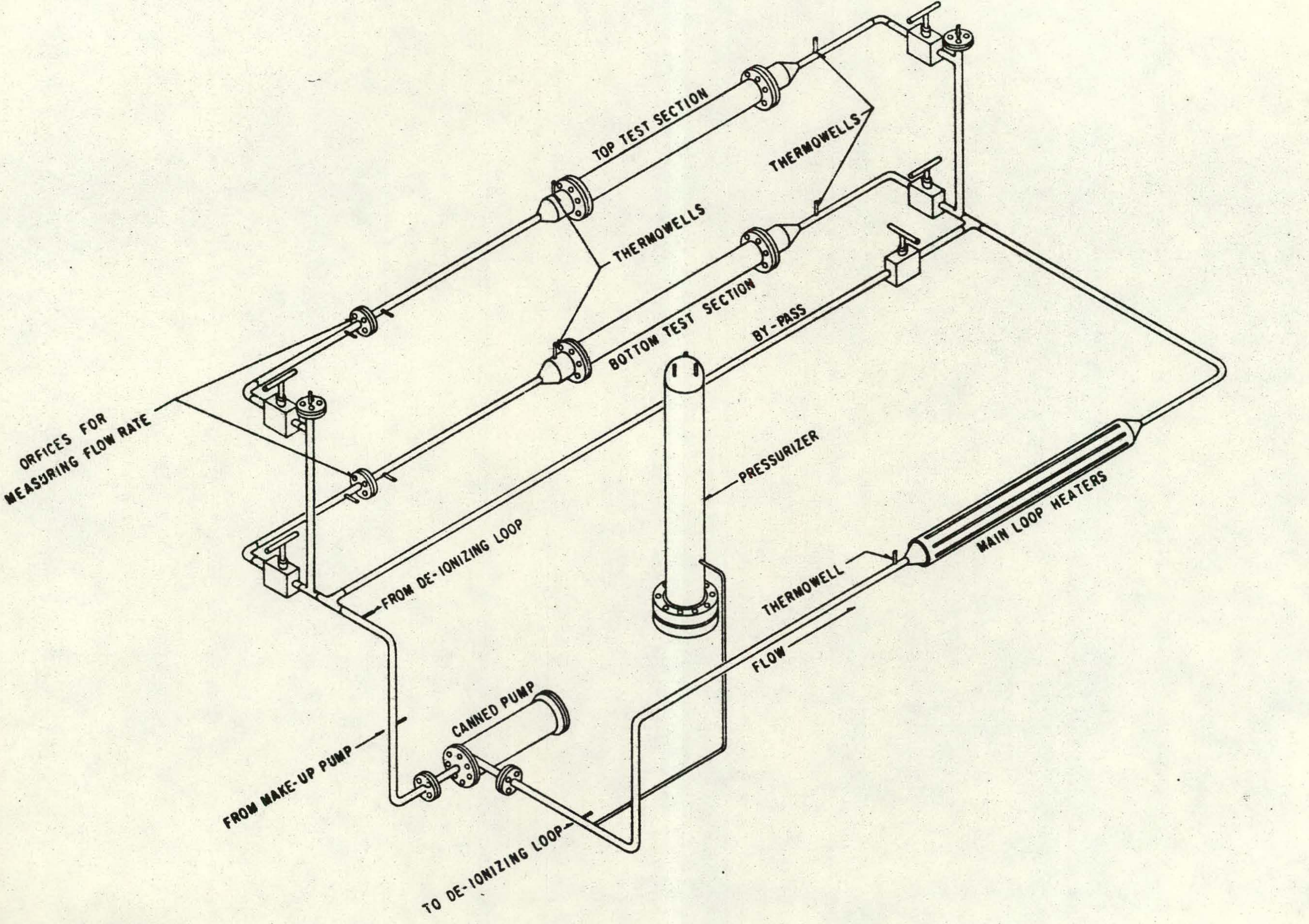


Figure 5

SCHEMATIC DIAGRAM OF CORROSION TEST LOOP

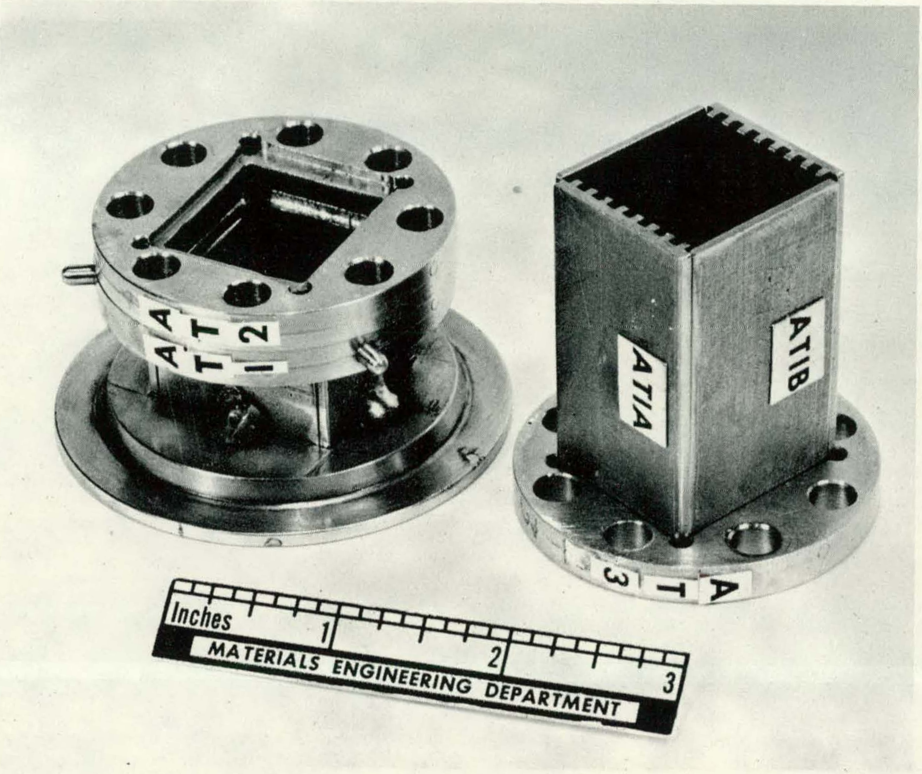


Figure 6

Coupon Holder and Holder Assembly End Flange

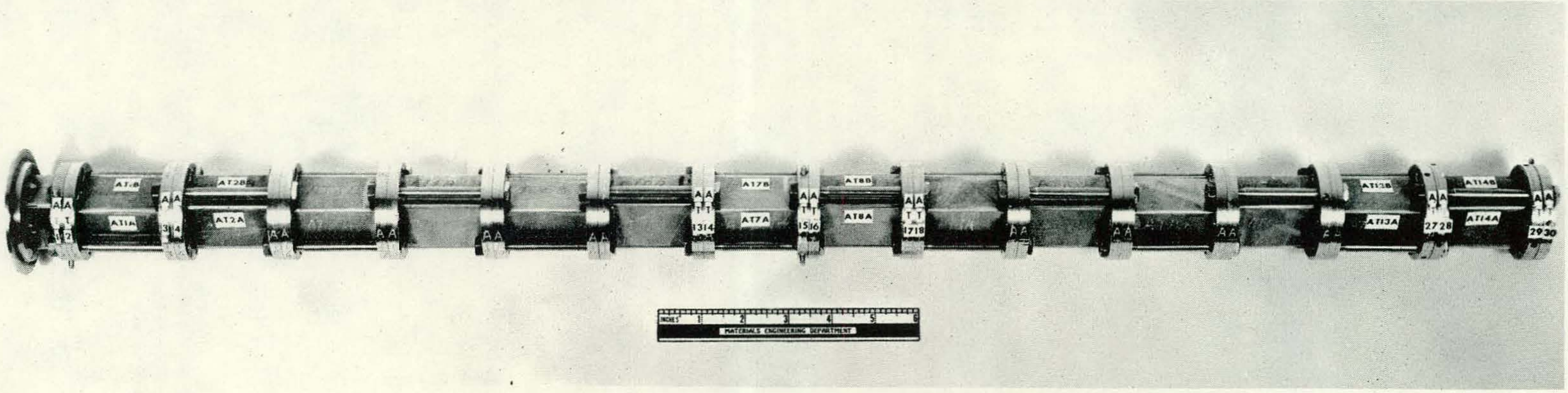


Figure 7

Coupon Holder Assembly

arranged for either vertical or horizontal orientation of coupon specimens. A special flange, shown in Figure 6, was used on the upstream end of each holder assembly to direct flow through the holders and over the test specimens. Pins were used to center the assembly along the length of the test section.

The pressurizer was a dead-ended cylinder joined to the loop on the discharge side of the canned-motor pump. It was constructed of four-inch, schedule 160, type 347 stainless steel. Immersion heaters entering through the bottom were used to supply heat for pressurization of the system. System pressure was maintained within ± 20 psi by a pressure controller-recorder which acted through control of the immersion heaters. Pressurizer level indication was obtained with an external circuit through a differential pressure cell. Pressurizer level and pressure were continuously recorded.

A side stream of approximately 1.25 gallons per hour was continuously diverted from the main loop, cooled to within a few degrees of room temperature, circulated through the purification, sampling and chemical injection system and returned to the loop. A mixed-bed ion exchange resin was used in the purification system for corrosion product removal. Bombs were provided for sampling of side stream fluid and injection of lithium hydroxide solution, boric acid solution and gaseous hydrogen, as required to maintain specified water composition. Conductivity probes were available in the side stream before and after the resin column to follow conductivity changes.

Initial loop fill was by evacuation technique. All water used for the initial charge and for make-up was distilled, demineralized, and finally de-aerated by prolonged boiling in a stainless steel tank to an oxygen content of less than 0.14 parts per million. A Milton-Roy controlled volume chemical pump (Model-43-45-SM) was used for make-up water injection.

B. Test Conditions

Loop water temperature, as controlled at the upstream end of the heater section, was maintained at 600°F ± 10°F in all tests. System pressure was maintained at 2000 psig ± 20 psi. Flow velocity, based on 0.5 in^2 flow area per test section, was maintained at seven feet per second.

Charge and make-up water characteristics were as follows:

Test No.	MEDA-1	MEDA-2	MEDB-1	MEDB-2
O_2, ppm	0.12	0.11	0.11	0.10
Specific resistivity, ohm-cm	4.4×10^5	7.3×10^5	11.3×10^5	5.6×10^5

Test duration and average loop water composition for each of the four tests are summarized below:

TABLE I

Average Loop Water Composition

Test No.	MEDA-1	MEDA-2	MEDB-1	MEDB-2
Exposure time, hr.	1560	1056	554	418
B (as boric acid), ppm	38.5 ± 1.8*	40.6 ± 1.6**	1587 ± 52**	1660 ± 79**
H_2, ml (STP)/kg solution	26.1 ± 3.6	28.7 ± 4.3	31.2 ± 3.6	31.4 ± 3.4
pH	9.8 ± 0.1	6.9 ± 0.3	9.7 ± 0.1	9.9 ± 0.1
Li (as LiOH), ppm	20.9 ± 3.9*	0	666 ± 73**	705 ± 21*
O_2, ppm	0.045	0.037	0.018	0.010
Sp. resistivity, ohm-cm	4429**	-	-	-

---

* average of values entering and leaving the purification system

** average values leaving the purification system

No significant difference was found in lithium and boron concentrations entering and leaving the purification system in Test MEDA-1. In subsequent tests, samples for analysis were generally taken at the exit from the purification system.

The analytical procedures used are described in detail in Appendix I.

C. Test Specimens

All specimens were prepared from quarter-hard, cold rolled stainless steel conforming to AISI Type 304. A metallographic examination showed the material to be of normal microstructure with relatively few non-metallic inclusions. The chemical analysis of the material was as follows:

Cr = 18.4%
Ni = 8.92
C = 0.058
Si = 0.73
S = 0.021
P = 0.025
Mn = 0.79

Two types of specimens were exposed in this investigation. Coupon specimens (2" x 1-1/8" x 1/16") were used to study general corrosion behavior. U-bend specimens were exposed to test susceptibility to stress corrosion. U-bend specimens were prepared from 4-1/2" x 3/8" x 1/16" strips. A 0.4" radius was formed in the center of each strip by bending over a 3/4" mandrel and was maintained with a threaded nut and bolt. The microstructure of the U-bend specimens before exposure was found to vary from a moderately stressed material where it had not been deformed to a severely stressed structure at the point of maximum deformation with a corresponding increase in hardness from 21 to 28 Rockwell C scale.

The coupons were divided into four groups, each of which received a different surface treatment, as follows:

Treatment	Average Initial Roughness* microinches (rms)
Surface grinding	16.22
Sanding (120 grit paper)	9.07
Electrolytic descaling	6.72
None (as-received)	6.32

* Measured with Brush Development Company Surface Analyzer (Model BL-103)

Surface roughness measurements were made after exposure in Test MEDA-1 only. Since this effect was found to be minor and these measurements were time-consuming and expensive, they were not made in subsequent tests.

The effect of preferred orientation of metal grain structure as a function of rolling direction was studied. Specimens were randomly distributed with regard to rolling direction in Test MEDA-1. The long dimension of all specimens was always oriented parallel to the direction of flow. All specimens were cut with the long dimension parallel to the rolling direction in Test MEDA-2. In Tests MEDB-1 and MEDB-2, all specimens in the top test section and half the coupons in the bottom section were cut with the long dimension parallel to the rolling direction. Half of the specimens in the bottom test section were cut with the long dimension perpendicular to the rolling direction.

A number was stamped on each specimen for identification. Coupon specimens were cleaned in a 1% Alconox solution and weighed as described in Appendix I. U-bend specimens were similarly cleaned but were not weighed.

V. EXPERIMENT DESIGN

Cleaned and weighed coupon specimens were placed in holders according to the following arrangement:

A descaled specimen occupied the middle (No. 4) position in a holder. Two sanded, two ground and two untreated (as-received) specimens were then positioned randomly within the holder with the condition that one of each type was on either side of the middle position. This group of seven coupons in each holder comprised a block which was inserted and removed from the test as a unit. In Tests MEDB-1 and MEDB-2, the pair of similar finish specimens in each holder of the bottom test section consisted of one coupon cut with the long dimension parallel to the rolling direction and the other coupon cut with the long dimension perpendicular to the rolling direction.

The holders, shown as a joined assembly in Figure 7, were oriented such that the coupon faces were disposed vertically in the odd numbered holders and horizontally in the even numbered holders. The holders were numbered serially with the extreme upstream position being No. 1 and the extreme downstream position No. 14. In the bottom test section, which in all tests was designed to remain undisturbed during the entire duration of each test, only holders 1, 2, 13 and 14 were occupied by coupon specimens. The other positions held U-bend specimens. In the top test section, which in all tests was opened periodically for removal and replacement of specimens, positions 1, 2, 3, 4, 11, 12, 13 and 14 were occupied by coupons with the remainder being occupied by U-bend specimens.

The schedule for replacement of coupon specimen holders in Test MEDA-1 is shown in Table II. Similar schedules were arranged for Tests MEDA-2, MEDB 1 and MEDB-2. These tests were not run as long as Test MEDA-1 and the schedules for coupon replacement were correspondingly shortened. All coupons removed from the test were washed, dried and weighed in accordance with the procedure described in Appendix I to obtain the "exposed" weight change. U-bend specimens were not weighed. All U-bend specimens and one out of every four similar coupon specimens were examined metallographically. The remaining coupons were electrolytically descaled[4] as described in Appendix I to determine the "descaled" weight change. No detectable weight change was found on 304 stainless steel blank specimens after electrolytic descaling. It should be noted that the electrolytic descaling procedure was not completely effective in scale removal. A very faint film of scale was retained.

The descaled weight change data was modified as a result of a more effective chemical treatment for descaling. This treatment employed a two step procedure involving a basic potassium permanganate solution and an ammonium citrate solution[7]. The laboratory procedure is described in Appendix I.

The chemical descaling solutions effectively removed the residual corrosion scale from all coupons. A weight bias was determined for each test group in order to adjust the descaled weight values for the attack of the descaling solutions on the basis metal. The bias was found to average 1.3 mg/dm^2 for the test groups. All the descaled weight values given in the tables have been corrected for this bias. The descaled weight change values used were based on the difference between the original coupon weight and the weight after chemical descaling.

TABLE II

Coupon Specimen Replacement Schedule for Test No. MEDA-1

Coupon** Group No.	Test Section	Day of Test (Running Time Only) 0	2nd	6th	14th	30th	65th	Total Days Exposed
A	Top	In	Out	-	-	-	-	2
B	Top	In	*	Out	-	-	-	6
C	Top	In	*	*	Out	-	-	14
D	Top	In	*	*	*	*	Out	65
E	Top	-	In	Out	-	-	-	4
F	Top	-	In	*	Out	-	-	12
G	Top	-	-	In	Out	-	-	8
H	Top	-	-	In	*	Out	-	24
I	Top	-	-	In	*	*	Out	59
J	Top	-	-	-	In	Out	-	16
K	Top	-	-	-	In	*	Out	51
L	Top	-	-	-	-	In	Out	35
M	Bottom	In	-	-	-	-	Out	65

---

* Coupons exposed to air on this day for 4 - 8 hours.

** See Table III.

Corrosion behavior of the test material was evaluated on the basis of "exposed" and "descaled" weight changes. The exposed weight change is defined as the weight difference between the exposed specimen and the original specimen and represents the weight of metal lost together with the weight gained by retention of scale. The descaled weight change is defined as the weight difference between the original specimen and the descaled specimen. The descaled weight change is a measure of the weight of metal lost by corrosion. The algebraic difference between the exposed weight change and the descaled weight change should be the weight of scale retained on the specimen after exposure[5]. The weight of metal released to the test fluid was calculated on the basis that the descaled weight change represented the total metal corroded and that the composition of the scale retained was represented by Fe_3O_4.[5] The amount of iron in the scale was computed and subtracted from the descaled weight loss to obtain the weight of metal released.

VI. RESULTS

A. Weight Changes as a Function of Position and Time for Holder Units in Test MEDA-1:

Exposed and descaled weight change averages for specimens in holder units as a function of position in the test section and of time of introduction and removal are illustrated in Table III for Test MEDA-1 (39 ppm boron at pH = 9.8). No trend with position or with time is evident. Specimen holder units in the bottom test section yield generally similar results to those in the top test section.

B. Weight Changes vs. Exposure Time for All Tests:

Weight change data (averages for all specimens regardless of position, finish, etc.) as a function of time of exposure are summarized for Tests MEDA-1 (39 ppm boron at pH = 9.8) and MEDA-2 (41 ppm boron at pH = 6.9) in Table IV and are shown graphically in Figures 8 and 9, respectively. Similar data is summarized for Tests MEDB-1 and MEDB-2 (approximately 1600 ppm boron at pH = 9.8) in Table V and are shown graphically in Figures 10 and 11, respectively. Test MEDA-1 shows no significant trend with time after the first two days whereas Test MEDA-2 shows a continuing increase in weight loss with time during the course of the test.

Tests MEDB-1 and MEDB-2 show a sharp initial rise in weight loss with time which apparently tends to level out thereafter. Included in Tables IV and V are calculated values for scale retained and metal released to the fluid stream. Constants A and B of the regression relationship, $Y = A + B \log t$ are shown in Table VI for all tests. These are derived from the logarithmic plots shown in Figures 12, 13, 14 and 15.

TABLE III

Averages of Exposed and Descaled Weight Changes in Test MEDA-1

Water Composition: B (as boric acid) = 38.5 ppm, pH=9.8

Coupon Group	Time, hr. In	Time, hr. Out	* Exposed Weight Change - mg/dm^2 Holder No. 1	2	3	4	11	12	13	14	* Descaled Weight Change - mg/dm^2 Holder No. 1	2	3	4	11	12	13	14
A	0	48	-2.3		-1.5				+0.8	+2.0	-6.5		-8.3				-7.8	-6.7
B	0	144		-1.9				-1.0				-7.8				-9.8		
C	0	336					0.0								-9.5			
D	0	1560				-0.6								-12.5				
E	48	144	+0.4							+0.9	-10.1							-11.1
F	48	336			+1.8				+1.4				-10.5				-12.1	
G	144	336	+1.1								-8.8							
H	144	720			+1.3			-0.4				-8.5					-8.1	
I	144	1560								-1.4								- 9.1
J	336	720	+0.3				0.0				-7.3				-7.2			
K	336	1560			+0.5				-3.0				- 5.2				-7.1	
L	720	1560	-1.8	-1.8			-4.8	-3.2			-7.1	-6.5				-7.2	-7.9	
M**	0	1560	-0.5	+0.4					+1.7	+2.4	-11.6	-11.7					-14.1	-12.6

* Negative signs indicate weight losses

** Bottom test section. This section was undisturbed during entire duration of test.

TABLE IV

Summary of Weight Change Data
(Tests MEDA-1 and MEDA-2)

Total Exposure Time, hr.	TEST NO. MEDA-1				TEST NO. MEDA-2			
	Average** Wt. Change-mg/dm^2		Scale Retained mg/dm^2	Metal Released, mg/dm^2	Average** Wt. Change-mg/dm^2		Scale Retained mg/dm^2	Metal Released mg/dm^2
	Exposed	Descaled			Exposed	Descaled		
48	-0.3	-7.2	6.8	2.3	-0.4	-11.9	11.5	3.6
96	+0.6	-10.6	11.4	2.5	-1.3	-15.2	13.8	5.1
144	-1.4	-8.7	7.2	3.5	-0.6	-13.3	12.7	4.2
192	+1.1	-8.7	9.9	1.6	-4.9	-21.7	16.6	9.7
240					-5.5	-23.9	18.4	10.6
288	+1.6	-11.4	12.9	2.0	-5.1	-23.4	18.4	10.2
336	0.0	-9.5	9.5	2.6				
384	+0.2	-7.2	7.6	1.9	-5.8	-23.1	17.4	10.6
576	+0.5	-8.4	8.7	2.0	-7.1	-25.4	18.3	12.1
624					-7.3	-26.8	19.5	12.8
840	-3.0	-7.2	4.2	4.2				
960					-7.8	-27.3	19.3	13.4
1224	+0.1	-6.1	6.5	1.6				
1416	-1.4	-9.1	8.0	3.6				
1560	-0.6	-12.5	11.8	3.8				
Entire Test Duration*	+1.0	-12.5	13.3	2.8	-9.9	-31.9	22.3	15.8

* Specimens in bottom test section. These were not disturbed during entire duration of test.

** Negative values are weight losses.

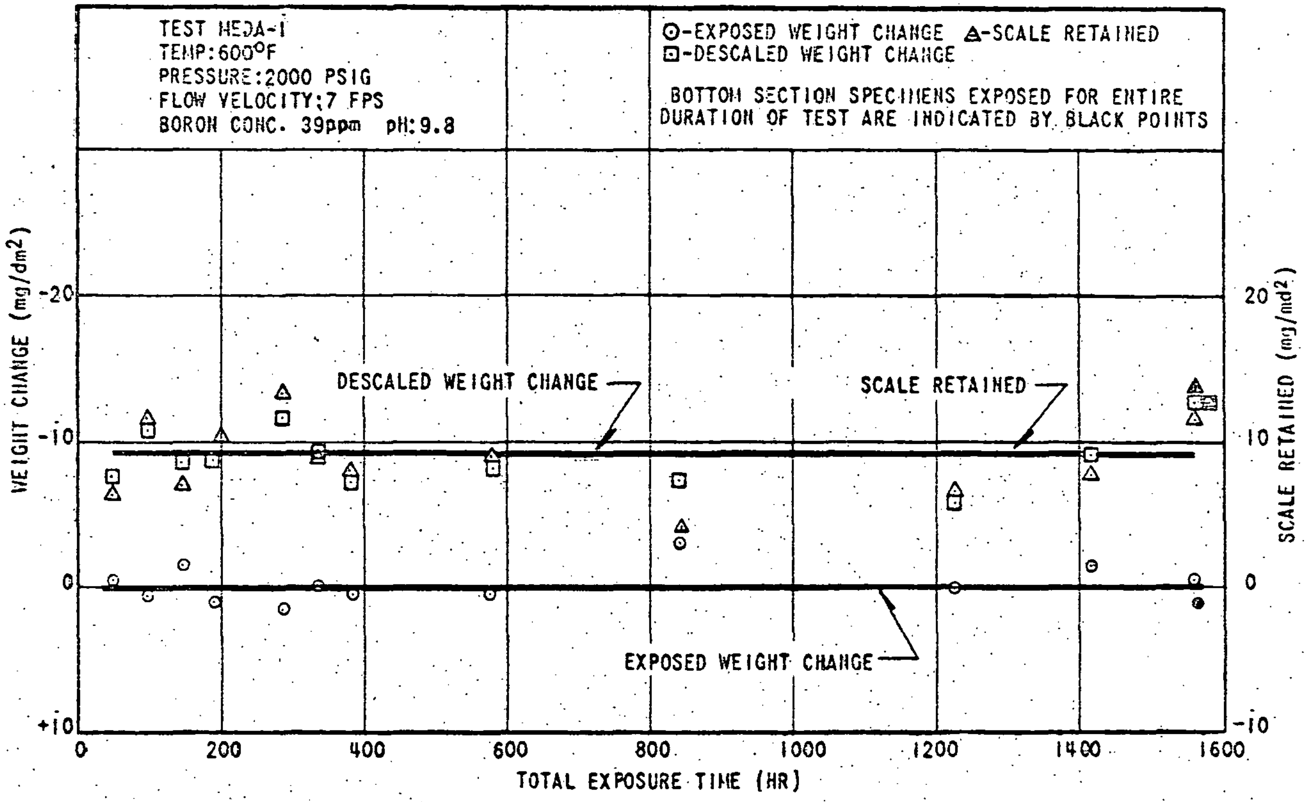


FIGURE 8 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF EXPOSURE TIME (TEST HEDA-1)

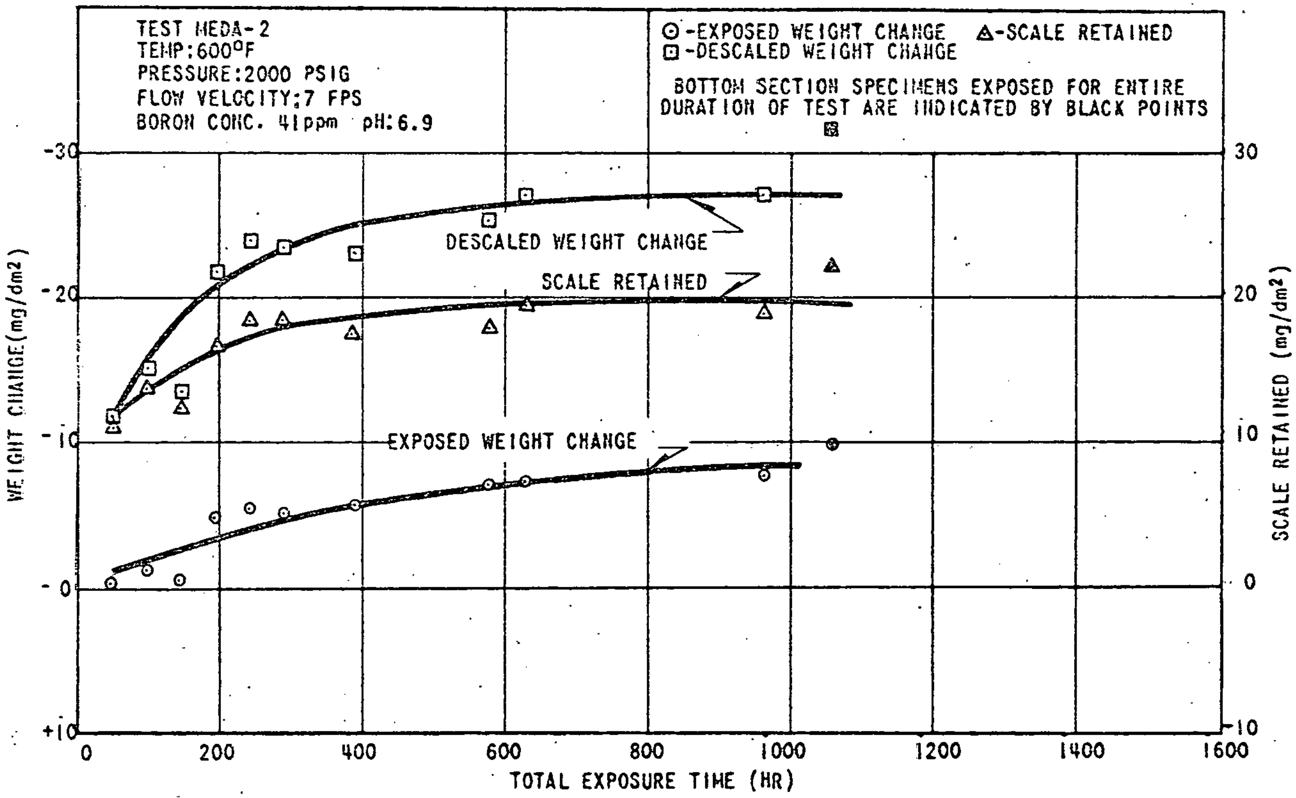


FIGURE 9 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF EXPOSURE TIME (TEST MEDA-2)

TABLE V

Summary of Weight Change Data
(Tests MEDB-1 and MEDB-2)

Total Exposure Time, hr.	TEST NO. MEDB-1				TEST NO. MEDB-2			
	Average Wt.Change* - mg/dm^2		Scale Retained mg/dm^2	Metal Released, mg/dm^2	Average Wt.Change*-mg/dm^2		Scale Retained mg/dm^2	Metal Released mg/dm^2
	Exposed	Descaled			Exposed	Descaled		
48	-3.4	-20.1	16.7	8.0	-2.9	-17.4	14.5	7.0
96	-4.9	-22.9	18.0	9.8	-5.1	-22.9	17.7	10.1
144	-5.3	-23.4	18.1	10.4	-4.8	-23.0	18.1	9.9
192	-6.8	-27.4	20.7	12.4				
216	-9.5	-34.6	25.0	16.5				
264					-8.4	-30.5	22.2	14.5
288	-6.1	-24.9	18.8	11.3				
360					-7.5	-27.2	19.7	13.1
408	-6.8	-30.1	23.1	13.4	-6.0	-28.0	21.5	12.5
552	-6.8	-27.2	20.7	12.2				
Entire Test Duration**	-4.2	-21.8	17.6	9.1	-4.0	-21.6	17.8	8.8

* Negative values indicate weight losses.

** Specimens in bottom test section. These were not disturbed during the entire duration of each test.

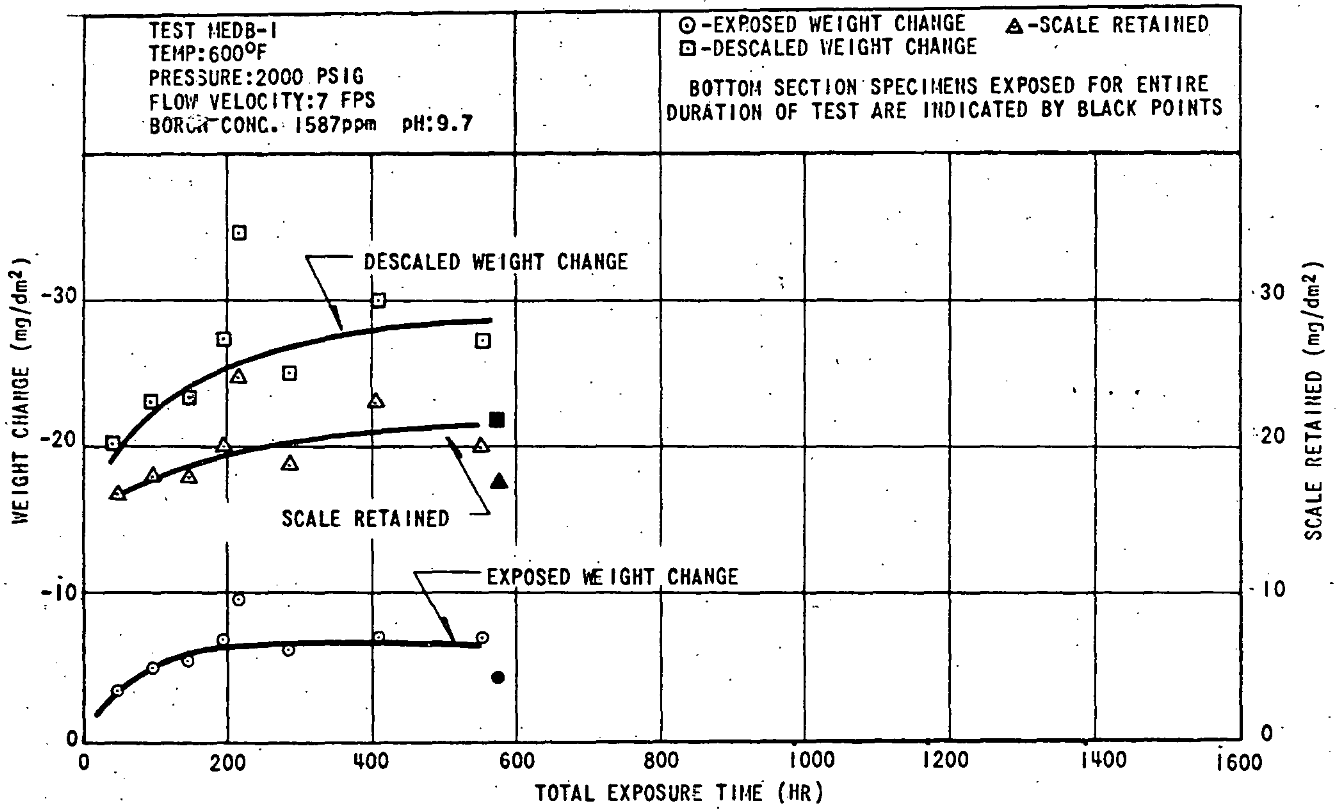


FIGURE 10 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF EXPOSURE TIME (TEST MEDB-1)

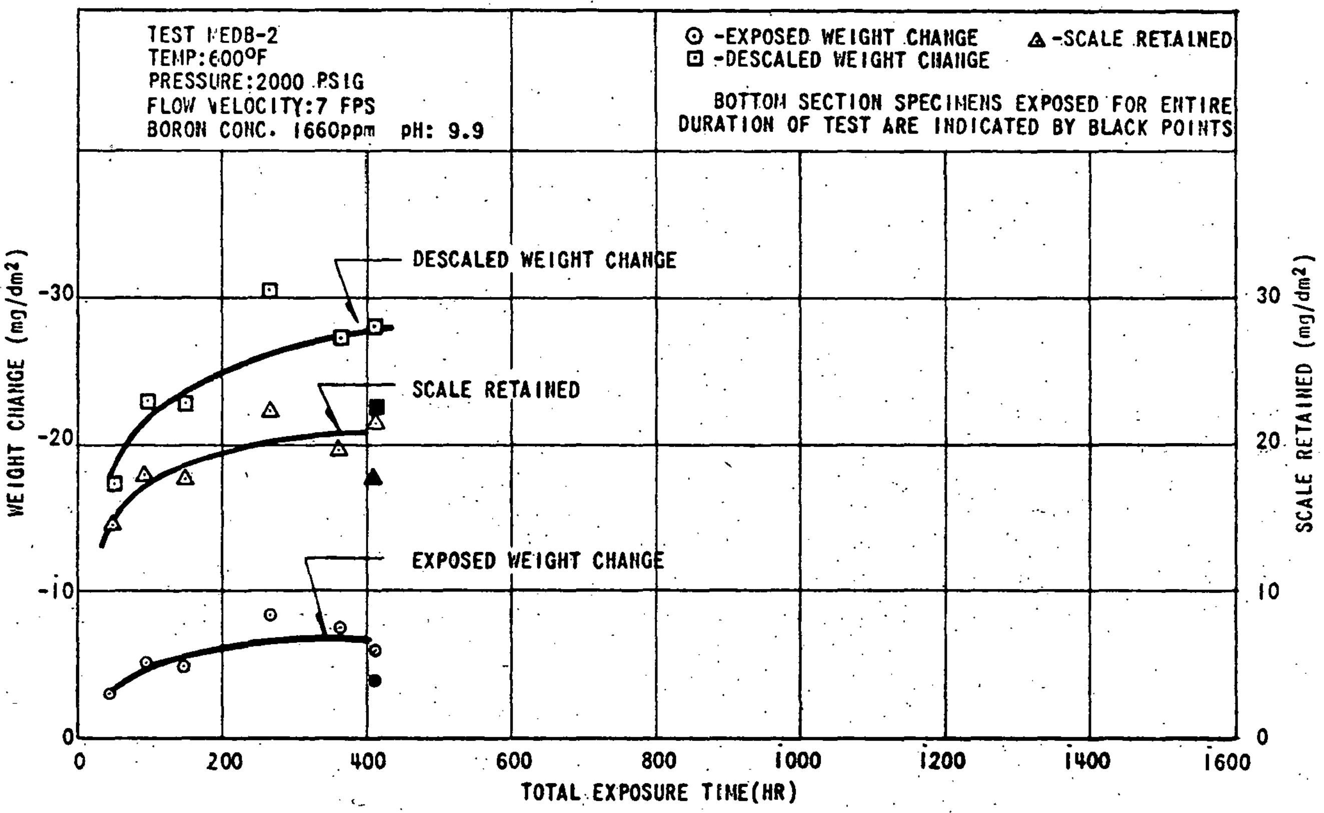


FIGURE 11 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF EXPOSURE TIME (TEST MEDB-2)

C. Weight Changes vs. Surface Finish and Position for All Tests:

Averages of the weight change data for the various surface finishes and positions, are shown in Table VII for all tests. Significant differences appear between different surface finishes but these are not consistent from test to test. The upstream position appears to be more subject to corrosive attack than the downstream position in all tests except test MEDA-1 where no significant position effect was found.

D. Surface Roughness Changes in Test MEDA-1:

Surface roughness changes are summarized in Table VIII for specimens exposed in Test MEDA-1. These measurements were made before exposure and after electrolytic descaling following exposure. An increase in roughness is found as a result of exposure and descaling.

E. Effect of Rolling Direction:

A comparison of weight changes for specimens exposed during the entire course of Tests MEDA-2, MEDB-1 and MEDB-2 is shown in Table IX to illustrate the effect of specimen orientation as regards rolling direction, with respect to the direction of fluid flow. Parallel orientation of rolling direction with fluid flow increases the extent of attack.

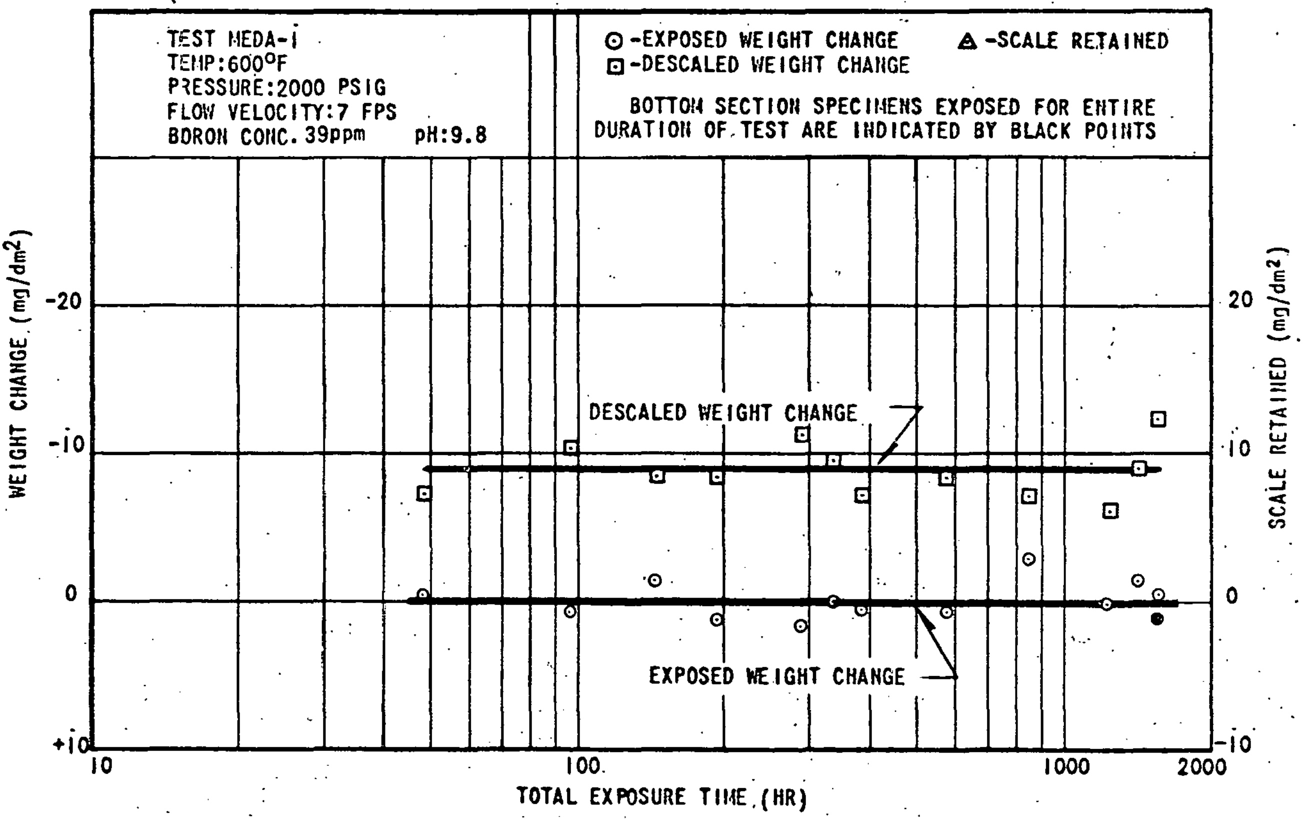
TABLE VI

*Constants of the Regression Relationship Y = A + B log (t)

	Water Composition		Exposed Weight Change, mg/dm^2		Descaled Weight Change, mg/dm^2		Scale Retained mg/dm^2	
Test No.	B, ppm	pH	A	B	A	B	A	B
MEDA-1	39	9.8	-	0	-	0	-	0
MEDA-2	41	6.9	+ 12.8	- 7.2	+ 11.5	- 13.7	+ 0.4	+ 6.8
MEDB-1	1587	9.7	+ 0.5	- 2.9	- 8.7	- 7.5	+ 9.3	+ 4.7
MEDB-2	1660	9.9	+ 3.9	- 4.4	- 3.7	- 9.0	+ 5.5	+ 5.8

* Derived from Figures 12, 13, 14, and 15

FIGURE 12 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF THE LOGARITHM OF EXPOSURE TIME (TEST MEDA-1)



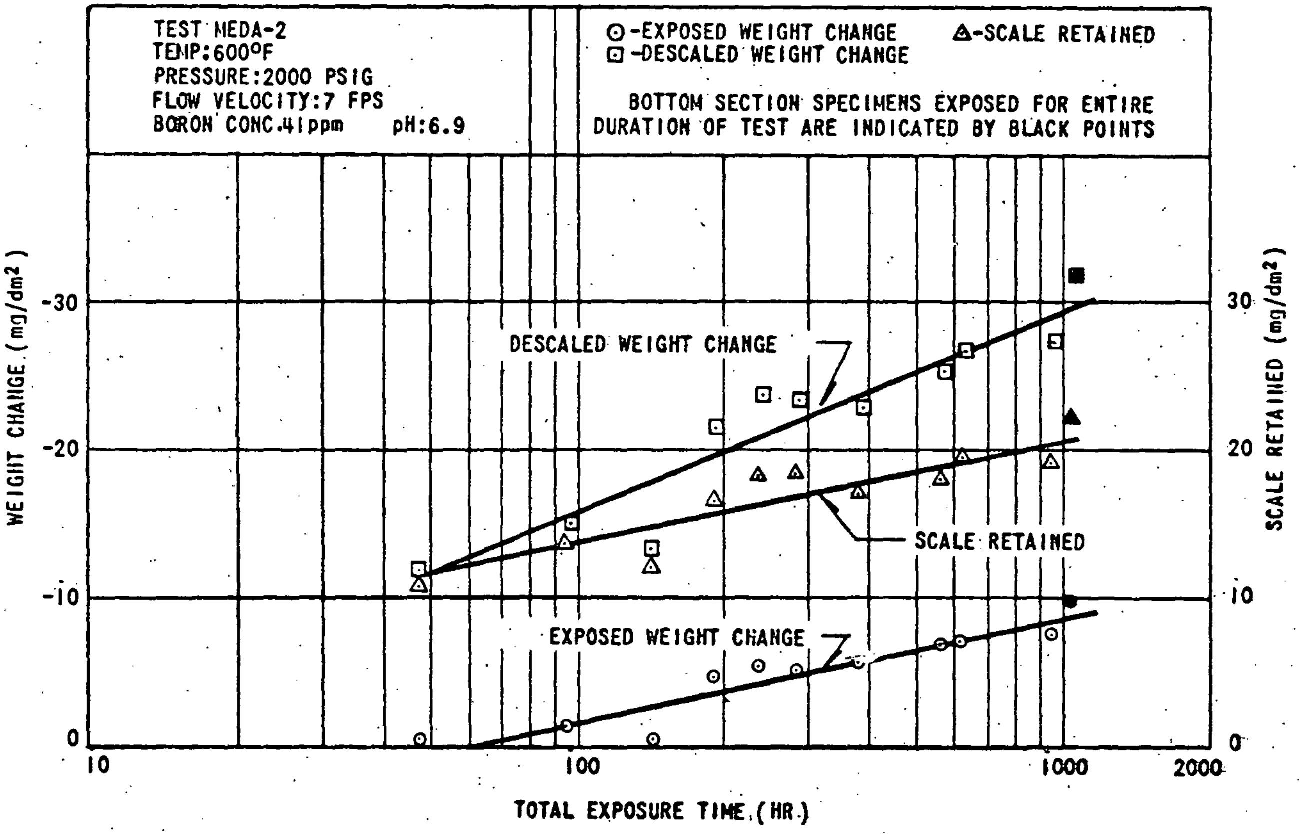


FIGURE 13 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF THE LOGARITHM OF EXPOSURE TIME (TEST MEDA-2)

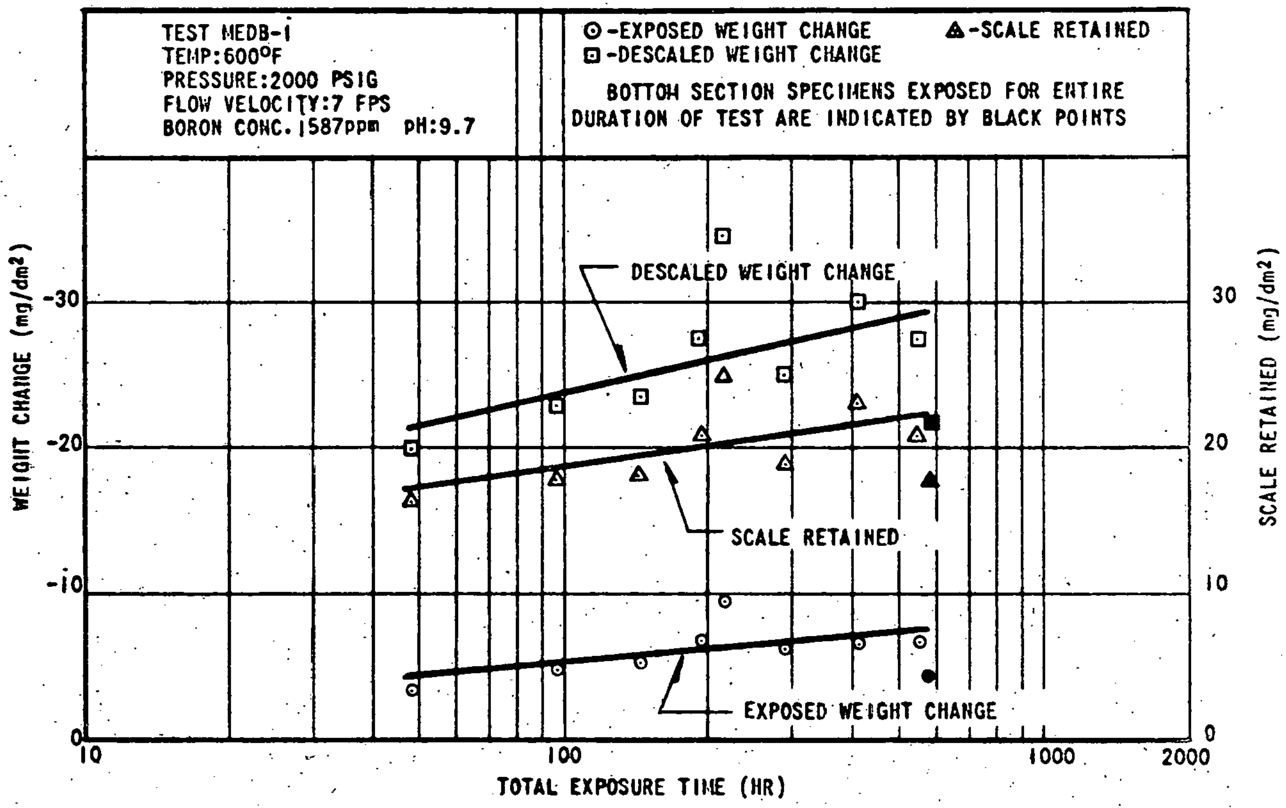


FIGURE 14 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF THE LOGARITHM OF EXPOSURE TIME (TEST MEDB-1)

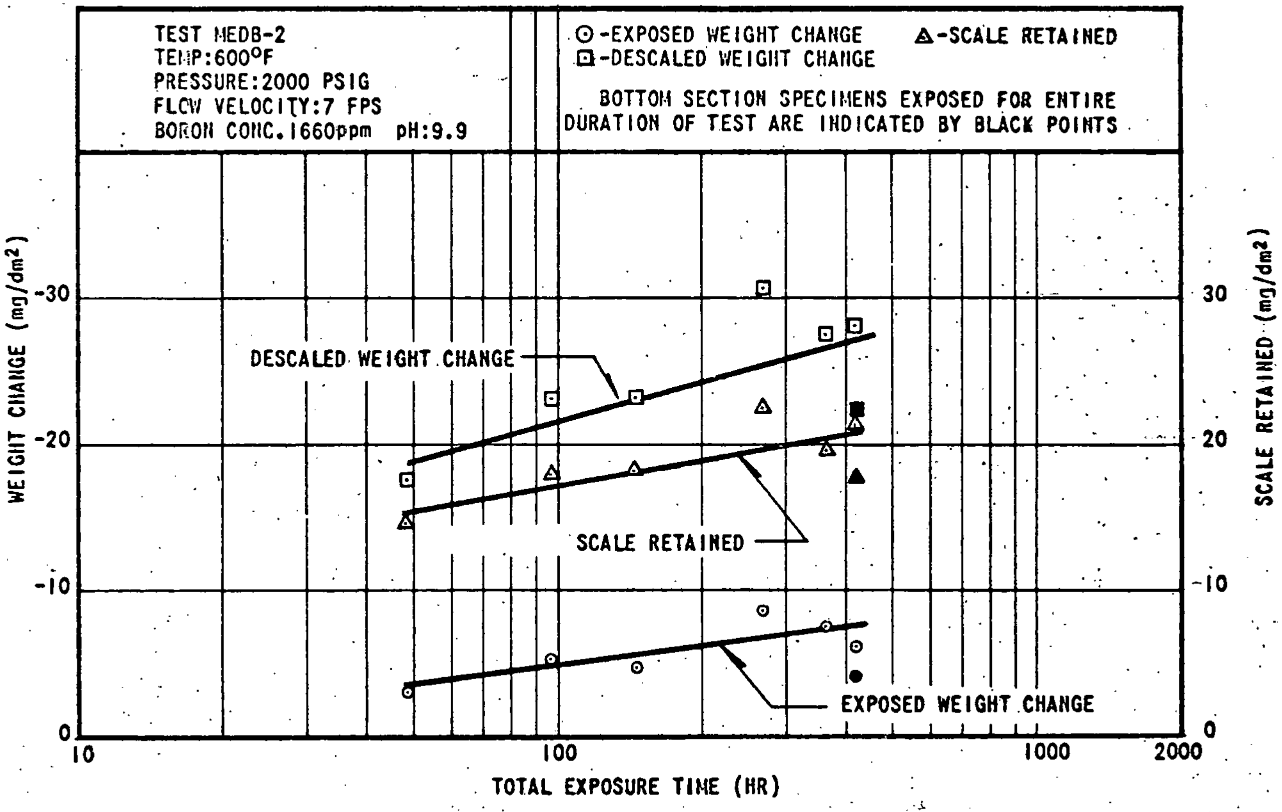


FIGURE 15 - WEIGHT CHANGES OF 304 STAINLESS STEEL IN WATER AS A FUNCTION OF THE LOGARITHM OF EXPOSURE TIME (TEST MEDB-2)

TABLE VII

Average Weight Change as a Function of Special Effects

Effect	*Exposed Weight Change (mg/dm^2)				Descaled Weight Change (mg/dm^2)			
	Test No. MEDA-1	Test No. MEDA-2	Test No. MEDB-1	Test No. MEDB-2	Test No. MEDA-1	Test No. MEDA-2	Test No. MEDB-1	Test No. MEDB-2
Overall	- 0.3	- 4.9	- 5.6	- 5.1	- 9.0	- 22.2	- 25.0	- 23.5
As-received	- 0.1	- 4.2	- 5.2	- 5.7	- 8.8	- 20.4	- 24.5	- 26.8
Descaled	+ 1.1	- 3.8	- 4.4	- 4.0	- 7.8	- 19.1	- 24.2	- 20.7
Sanded	- 0.6	- 6.1	- 6.3	- 6.2	- 9.3	- 27.5	- 26.4	- 24.7
Ground	- 0.5	- 4.5	- 5.7	- 3.8	- 9.1	- 18.8	- 24.1	- 20.0
Upstream	- 0.3	- 6.0	- 6.6	- 5.9	- 8.6	- 23.0	- 27.1	- 25.5
Downstream	- 0.2	- 3.8	- 4.6	- 4.3	- 9.3	- 21.4	- 22.8	- 21.5
Bottom Section	- 0.9	- 9.7	- 4.3	- 3.7	- 12.4	- 31.9	- 21.8	- 21.6
Top Section	- 0.2	- 4.2	- 6.2	- 5.9	- 8.4	- 20.7	- 26.4	- 24.5

* Negative values represent weight losses.

TABLE VIII

Surface Roughness* Change as a Function of Surface Finish (Test MEDA-1)

Surface Finish	Average Initial Roughness, Microinches (rms)	Average Final Roughness, Microinches (rms)	% Increase in Roughness**
As-received	6.32	7.39	17
Descaled	6.72	7.53	12
Sanded	9.07	9.88	9
Ground	16.22	18.23	12

* measured in microinches (rms)

** increase over initial roughness after electrolytic descaling of exposed specimens.

TABLE IX

*Average Weight Loss as a Function of Orientation of Rolling Direction of the Metal Coupons with Respect to the Flow Direction of the Test Fluid

Test No.	Test Section	Orientation	No. of Specimens	Exposure, hr.	Weight change, mg/dm^2**		Scale Retained mg/dm^2	Metal Released mg/dm^2
					Exposed	Descaled		
MEDA-2	Top	Parallel	8	960	- 8.0	- 27.3	19.3	13.4
	Bottom	Parallel	17	1056	- 9.5	- 31.9	22.3	15.8
MEDB-1	Top	Parallel	8	552	- 6.4	- 27.2	20.7	12.2
	Bottom	Parallel	22	576	- 4.4	- 22.2	17.7	9.3
	Bottom	Perpendicular	23	576	- 4.0	- 21.3	17.5	8.9
MEDB-2	Top	Parallel	8	408	- 6.0	- 28.0	21.5	12.5
	Bottom	Parallel	22	408	- 4.3	- 23.0	18.4	9.7
	Bottom	Perpendicular	23	408	- 3.1	-20.3	17.2	7.8

* Specimens exposed in top and bottom test sections for the entire duration of each test. Note that top test section specimens were periodically exposed to air at scheduled test section openings. Bottom test sections were not exposed to air for duration of test.

** Negative values indicate weight losses.

VII. DISCUSSION OF RESULTS

No change in the microstructure of the stainless steel specimens (either coupon or U-bend) was found as a result of exposure to any of the conditions tested. Intergranular or transgranular cracking was not observed. In one instance, pitting was found which was shown to be due to the presence of non-metallic inclusions.

Tests MEDA-1 and MEDA-2 were performed under similar conditions and at a boron concentration of 40 parts per million (present as boric acid) except that in Test MEDA-1, the pH value was maintained at 9.8 with lithium hydroxide whereas in Test MEDA-2, with no pH adjustment, the pH value averaged 6.9. No significant exposed weight change was detected in Test MEDA-1 (Tables III and IV; Figures 8 and 12) and no significant trend of exposed weight change with time was noted. Similarly, the descaled weight changes, beginning with the first inspection at 48 hours exposure, yielded an average weight change of -9.0 mg/dm^2 with no significant trend as a function of time. The results obtained from specimens exposed in the bottom test section, which were not disturbed during the entire course of the experiment, were in good agreement with those obtained in the top test section. The weight of scale retained (measured by the algebraic difference between the exposed and descaled weights) remained essentially constant and equal to the descaled weight change (-9.0 mg/dm^2). In Test MEDA-2, however, exposed and descaled weight changes varied with time (Table IV and Figures 9 and 13) according to a regression relationship of the type:

$$Y = A + B \log (t)$$

where Y is the weight change per unit area (mg/dm^2), t is the exposure time in hours and A and B are contants determined from the data by a least squares procedure. Values of constants A and B are shown in Table VI. These constants are strictly valid only within the time interval from 48 hours to the total exposure time in the test. Constant A is related to the corrosion suffered by the stainless steel during the initial two-day period by a corrosion mechanism which may be presumed to become inactive within that period of time. Constant B is related to corrosion occurring after the first two days as defined by the expression, $dY/dt = B/(t)$ where dY/dt is the corrosion rate.

Tests MEDA-1 and MEDA-2 may be compared at 1000 hours of exposure, with data from the curves in Figures 12 and 13. This comparison is shown in Table X.

More scale appears to have been retained at the lower pH condition together with an increase in metal corroded as compared to the higher pH condition. The B constant for the regression relationship is essentially zero in the high pH condition whereas a relatively high rate is indicated by the B constant for the low pH condition.

Test MEDB-1 and MEDB-2 are compared with Test MEDA-1 at 400 hours exposure time, using the curves shown in Figures 12, 14 and 15 to show the effect of increasing boron concentration at the same pH level. (Table XI).

TABLE X

Comparison of Results of Tests MEDA-1 and MEDA-2 at 1000 Hours of Exposure

(Constant boron concentration with pH variation)

Test No.	MEDA-1	MEDA-2
B, ppm	39	41
pH	9.8	6.9
Exposed weight change, mg/dm^2	0	- 8.9
Descaled weight change, mg/dm^2	- 9.0	- 29.5
Scale retained, mg/cm^2	9.0	20.9
Constant B (Table VI) for descaled weight changes	0	-13.7

TABLE XI

Comparison of Results of Tests MEDA-1, MEDB-1 and MEDB-2 at 400 Hours of Exposure

(Constant pH with varying boron concentration)

Test No.	MEDA-1	MEDB-1	MEDB-2
B, ppm	39	1587	1660
pH	9.8	9.7	9.9
Exposed weight change, mg/dm^2	0	-7.1	-7.5
Descaled weight change, mg/dm^2	-9.0	- 28.0	- 27.0
Scale retained, mg/dm^2	9.0	21.5	21.0
Constant B (Table VI) for descaled weight changes	0	- 7.5	- 9.0

The effect of increasing boron concentration at constant, elevated pH appears to increase the extent and rate of corrosion.

No effect due to position of the holders within the test section (upstream-downstream effect) was found in Test MEDA-1. In Test MEDA-2 and in Tests MEDB-1 and MEDB-2, corrosive attack was consistently more severe at the upstream end of the test section (Table VII). No satisfactory explanation for this result has been obtained although its existence should be noted in the design of future experiments.

Although significant differences appear in Table VII for the weight losses corresponding to different surface finishes, these are not consistent from test to test and may be due to variations in the preparation of batches of specimens. The change in roughness as a function of initial surface finish was measured in Test MEDA-1 (Table VIII). The roughness increases after exposure but the increase depends on the initial surface roughness.

The effect of orientation of the rolling direction of the coupon specimens with respect to the direction of flow of the test fluid was studied in Tests MEDB-1 and MEDB-2 as shown in Table IX. In Test MEDA-1, specimens were randomly distributed with respect to rolling direction. In Test MEDA-2, the specimens were all oriented with the rolling direction parallel to the flow direction. In Tests MEDB-1 and MEDB-2, all top section specimens had parallel orientation whereas in the bottom section half were oriented in a parallel manner and half were oriented in a perpendicular manner. Specimens with parallel orientation were attacked more severely than specimens with perpendicular orientation. No explanation for this effect is currently available. An observation concerning the effect of rolling direction on stress corrosion cracking of niobium stabilized 18-8 type stainless steel, containing between 11 and 12% nickel has been reported.[6] Two stressed specimens were exposed to water containing sodium chloride (18 ppm chloride). One specimen cut with the "grain" of the metal parallel to the length of the strip failed by cracking in four hours. The other specimen, with the "grain" of the metal perpendicular to the length of the specimen, remained in the solution for 50 days with no apparent effect except slight pitting.

VIII. GENERAL OBSERVATIONS

Periodic analyses were made to determine the iron, nickel and chromium content of loop water entering and leaving the purification system. In Tests MEDA-1, MEDB-1 and MEDB-2, mixed-bed resins consisting of 80% cation resin in the lithium form were used. In Test MEDB-1, the anion resin was initially in the hydroxyl form whereas in Test MEDB-1 the anion resin was initially saturated with boric acid. Fresh resin beds were used in Tests MEDA-1 and MEDB-1. The resin was not replaced in the transition from Test MEDB-1 to MEDB-2. A fresh hydrogen-hydroxyl form mixed-bed resin was used in Test MEDA-2 since this test was made without lithium hydroxide addition.

Trends could not be definitely established for chromium and nickel because of the low concentration level at which they occurred in all tests. Average values for chromium and nickel entering and leaving the purification system were:

Test No.		MEDA-1	MEDA-2	MEDB-1	MEDB-2
Cr (ppm),	entering	0.002	0.003	0.004	0.003
	leaving	0.002	0.003	0.003	0.003
Ni (ppm),	entering	0.010	0.012	0.020	0.009
	leaving	0.006	0.010	0.020	0.007

The results for iron are summarized in Table XII. In Test MEDA-1, iron concentration decreased sharply within the first few days as a result of a sharply decreasing corrosion rate with relatively effective assistance from the purification system. Similarly, the fresh mixed-bed lithium-borate form resin in Tests MEDB-1 appears to have been effective in maintaining iron at a low level. The same resin-bed was re-used in Test MEDB-2 without regeneration. In this case, the resin bed appeared to have no effect on the level of iron concentration and essentially complete break-through occurred immediately. In Test MEDA-2, the fresh mixed-bed hydrogen-hydroxyl form resin appears to have been completely ineffective in iron removal due to channeling.

Leakage at main loop valves (packing glands) and at flanged joints occurred in Test MEDA-1 and was so severe in Test MEDB-1 to warrant premature termination of the latter test. In Tests MEDA-2 and MEDB-2, the valve packing problem was solved after several trials with various packings by the use of bulk form Carbonite (a graphitized asbestos material manufactured by the Anchor Packing Co.). Tight valves were obtained with this material after several thermal cycling and tightening operations. The flanged joint leakage problem was not solved satisfactorily. Massive deposits of material containing lithium and boron were found externally at these joints in Tests MEDB-1 and MEDB-2. During the course of Test MEDB-1, considerable internal deposition of white, crystalline-appearing material was found at the upstream end of the upper test section only at the 14-day scheduled opening as shown in Figures 16, 17, 18, and 19. This had not been found previously nor was it present subsequently. The composition of this material was 6.4 w/o Li and 19.3 w/o B corresponding to a lithium-boron ratio of 0.33. Loop water composition in this test involved an average lithium-boron ratio of 0.42. An X-ray pattern could not be obtained on the deposited material. This material is, therefore, not related to crystalline deposits which have been reported to form in high temperature water systems containing lithium hydroxide and boric acid[2]. These reported deposits yield X-ray patterns and were found to correspond in chemical composition to anhydrous lithium metaborate ($LiBO_2$) in which the lithium content is 14 w/o and the boron content is 22 w/o with a lithium-boron ratio of 0.64. At the termination of the test (MEDB-1), no internal deposition was found in the bottom test section which had been onstream during the entire test. It is concluded that improper let-down of

TABLE XII

Purification System Removal of Iron

Time, hr.	TEST MEDA-1		TEST MEDA-2		TEST MEDB-1		TEST MEDB-2	
	Fe, ppm		Fe, ppm		Fe, ppm		Fe, ppm	
	Entering	Leaving	Entering	Leaving	Entering	Leaving	Entering	Leaving
24	.185	.036						
48	.099	.034	.070	.060				
72					.365	.048	.055	.045
96								
120					.240	.048	.055	.035
144	.030	.020						
168	.042	.018	.075	.057	.165	.021	.030	.040
192			.069	.050				
216					.120	.017	.035	.025
240			.040	.035				
264					.090	.020	.035	.030
288	.022	.006	.040	.045				
312	.022	.009			.085		.035	.025
336	.017	.009	.045	.040				
360	.019	.003			.060	.016	.040	.030
384	.013	.003						
408	.014	.003	.045	.025	.012	.005	.030	.030
432	.015	.003	.035	.030				
456	.015	.006			.005	.006		
480	.001	.007	.035	.057				
504	.012	.002			.009	.007		
528	.011	.002	.015	.030				
552	.010	.004			.009	.005		
576	.008	.004	.030	.015				
624	.018	.004	.025	.040	.009	.005		
720	.031	.004	.025	.030				
840			.040	.030				
960			.035	.025				
1080	.013	.007	.035	.030				
1152			.035	.030				
1560	.013	.007						

the upper test section at the 14-day opening resulted in evaporation of test fluid contained in the section at that time. Lithium tetraborate pentahydrate ($Li_2B_4O_7 \cdot 5\ H_2O$) contains 5.6 w/o lithium and 17.4 w/o boron with a lithium-boron ratio of 0.32. This material is reported to be amorphous. The material deposited internally appears to be quite similar to lithium tetraborate pentahydrate.

At the termination of Test MEDB-1, a white film was found internally around the bottom portion of the pressurizer as shown in Figures 20 and 21. Material deposited on the heaters (Figure 20) contained 2.5 w/o lithium and 4.1 w/o boron. Material deposited on the pressurizer wall (Figure 21) contained 6.5 w/o lithium and 12.3 w/o boron. The amount of material deposited in the pressurizer and the volume of solution from which it appeared to have formed indicate that this deposit resulted from evaporation during the course of the shutdown operation.

Further evidence supporting the conclusion that improper operation during Test MEDB-1 was responsible for internal deposits is as follows:

1. Test MEDB-2 was performed to check the observations made in Test MEDB-1 concerning internal deposits. Although massive deposition of lithium-boron containing material occurred externally at all flanged joints, no internal deposition was observed either in the test sections or in the pressurizer.

2. Previously reported lithium metaborate deposits[2] had been obtained under autoclave conditions. A static autoclave test was carried on for 1000 hours at 600°F with 1600 ppm boron (as boric acid) adjusted to a pH value of 9.5 with lithium hydroxide (720 ppm lithium). The autoclave was opened at 200 hour intervals for specimen inspection. The water was analyzed for lithium and boron and pH values were obtained at each opening. Fresh water of the specified composition was used for each test period. No significant changes in water composition were noted and no evidence of deposition of lithium-boron containing material was observed.

Malfunctioning of the pressurizer level indicator forced two shut-downs during Test MEDA-1. Periodic venting of the pressurizer vapor phase appeared to relieve the condition which may have been due to hydrogen accumulation in the vapor phase. During the course of these shutdowns and at the conclusion of the test, the pressurizer was dismantled and examined. No evidence for deposition of lithium-boron compounds was obtained. No evidence for such deposition was noted during the frequent routine openings of the test sections during the test.

Chemical and water make-up data for all runs are summarized in Table XIII.

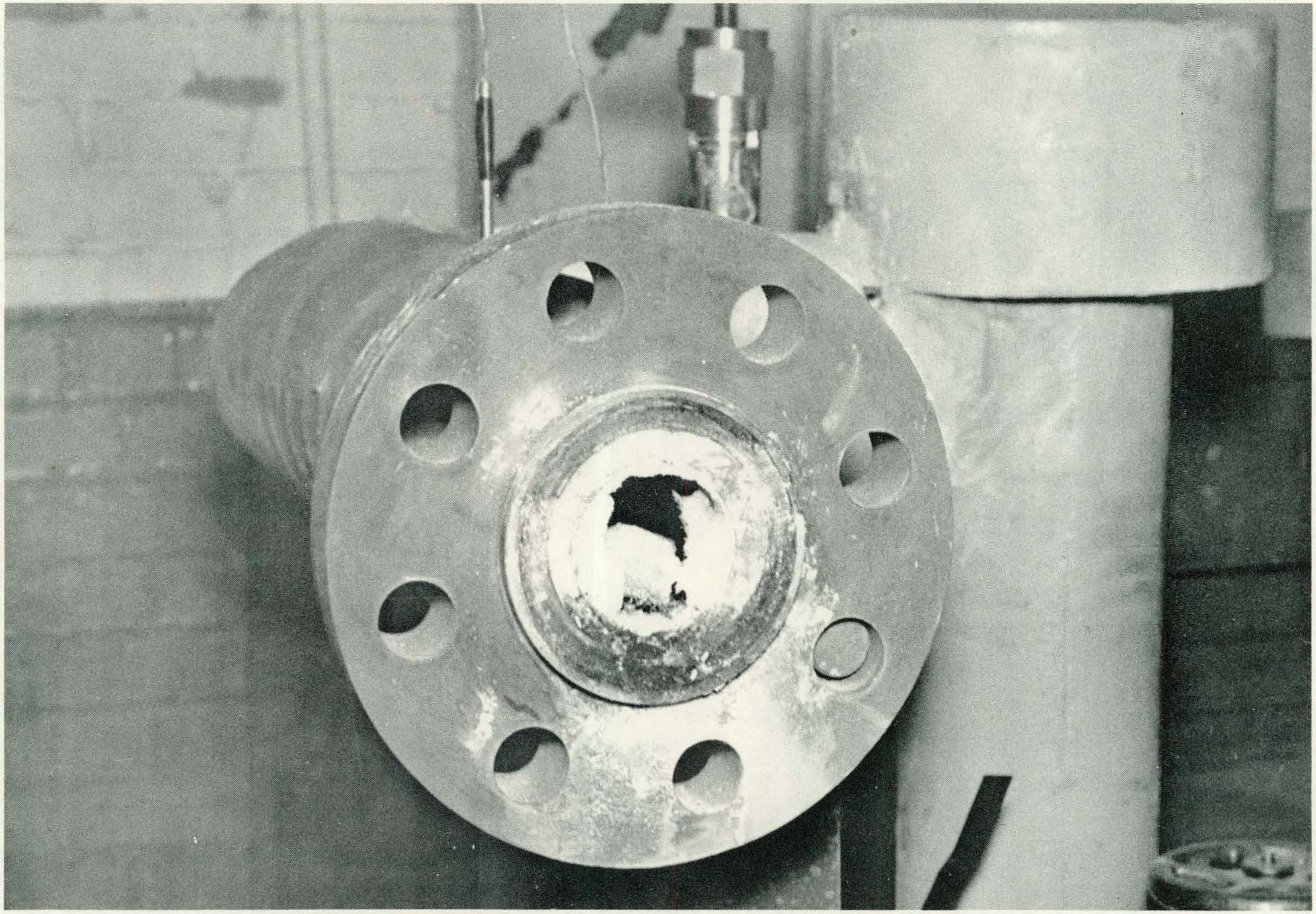


Figure 16 - Upstream Loop Flange Deposit (Test MEDB-1)

A white, low density, crystalline appearing material containing lithium and boron is shown. This was found internally adjacent to the upper test section upstream flange at the scheduled 14-day test section opening in Test MEDB-1 (1585 ppm boron at pH = 10).

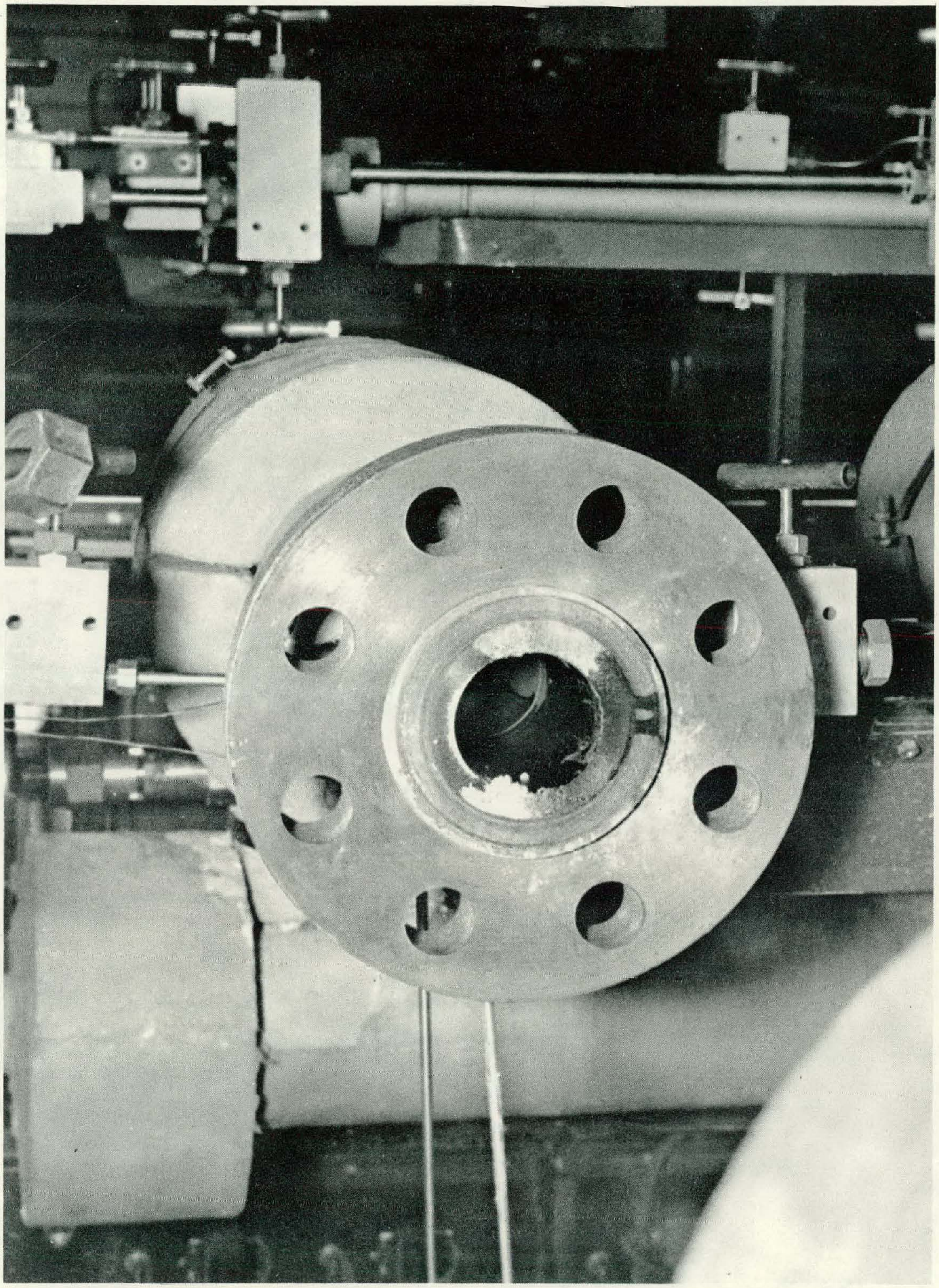


Figure 17 - Downstream Loop Flange Deposit (Test MEDB-1)

A small quantity of translucent film was found internally. This material which contained lithium and boron was found internally adjacent to the upper test section downstream flange at the scheduled 14-day test section opening in Test MEDB-1 (1587 ppm boron at pH = 10).

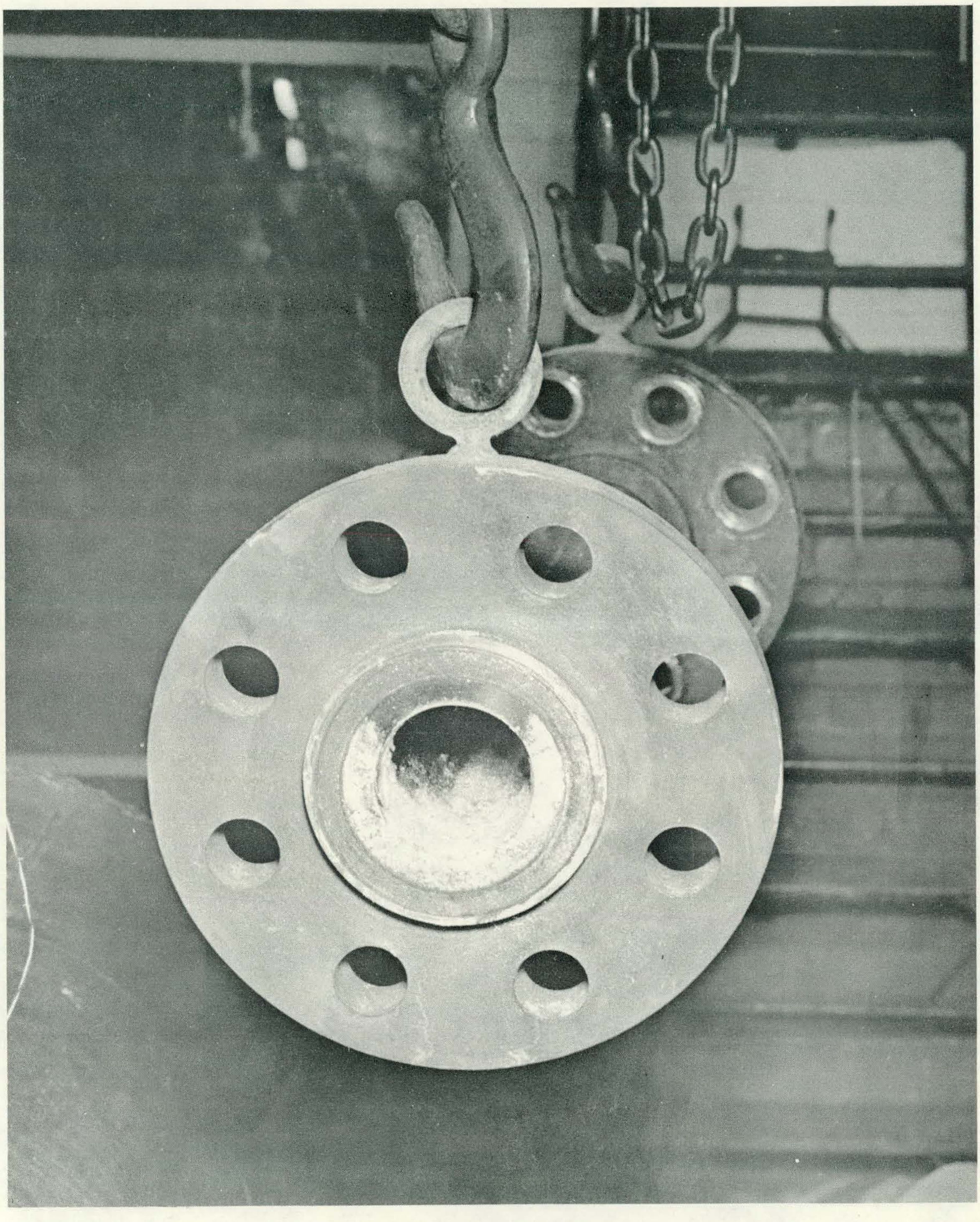


Figure 18 - Upstream Test Section Flange Deposit (Test MEDB-1)

The test section is shown with the holder coupon removed. This end of the test section was adjacent to the flange shown in Figure 16. The white material shown was of the same composition as the material shown in Figure 16.

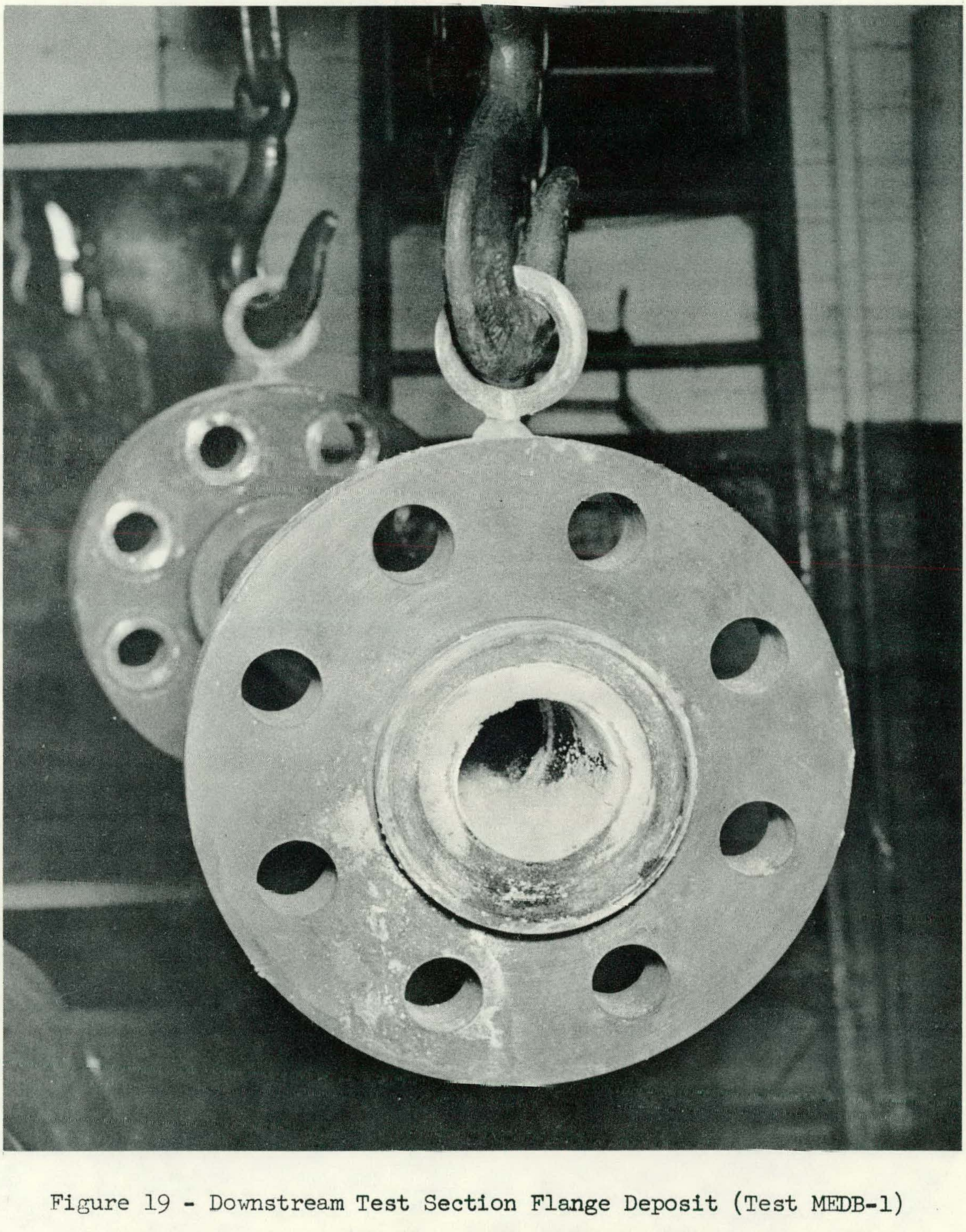


Figure 19 - Downstream Test Section Flange Deposit (Test MEDB-1)

The test section is shown with the coupon holder removed. The flange shown is the companion flange to the one shown in Figure 17. Only a thin film of white material was found at this location.

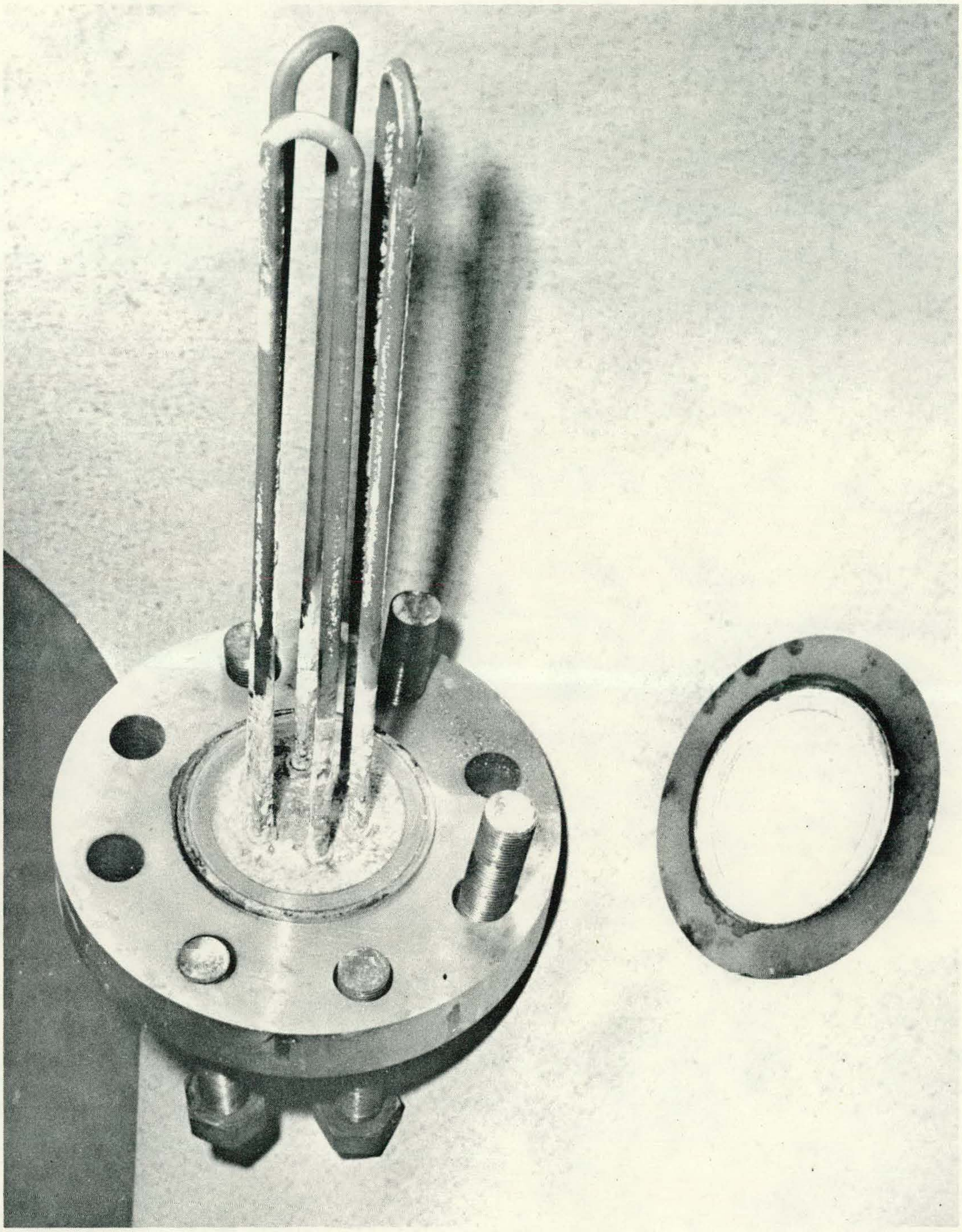


Figure 20 - Pressurizer Base Flange and Immersion Heater Deposit
(Test MEDB-1)

A white deposit is shown which was found at the termination of Test MEDB-1. The material contained lithium and boron and was apparently formed during the shut-down operation.

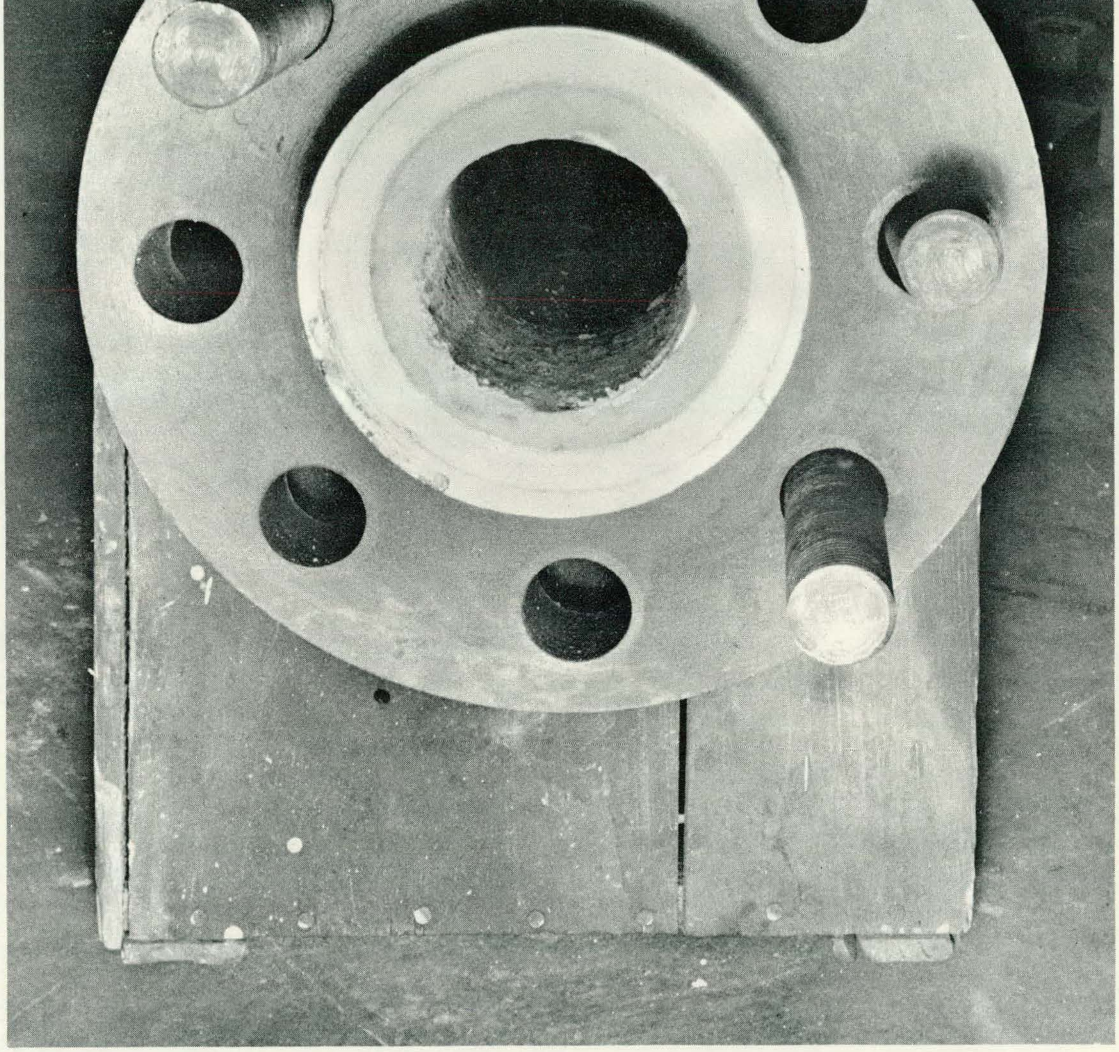


Figure 21 - Pressurizer Wall Deposit (Test MEDB-1)

A white deposit of material is shown containing lithium and boron which was found in conjunction with the deposit shown in Figure 20 at the termination of Test MEDB-1.

TABLE XIII

Chemical and Water Make-up Data

Test No.	MEDA-1	MEDA-2	MEDB-1	MEDB-2
Total water lost, liters	414	239	150	67
*Water removed, liters	312	127	52	28
Water lost by leakage, liters	102	112	98	39
Boric acid added, gm.	120	40	1440	565
**Boric acid content of water removed, gm.	69	29	468	261
Boric acid lost, gm.	51	11	972	304
LiOH · H_2O added, gm.	76	0	790	260
**LiOH · H_2O content of water removed, gm.	39	0	508	115
LiOH · H_2O lost, gm.	37	0	282	145
H_2 added, ml (STP)	51,142	56,082	25,948	21,268
H_2 content of water removed, ml (STP)	8143	3645	1610	864
H_2 lost, ml (STP)	42,999	52,437	24,338	20,404

* for sampling and purging

** based on average concentration in loop water during the run

IX. SUMMARY

The corrosion of Type 304 stainless steel in water containing boric acid at 600°F, 2000 psig and at a flow velocity of seven feet per second was investigated as a function of boron concentration and of alkalinity. No evidence of microstructural attack was observed on coupon specimens or on U-bend specimens under any of the conditions tested.

At a boron concentration of 39 parts per million with pH maintained at a value of 10 with lithium hydroxide, no trend of corrosive attack with time was noted after the first two days of exposure. Specimens exposed under these conditions showed no change in weight after exposure (exposed weight change). The loss of metal due to corrosion, as measured by the descaled weight change, was approximately -9 mg/dm^2 without regard to the length of time exposed after the first two days. The location of coupons within a holder, the location of the holders (i.e., upstream or down stream) and periodic exposure of the specimens to air during the test run had no apparent effect on the total corrosion of the coupons. The surface finish of the coupons was found to have an effect on the total amount of corrosion but the effect was not found to be consistent. All coupons showed an increase in surface roughness after exposure which was not significantly affected by length or period of exposure or by time of introduction or removal of coupons.

At a boron concentration of 41 parts per million, without pH control, and at a boron concentration of approximately 1600 parts per million with the pH maintained at 10 with lithium hydroxide, the rate of corrosion was found to be expressible by the expression $Y = A + B \log t$ where Y is the weight change per unit area, t is the exposure time (greater than 48 hours and equal to or less than the total exposure time) and A and B are constants. The corrosive attack on the coupons was greater in high boron content water than in low boron content water at a constant pH value of 10. After the first two days of exposure, the corrosion rate was found to be lower in high boron content water at pH = 10 than in low boron content water without pH adjustment based on the B constants shown in Tables X and XI. The surface finish was found to have an effect on the total amount of corrosion but the effect was not consistent from test to test. The fore (or upstream) part of the test section was found to be a more corrosive environment than the aft (or downstream) region. The corrosion suffered by coupons was more severe when the coupons were exposed so that their rolling direction was parallel to the direction of fluid flow.

Internal deposition of material containing lithium and boron was observed during Test MEDB-1 (1587 ppm B, pH = 9.7 with lithium hydroxide). No deposition was obtained in Test MEDB-2 (1660 ppm B, pH = 9.9 with lithium hydroxide) which was made to determine the cause of this deposition. No deposition was observed in a test performed under essentially the same conditions (except for flow) in a static autoclave. It has been assumed that the manner of let-down to atmospheric pressure was responsible for the deposition obtained.

X. REFERENCES

1. "Corrosion and Stability Tests on Chemical Poisons in High Temperature Water", Breden and Abers, September 1, 1953, ANL-5147 (Rev.)

2. "A Study of Chemical Control for PWR", Edited by Z. M. Shapiro, April 8, 1955.

3. "Corrosion and Wear Handbook", Edited by D. J. DePaul - TID 7006/March 1957.

4. "Corrosion Handbook", Uhlig.

5. "Corrosion of Type 304 Stainless Steel with Varying Carbon Content in Reference Primary Coolant Water", E. Rau, Bettis Technical Review 1 No. 3, 23-38 (1957).

6. "Symposium on Stress Corrosion Cracking of Metals", 1944, ASTM-AIME, p. 430.

7. "A Study of Decontamination Agents for Use in the Yankee Reactor", R. M. Watkins, November 1958, YAEC-90

XI. ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. J. Penkrot of the Chemical Laboratory of the Westinghouse Materials Engineering Departments who supervised the loop operations and to Mr. B. Sinwell of the Physical Testing Laboratory of the Materials Engineering Departments who was concerned with the mechanical phases of loop operations. Messrs. R. C. Garretson and G. A. Eator of the Materials Engineering Departments were extremely helpful in this investigation. The authors wish to thank Mrs. D. J. Rahn of the Technical Service Laboratories of the Westinghouse Atomic Power Department for metallographic examination of the corrosion specimens.

APPENDIX I

LABORATORY PROCEDURES

A. Electrolytic Descaling Procedure

In order to determine the change in weight of metal after it has been exposed to a corrosive environment, it is necessary to remove the scale that has formed on the surface of the base metal. This is done by electrolytically descaling the specimen in an inhibited acid bath, as follows:

Required:
- 1 - Descaling apparatus consisting of a 2-liter beaker, pure carbon anode (spectroscopic grade), silver lined Bakelite alligator clips (cathodes), and necessary wiring.
- 1 - Rectifier.
- 1 - Hot plate and thermometer.
- 1 - 2-liter beaker for rinse water.
- - H_2SO_4 (5% by weight) in distilled water, (28 ml conc. acid per 972 ml water, or 56 ml of 1-1 acid to 944 ml water).
- - Inhibitor (Rodine 77 for sulfuric acid).

Procedure: The specimens to be descaled are held by the alligator clips, so that they are equi-distant from the carbon rod. The carbon rod is then attached to the positive (+) terminal of the rectifier, and the specimens to the negative (-) terminal. The specimens are then immersed in a 74°C 5% sulfuric acid solution, which contains 2 ml of inhibitor (Rodine 77) per liter of solution, and exposed to a current density of 4.7 amperes per specimen (1.0 amps per sq. in. or 15 amps per sq. dm.) for a period of 3 minutes. At the end of this period, the specimens are to be quickly removed and placed in a beaker of cold tap water.

Note 1: The descaling solution should be discarded and the equipment thoroughly cleaned after 100 specimens have been descaled.

Note 2: Following are the ammeter settings for conventional corrosion specimens (1/16 x 1-1/8 x 2):

No. of Specimens*	Amperes
1	4.7
2	9.4
3	14.2
4	18.9
5	23.6

* Instead of varying the current, blank specimens may be used to fill up the holders.

Following the descaling and initial rinsing, all specimens are to be washed according to the procedure described below.

B. Washing Procedure - Test Coupons

The following procedure is to be followed prior to weighing new, exposed, or descaled test coupons.

1. Specimens are not to be handled with the bare fingers. Rubber gloves will be worn, and when possible specimens will be handled with wire hooks or with tongs or tweezers, the tips of which are covered with plastic "spaghetti."
2. Wash the specimens for one-half minute in a 1% solution of Alconox (a product of Alconox, Inc.) in water, using a camel's hair brush. Care must be exercised to thoroughly scrub all edges and the entire surface on each side.
3. Thoroughly rinse specimens for five seconds in flowing tap water.
4. Rinse specimens at least six times in each of two beakers of distilled, de-ionized water.
5. Rinse specimens at least six times in each of three beakers of acetone (CP grade).
6. Air dry specimens, then place in oven (150 - 200°F) for a minimum of one-half hour.
7. Transfer specimens to a desiccator and allow to cool.
8. Weigh specimens to the nearest 0.1 milligram.

C. Determination of Boron in Loop Water

1. (a) For 40 ppm B, transfer 100 ml sample to a 250 ml beaker.
   (b) For 1600 ppm B, transfer 25 ml sample to a 250 ml beaker.
2. Using a pH meter, adjust pH to 6.5.
3. Titrate to pH 8.5 with 0.1000 N NaOH solution.
4. Add one gram of mannitol. If pH drops below 8.5, the boron has been only partially titrated in step 3. Therefore, titrate with 0.1000 N NaOH again to pH 8.5.
5. Repeat step 4 until the pH does not drop with a further addition of one gram of mannitol.

Calculation:

$$\frac{0.01082 \times \text{N of NaOH} \times \text{ml NaOH} \times 10^6}{\text{Sample Volume}} = \text{ppm B}$$

D. Determination of Nickel in Loop Water

1. Transfer 100 ml sample to a 250 ml beaker.
2. Make just slightly acid and then boil down to 5 ml volume.
3. Adjust to pH 5-6 using either 10% HCl or 10% NH_4OH as necessary.
4. Add a saturated solution of bromine water dropwise until a faint yellow color appears. Then add 4 drops in excess.
5. Add 0.5 ml of 10% sodium dimethylglyoximate solution.
6. Add 5% NaOH solution dropwise until the yellow bromine color disappears or any precipitate dissolves. (pH 8)
7. Transfer to 50 ml volumetric flasks, dilute to the mark with water and mix thoroughly.
8. Read the transmission in a colorimeter at 490 mμ using a water blank as a reference solution to calibrate the instrument for 100% transmission.

The curve is prepared by analyzing seven samples containing 0, 5, 10, 15, 20, 25, and 30 micrograms of nickel by the method. The above solution concentrations are based on a 2 cm absorption cell.

Calculations: $$\frac{\text{Micrograms of Ni from Curve}}{\text{Sample Volume}} = \text{ppm Ni}$$

E. Determination of Iron in Loop Water

1. Transfer 100 ml sample to 250 ml beaker.
2. Make just slightly acid and boil down to 10 ml volume.
3. Adjust pH to 7.5 ± 0.5 with 10% NH_4OH. Cool.
4. Add 0.5 ml of 1% aqueous ortho-phenanthroline solution and then 1 ml of 6% sodium hydrosulfite solution.
5. Swirl the solution for two minutes.
6. Transfer to a 25 ml volumetric flask, dilute to the mark with water and mix thoroughly.
7. Let stand five minutes for full color development.
8. Read the transmission in a colorimeter at 490 mμ using a water blank as a reference solution to calibrate the instrument for 100% transmission.

The curve is prepared by analyzing six samples containing 0, 10, 20, 30, 40, and 50 micrograms of iron. The above solution concentrations are based on a 2-cm absorption cell.

Calculations: $\dfrac{\text{Micrograms of Fe from Curve}}{\text{Sample Volume}} = \text{ppm Fe}$

F. Determination of Chromium in Loop Water

1. Transfer 100 ml sample to a 250 ml beaker.

2. Make just slightly acid and boil down to volume.

3. Add 7 ml 10% H_2SO_4, 1 ml of 1% $AgNO_3$ solution and 15 drops of .3% $KMnO_4$ solution.

4. Boil for three minutes to oxidize chromium.

5. Remove from hot plate and add immediately two drops of 10% sodium azide solution. Then boil for 1/2 to 1 minute. The boiling time is important at this step.

6. Remove from hot plate and cool to 20°C.

7. Transfer to 50 ml volumetric flask.

8. Add 2.0 ml of 0.4% diphenylcarbazide in methyl alcohol to the volumetric flask.

9. Dilute to the mark with water and mix thoroughly.

10. Read the transmission in a colorimeter at 550 $m\mu$ using a sample determination containing all the reagents used in the procedure with the exception of the diphenylcarbazide solution as a reference solution to calibrate the instrument for 100% transmission.

The curve is prepared by analyzing seven samples containing 0, 4, 8, 12, 16, 20, and 24 micrograms of chromium. The above solution concentrations are based on a 2-cm absorption cell.

Caution:

Do not use any glassware that has been cleaned with chromic acid cleaning solution until it has been thoroughly rinsed with water. Check rinsings with diphenylcarbazide solution until a negative test is obtained for chromium.

Calculations: $\dfrac{\text{Micrograms of Cr from Curve}}{\text{Sample Volume}} = \text{ppm Cr}$

G. Chemical Descaling Procedure

Chemical descaling was accomplished as follows:

Descaling Solutions:

A. Aqueous solution of sodium hydroxide (3% by weight) plus potassium permanganate (18% by weight).

B. Aqueous solution of ammonium citrate (10% by weight).

Procedure:

The specimens are washed (procedure B) before they are chemically descaled. The two chemical solutions are heated and maintained near boiling (solution A at 210°F, solution B at 180°F). The specimens are placed in solution A for thirty seconds, rinsed with running water, and then placed in solution B for two minutes. After being in solution B for two minutes the specimens are removed, rinsed in water and scrubbed with tissue to remove the adhering film. The cleaned specimens are air dried and reweighed.

Specimens not completely descaled are given increasing exposure periods in the descaling solutions until the scale is satisfactorily removed. The descaling solutions should be discarded when they become appreciably discolored.

H. Miscellaneous Analytical Methods

1. pH was determined using a Beckman Industrial Type pH Meter.

2. Dissolved H_2 was determined by vacuum extraction, the volume being measured and converted to ml/l at STP.

3. Li was determined by flame photometry.

4. Dissolved O_2 was determined by Method 560 X-3, dated January 11, 1956, which was provided by the Chemical Laboratory, CTA, Bettis Plant, Clairton Site, Westinghouse Atomic Power Division.