APAE No. 43
Volume II

APPR-1
RESEARCH AND DEVELOPMENT PROGRAM
DECONTAMINATION PROGRAM
TASK II

VOLUME II
EVALUATION OF CHEMICAL AGENTS FOR NUCLEAR REACTOR DECONTAMINATION

ALCO PRODUCTS, INC.
POST OFFICE BOX 414
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APAE No. 43
Vol. II

DECONTAMINATION PROGRAM

TASK II

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EVALUATION OF CHEMICAL AGENTS FOR NUCLEAR REACTOR DECONTAMINATION

Contract No. AT (30-3)-326
Issued February 15, 1959

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ABSTRACT

The caustic permanganate-rinse decontamination treatment was investigated. Loop and metallurgical studies were performed to determine optimum operating conditions as well as the metallurgical effects of the treatment. A treatment with 10 percent sodium hydroxide and 5 percent potassium permanganate solution followed by a rinse with a 5 percent ammonium citrate, 2 percent citric acid and 1/2 percent Versene solution was chosen for the decontamination of a stainless steel steam generator. Decontamination factors of greater than 50 were obtained in loop tests using the above treatment. Corrosion and metallurgical results indicated a total penetration of less than 0.01 mil on annealed Type 304 stainless steel with no evidence of any deleterious effects.

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1.0 INTRODUCTION

The major problems associated with the buildup and removal of activated corrosion products in nuclear facilities were reviewed in Volume I of this report. It was concluded that from the standpoint of accessibility and practicality, chemical decontamination offered the most feasible method of decontaminating large facilities. Preliminary studies indicated that a caustic permanganate-rinse treatment may be an effective chemical method of removing activated corrosion product scale. Nitric acid, oxalic acid, citric acid, and ammonium citrate were found to be effective rinses. Nitric acid was not given further consideration because of the hazard involved in handling the chemical. Limited corrosion information on the decontamination treatment indicated no evidence of intergranular corrosion. However, a further evaluation of the caustic permanganate-rinse treatment was deemed necessary.

An investigation of the important parameters of the caustic permanganate-rinse decontamination treatment was conducted. These parameters (concentration, temperature, flow rate, and residence time) were evaluated in a decontamination test loop. The results of short and long term corrosion and metallurgical tests are given, as are the results of two simulated APPR-1 decontamination tests. Post decontamination effects (weight loss and activity pickup) are also presented in this report.

2.0 OBJECTIVE

An investigation of the caustic permanganate-rinse decontamination treatment and its applicability to the decontamination of a stainless steel steam generator.

3.0 SUMMARY AND CONCLUSIONS

It was found that a caustic permanganate solution followed by a rinse solution of either oxalic acid, citric acid, or ammonium citrate was effective in removing activated corrosion product scale from stainless steel. The oxalic acid was eliminated from final consideration because of the excess gas formation observed in loop tests and the resultant danger of pump cavitation.

A caustic permanganate solution, consisting of 10 percent sodium hydroxide and 5 percent potassium permanganate (by weight) was used at 225°F for 30 minutes and found to give satisfactory decontamination results, when followed by a rinse solution. Radiochemical analysis indicated that approximately 75 percent of the manganese-54 activity was removed by the caustic permanganate solution. It also appears that the major part of the chromium-51 and iron-59 activity is removed by this solution. The cobalt-60 and cobalt-58 activities are removed by the rinse solution.

An ammonium citrate concentration of 5 percent was found to be an

optimum concentration for decontamination. Treatment at a minimum temperature of 220°F for at least 30 minutes was required for effective removal of activated corrosion product scale. However, the extent of decontamination was found to be dependent upon flow velocity.

A citric acid concentration of 5 percent was also found to give satisfactor decontamination. A complexing agent (1/2 percent Versene) was added to enhance the complexing power of the solution. The minimum temperature required for effective decontamination was found to be approximately 170°F. Unlike the ammonium citrate solution, the extent of decontamination was not found to be dependent upon the flow velocity of the citric acid rinse solution. It was also found that the decontamination was increased when the contaminated metal surface was allowed to dry prior to the addition of the citric acid rinse.

The decontamination treatment with citric acid as a secondary rinse solution resulted in higher corrosion rates on sensitized stainless steel. The addition of 2 percent citric acid to 5 percent ammonium citrate resulted in less corrosion on sensitized stainless steel than was observed in the case of 5 percent citric acid. It was also found that the flow rate dependency was reduced as a result of the addition of citric acid. Since the main constituent of the combination solution is ammonium citrate, a temperature of 220°F and a residence time of 30 minutes at this temperature was chosen for the solution. This solution is most applicable as a secondary rinse solution for steam generator decontamination. A decontamination factor of 84 was obtained on Type 304 stainless steel tubing exposed to the caustic permanganate-citrate combination solution decontamination treatment during a simulated APPR-1 loop test.

The corrosion results (mils penetration) for the caustic permanganate-citrate combination solution treatment, based on a 30 hour exposure time, increase in the order: Inconel (0.002), annealed Type 304 stainless steel (0.008), sensitized Type 304 stainless steel (0.017), Babcock and Wilcox Croloy 16-1 (0.029), and AISI C1010 Carbon Steel (0.182). For stainless steel, it was found that increasing corrosion resulted in greater decontamination.

There was no evidence of any cracking or any significant amount of intergranular corrosion or localized attack on any metal specimens exposed in loop, dynamic autoclave, and static autoclave tests. Evidence of possible crevice corrosion was found in the root area of weld specimens subjected to long term static caustic permanganate solution at 77°F (25°C) and 122°F (50°C) for eight weeks. There was no evidence of crevice corrosion on weld samples exposed in the same solution at 203°F (95°C) for four weeks. The root area of the APPR-1 steam generator tube to tube sheet weldment would not be subjected to any solution during decontamination.

Activity buildup and weight loss on metal coupons re-exposed in the APPR-1 primary purification system following decontamination by the caustic permanganate-rinse method were found to be less than new metal coupons.

4.0 EXPERIMENTAL DECONTAMINATION LOOP

4.1 General Description

A chemical decontamination test loop of 7-gallons total volume was fabricated in the Nuclear Power Engineering Laboratory of Alco Products, Inc., (Fig. 1). The loop was designed to allow replacement of a section with a contaminated section exposed in APPR-1 (Fig. 2). Most of the loop was constructed from Type 304 stainless steel. Some of the components and a flowmeter were constructed of Type 316 stainless steel. A 5-gallon fill tank, located above the highest point in the system, was used as a pressurizer tank during loop operation. A 15-gallon stainless steel vessel was used for mixing the chemical solutions. The solution was then pumped into the fill tank where, if necessary, it could be heated before filling the loop (Fig. 3). The loop was filled by either gravity or by applying nitrogen pressure to the pressurizer from a gas cylinder. During the filling operation, the loop was bled at its highest point to eliminate trapped air. A circulating pump was used to maintain the desired flow rate throughout the contaminated section of the loop. To raise and maintain the temperature of the system, Calrod type strip heaters were utilized along the piping.

For sampling during operation of the loop, a Hagen Industrial Cooler (Model WC110) was used. A Brooks Purge Meter (Model 1350V) was installed to control sample flow. This sampling system was also applicable for evaluating a feed-bleed type of operation. Instrumentation was also included for measuring and controlling temperature, loop pressure, and flow rate. A 1x1-inch sodium iodide (Tl) gamma scintillation crystal, placed over the contaminated section, was used to determine the radioactivity at any time during a loop test.

4.2 Design Characteristics

4.2.1 Pump

A Chempump, Model S 3/4 HP, centrifugal pump with a flow range of 0-16 gpm was used to circulate the chemical solutions. This type of pump was selected to prevent any leakage of the chemical solutions at the pump. The pump was fabricated entirely of stainless steel with the exception of the bearings. These were fabricated of Graphitar No. 14, a compressed, pure carbon material. After approximately 15 hours of pump operation, a fine suspension of black particulate matter was found in the waste solutions. Upon disassembling the pump, it was found that the bearings had been eroded to such an extent by the caustic permanganate-rinse decontaminating solutions that they could no longer be used. Fig. 4 is a photograph of a new bearing (Top-Left) compared with the bearing removed from the decontamination loop pump after 15 hours of operation (Top-Right). The Graphitar No. 14 bearings were replaced with Type 304 stainless steel bearings (Fig. 4 (Bottom-Left) provided with removable Teflon sleeves (Fig. 4 Bottom-Right). All metal to Graphitar contact was therefore replaced with metal to Teflon contact. The Teflon sleeves could be replaced if excess wear

on the part should warrant such replacement.

In larger canned rotor pumps, it is possible to flush the bearings with demineralized water. In this manner, it is possible to maintain the concentration of the decontamination solution in the vicinity of the bearings low enough to prevent oxidation or other effects by the solution.

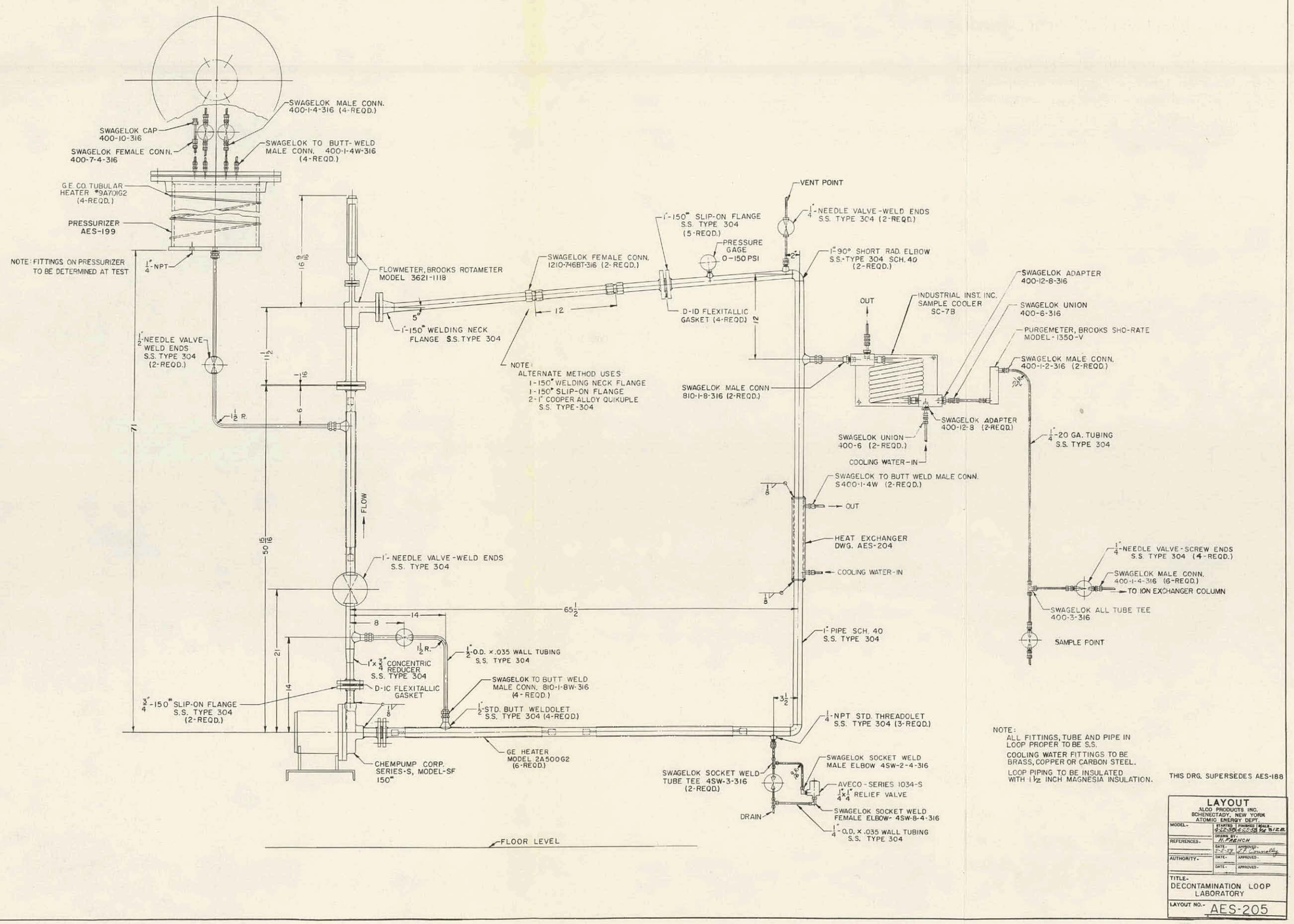

Fig. 1 Decontamination Test Loop Assembly Drawing

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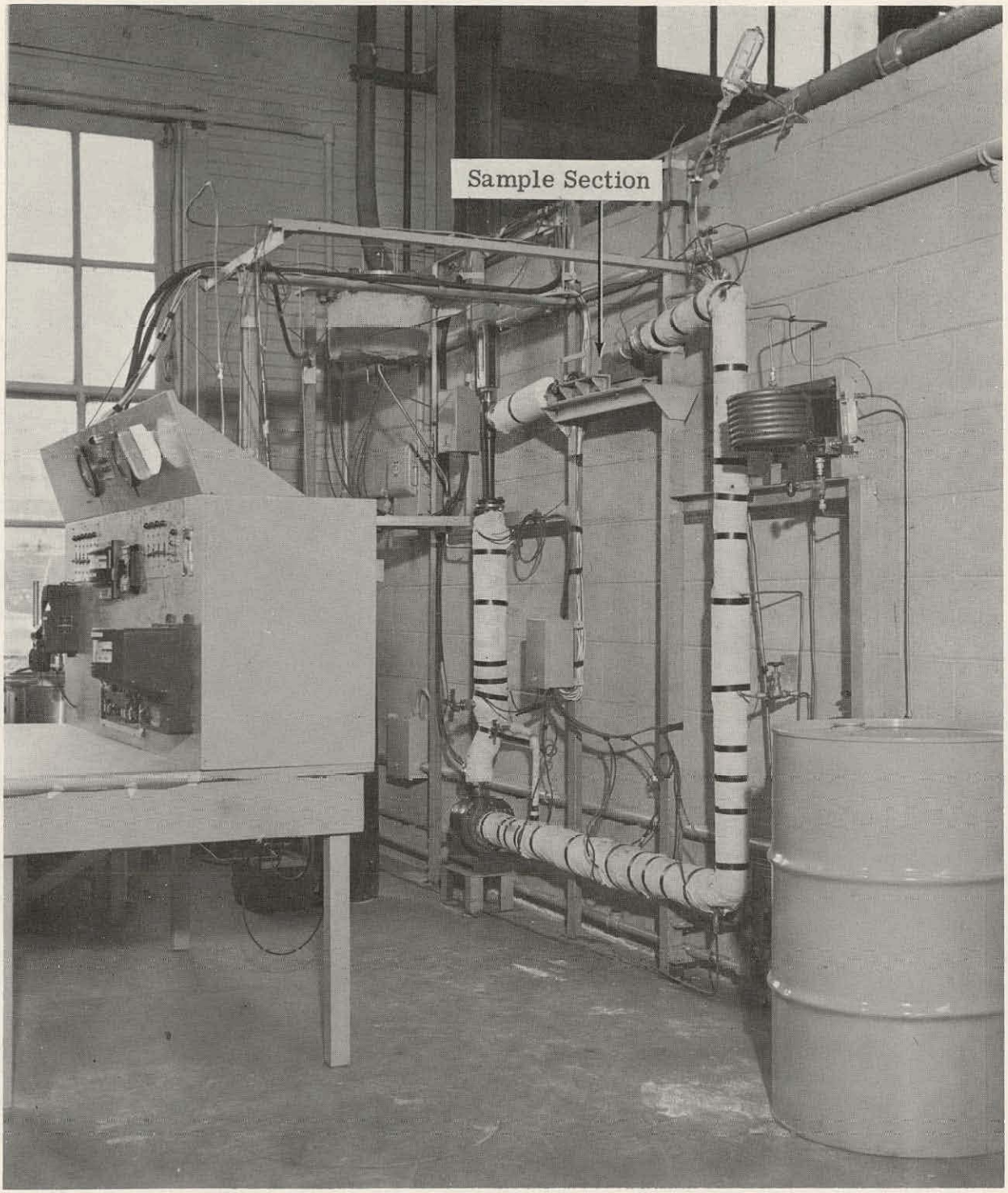

Fig. 2 - Photograph of Decontamination Test Loop

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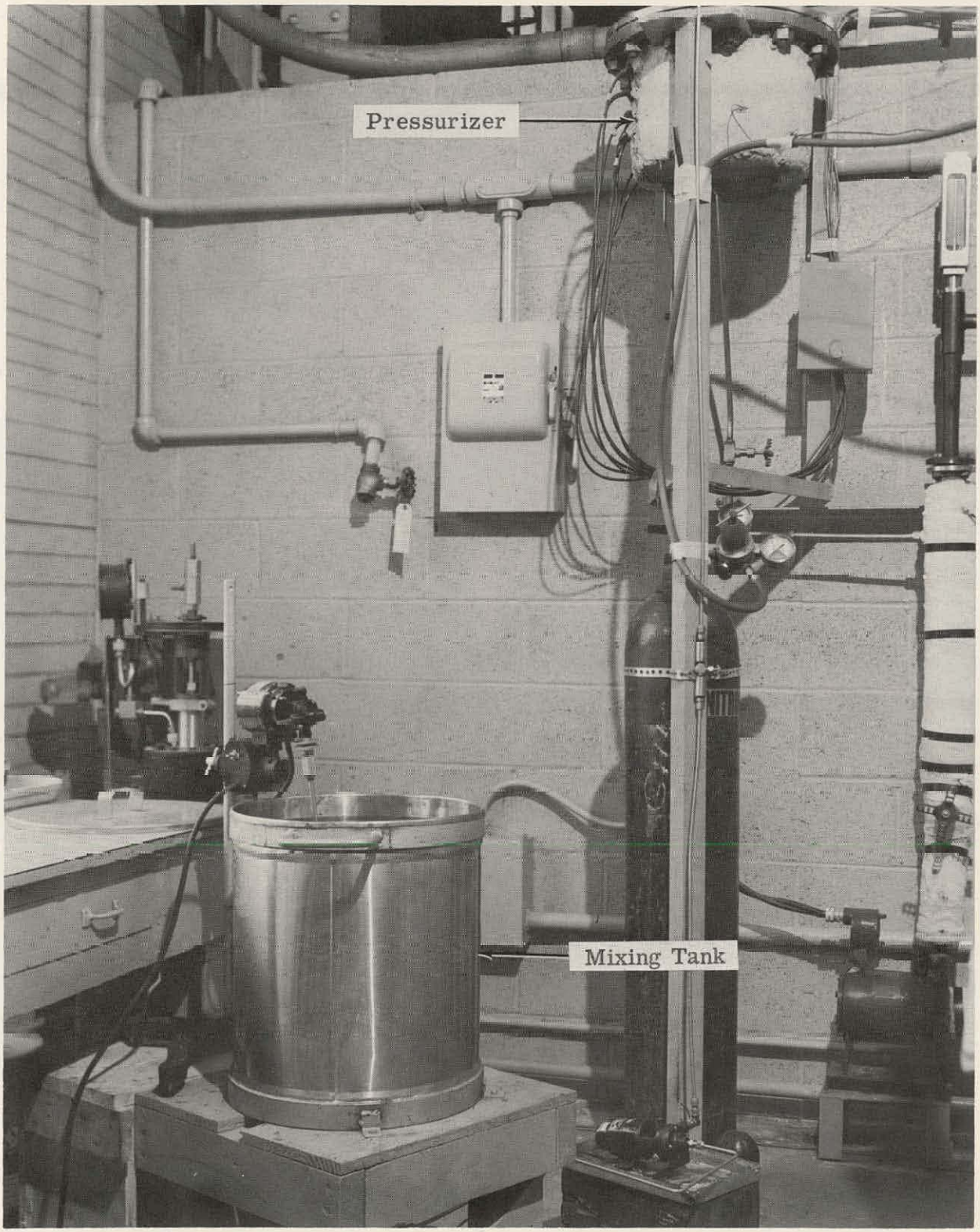

Fig. 3 - Photograph of Mixing Tank, Filling System, and Pressurizer for Decontamination Test Loop

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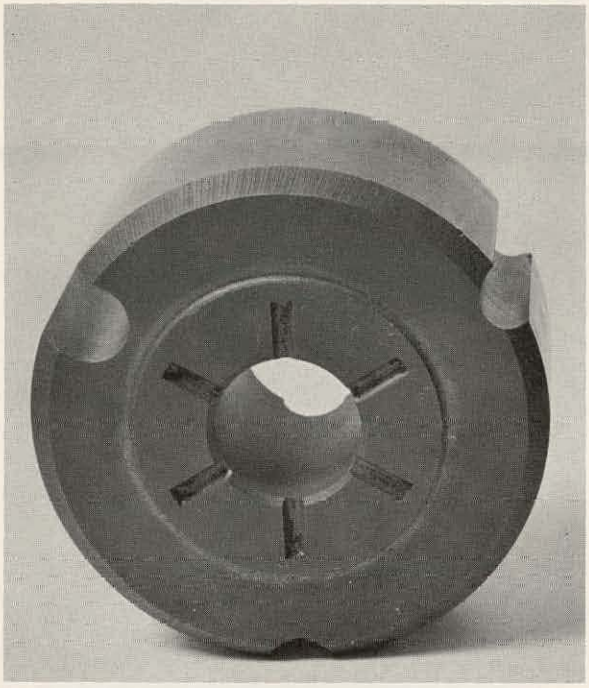
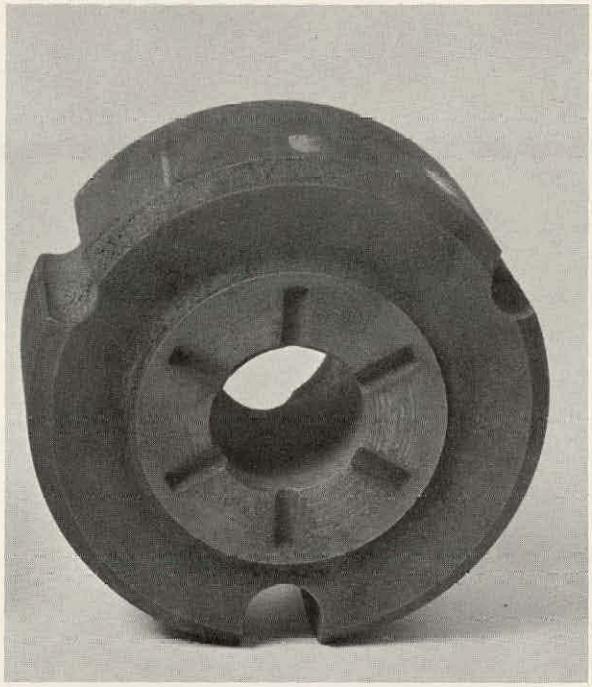
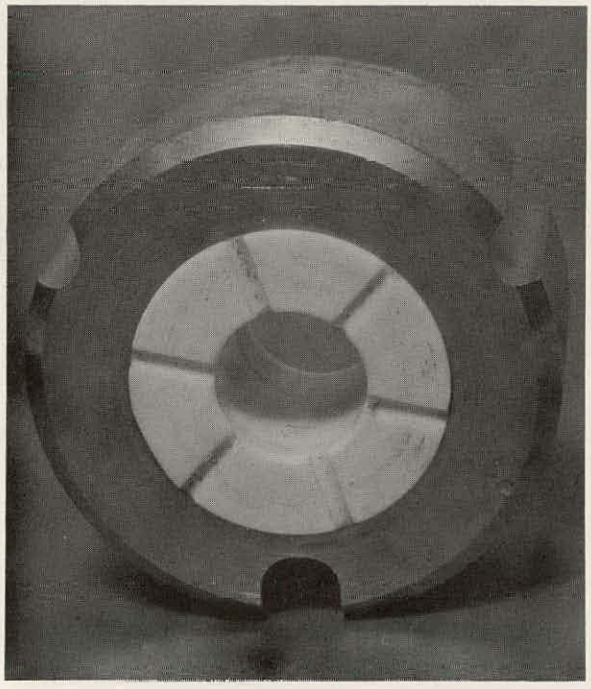


New Graphitar No. 14 Bearing



Graphitar No. 14 Bearing After 15 Hours Exposure to Decontamination Solutions



Replacement Stainless Steel Bearing

Teflon Insert

Fig. 4 - Photographs of Original and Replacement Bearings for Circulating Pump

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4.2.2 Flow Rate

The loop was designed to obtain a liquid velocity of 10 feet per second. This value was based upon an estimate of the pump size that would reasonably be available to decontaminate a large nuclear facility such as the APPR-1 steam generator. That facility would require a 4000 gpm pump to achieve a flow velocity of 10 feet per second through the heat exchanger tubes.

A Brooks rotameter was used to measure flow (gpm) in the loop. Two interchangeable floats were used; the first was used in the range of 0.5 gpm to 7.0 gpm, the second was used from 4 gpm to 16 gpm. Fluid velocity (fps) through the sample section of the loop was determined from flow rate and the cross section of the sample.

4.2.3 Temperature and Pressure

Preliminary bench-type screening results indicated that satisfactory decontamination results could be achieved at relatively low temperatures (185-205 ^{o}F) and pressures (atmospheric) utilizing the caustic permanganate - rinse decontamination treatment. This treatment, if practical, would thereby eliminate the hazard and expense associated with a high temperature and pressure system. The maximum loop temperature was therefore fixed at 300^{o}F, and the maximum pressure established at 100 psig. This pressure was sufficient to prevent any boiling at the maximum temperature. For safety purposes, a relief valve set at 100 psig was installed in the system.

Loop heat-up time and operating temperature were controlled by a Partlow (Model L) controller with individual on-off control for each heater. With this control system, the temperature was maintained within $\pm 5^{o}$F of any set point. A Minneapolis-Honeywell temperature indicator and a 12-point thermocouple switch were used to monitor the temperature at various points throughout the system. A small single pass heat exchanger was used to cool the solution in the loop to safe draining temperature.

4.2.4 Contaminated and Corrosion Sample Section

The loop was designed with provisions to evaluate corrosion and decontamination effects of the solution. The major part of the decontamination evaluation phase of the program was performed using 14-inch lengths of Type 304 stainless steel 3/4-inch 16 Gage BWG tubing.

The tubing was installed in the sample section of the loop with two modified Swagelok female connectors. With this installation, the tubing was an integral part of the loop.

For corrosion studies, 3 1/2 x 1/2 x 1/16 - inch coupons of various metals were used. A specially fabricated coupon holder of Type 304 stainless steel was used to hold the coupons in the loop (Fig. 5). The holder, with provisions for 18 coupons, was placed inside a 15-inch section of 1 1/2-inch Type 304 stainless steel pipe installed in the loop with two Cooper Alloy Quickupl connections. Its physical location in the loop was identical with the tubing, making it part of the loop.

4.2.5 Counting of Contaminated Samples

A 1 x 1 -inch sodium iodide (Tl) gamma scintillation crystal coupled to a photomultiplier tube was used to measure the radioactivity emanating from the contaminated sample section. The counting unit was connected to an RIDL scaler (Model 2001) located on the loop control panel. The crystal unit was placed in position approximately 2 inches over the contaminated section and inside a lead shield. A piece of asbestos was placed between the crystal face and the contaminated section to reduce thermal effects on the crystal. Lead bricks were used to inclose the entire section and to reduce background radiation. With this counting arrangement, the residual activity of the sample and the activity in solution near the sample could be measured at any time during a loop test. When the loop was drained, the activity due to the sample was determined.

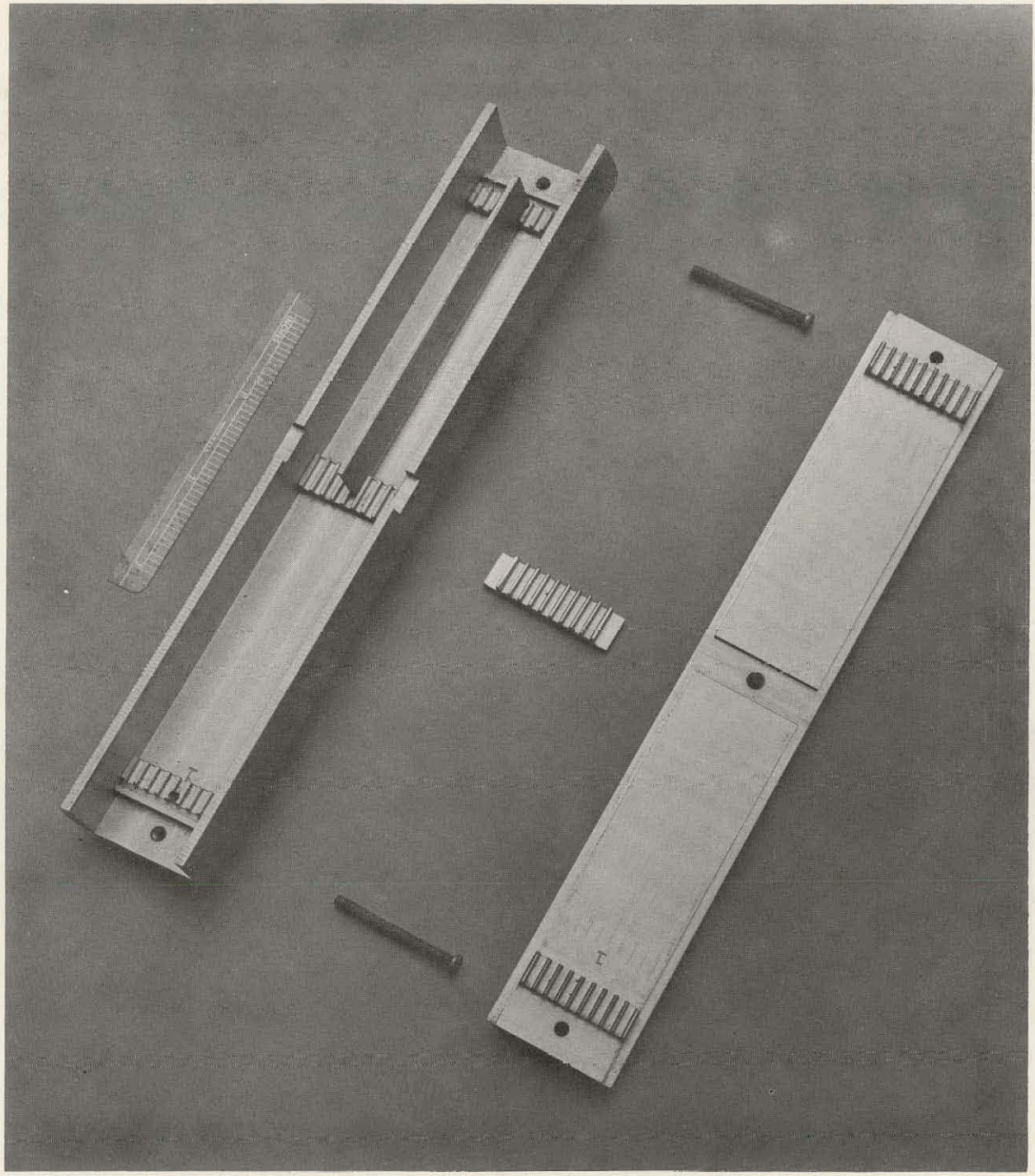

Fig. 5 - Photograph of Stainless Steel Sample Holder

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5.0 SOURCE OF CONTAMINATED AND CORROSION TEST SAMPLES

5.1 APPR-1 Primary Purification System Modification

In Volume I of this report, it was shown that metal samples exposed in the APPR-1 primary purification system at reactor operating conditions acquired a much more tenacious corrosion product scale than samples exposed at a lower temperature and pressure. Consequently, a revision was made to the APPR-1 primary system purification blowdown line to incorporate fifty feet of Type 304 stainless steel 3/4-inch 16 Gage BWG tubing and two additional sections of 1 1/2-inch flanged pipe to contain two coupon sample holders. The sample holders were identical to the one used in loop decontamination tests shown in Fig. 5. The sections of tubing and flanged pipe are shown in Fig. 6 and Fig. 7, respectively.

The purification system modification was used to supply contaminated samples for use in loop decontamination studies. The tubing was identical to that in the APPR-1 steam generator and represented, except for actual removal of sections of the steam generator, the most practical method for evaluating the effect of chemical solutions on steam generator surfaces. The metal coupons were removed during plant shutdowns, carefully wrapped in filter paper, and shipped to Schenectady. The coupons were counted, washed, and recounted before use in loop decontamination studies.

A section of tubing was also removed during these shutdowns. The tubing was cut into 3 1/2-foot lengths and shipped to Schenectady for use in the evaluation of decontamination parameters. After decontamination, representative samples of tubing and metal coupons were submitted for metallurgical examination. The remainder of the metal coupons were reinserted in the APPR-1 purification blowdown line for post decontamination exposure and subsequent corrosion rate and activity buildup studies.

5.2 Type and Heat Treatment of Metal Specimens

The 3 1/2 x 1/2 x 1/16 - inch specimens exposed in the APPR-1 purification blowdown line consisted of Type 304 stainless steel (annealed and sensitized), Babcock and Wilcox stainless steel Croloy 16-1 (a modified Type 430 stainless steel), and low carbon steel.

The Type 304 stainless steel coupons were fabricated from 1/16-inch thick flat stock in the annealed condition. The sensitized specimens were prepared by heating the specimens in a furnace at 1200°F for 10 minutes, followed by air cooling. The oxidation scale was removed by polishing with fine emery paper. All Type 304 stainless steel specimens possessed a 35-40 RMS surface finish.

The Babcock and Wilcox Croloy 16-1 specimens were fabricated from a 3/32-inch thick stock that was not heat treated by the vendor. The stock was initially machined to the correct width and length with the thickness 0.07-inch greater than specification. The specimens were than heat treated at 1700°F for one hour and air cooled, followed by reheating at 1300°F for one hour with a slow furnace cool to below 600°F. The specimens were than machined to the correct dimensions with about a 60 RMS surface finish.

The carbon steel specimens were fabricated from Alco Products Specification 30090 carbon steel strip. The material was in the hot rolled condition and chemical analysis indicated 0.076 percent carbon and 0.50 percent manganese. This material meets the specifications of AISI C1010 carbon steel.

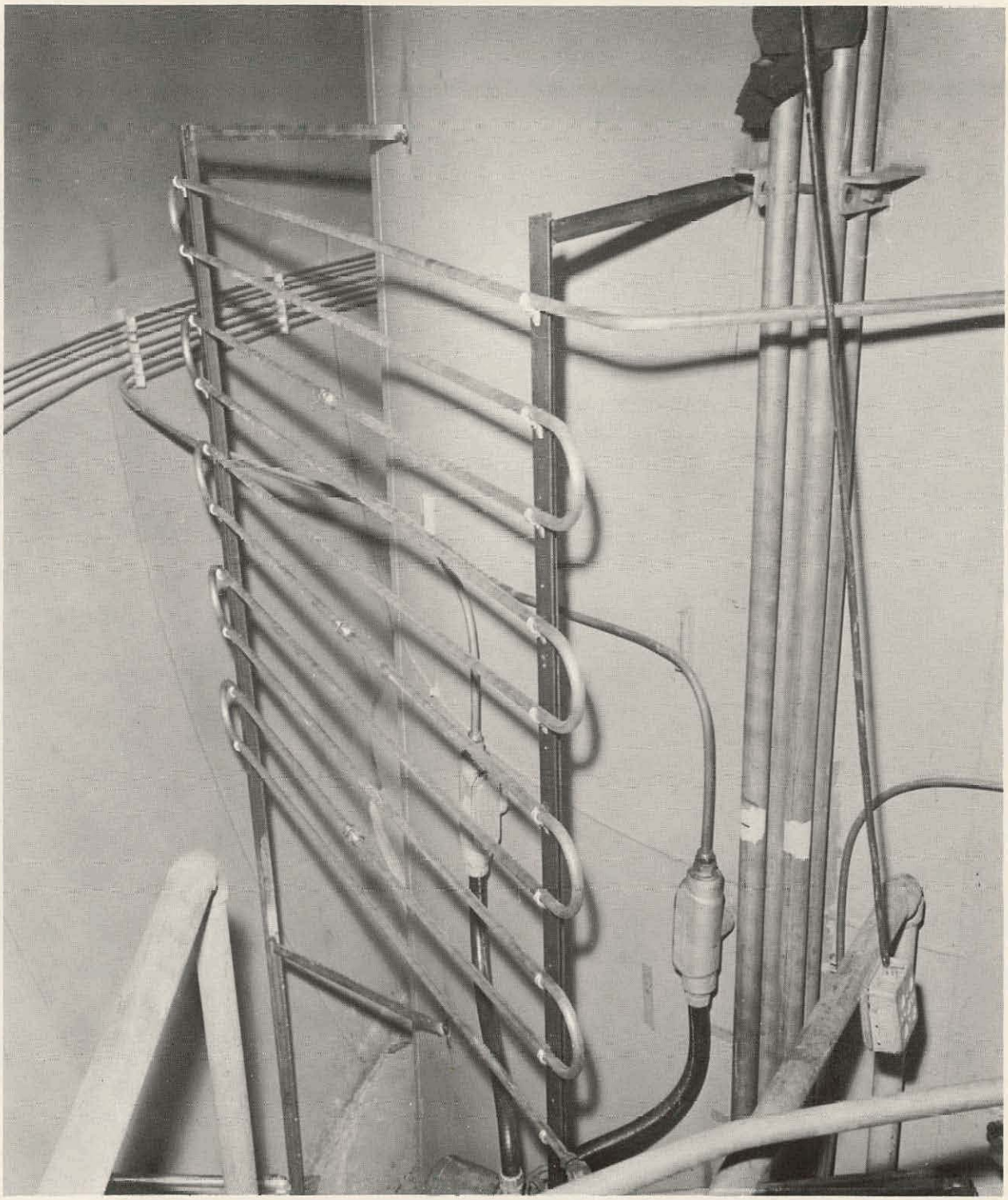

Fig. 6 - Photograph of Installed Section of Type 304 Stainless Steel Tubing - APPR-1 Primary Purification System

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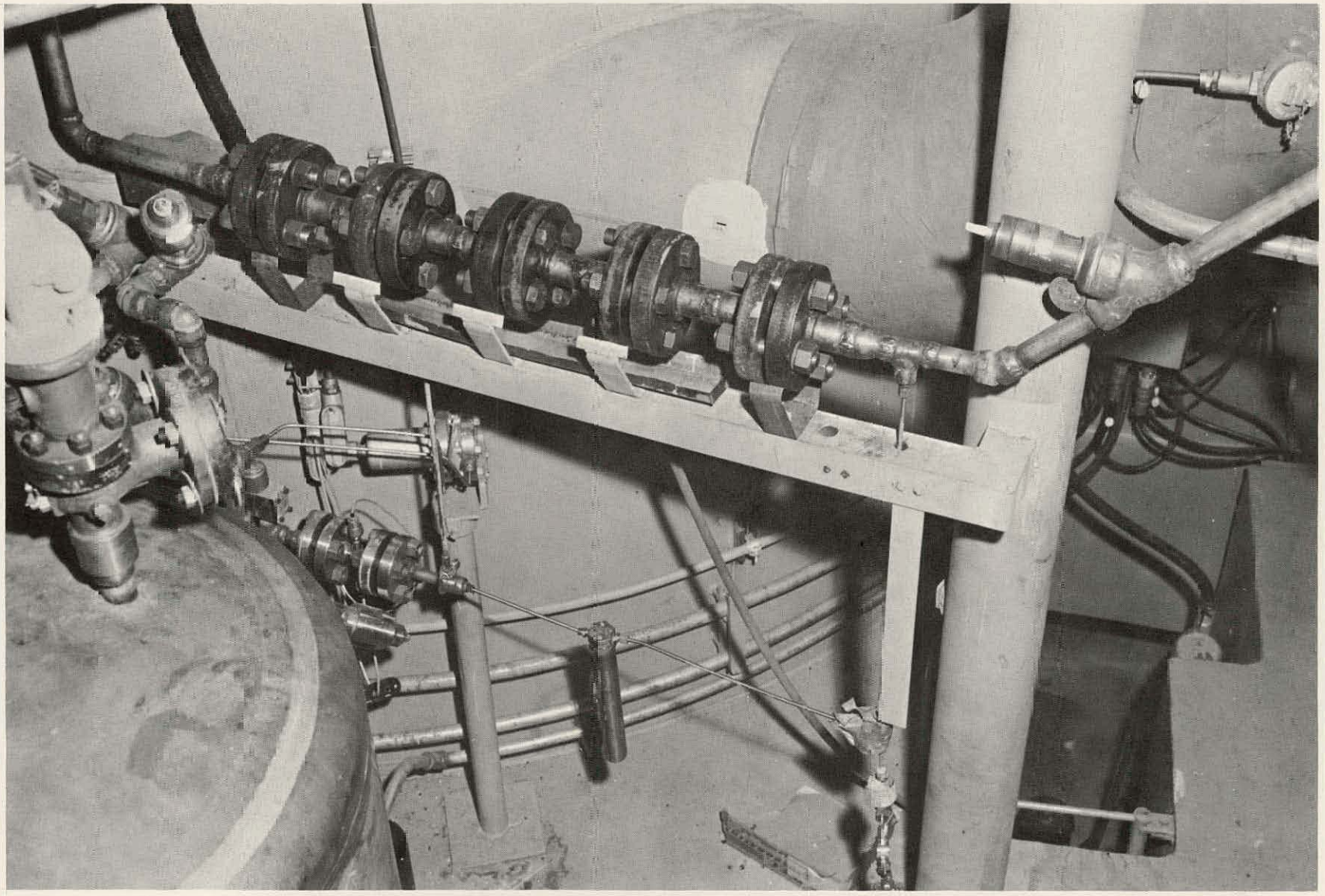

Fig. 7 - Photograph of Installed Section of Flanged Pipe Containing Coupon Sample Holders APPR-1 Primary Purification System

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PART I - LOOP DECONTAMINATION TESTS

6.0 DISCUSSION OF RESULTS

Preliminary screening results are presented in Volume I of this report. They indicated that a primary solution treatment of caustic permanganate (10 percent sodium hydroxide and 5 percent potassium permanganate) followed by a rinse of either nitric acid, oxalic acid, citric acid, or ammonium citrate was effective in removing activated corrosion product scale from stainless steel surfaces. Approximately 50 loop run tests were performed to permit a more complete evaluation of the caustic permanganate-rinse treatment. This included the determination of such parameters as concentration, temperature, flow rate, residence time and any others that may have appeared during the course of the work. Approximately 12 loop test runs were made with metal test specimens. The majority of these specimens were new; however, a number of contaminated specimens were used to evaluate relative decontamination of various metal surfaces. Finally, two simulated APPR-1 decontamination tests were performed to obtain corrosion and decontamination information.

A typical activity profile for a loop run is shown in Fig. 8. During the caustic permanganate (primary) solution phase of the decontamination there is some decrease in activity. There is another small decrease during the first water rinse phase. With the addition of the secondary solution rinse, there is a rapid decrease in activity. As will subsequently be shown, the rate of activity removal is highest at the critical temperature of the solution. A final water flush is used to remove any solution remaining after the secondary solution rinse phase of the decontamination treatment.

6.1 Decontamination Expressions

The effects of the variables involved in the decontamination, e.g. temperature, flow rate, residence time, were all evaluated in terms of one common measurement, viz., decontamination achieved. While there are many ways of expressing decontamination, two expressions were used in this investigation. These were decontamination factor (D. F.) and background factor (B. F.).

6.1.1 Decontamination Factor

The decontamination factor is defined as follows:

$$\text{Decontamination Factor (D. F.)} = \frac{\text{Net* Initial Activity}}{\text{Net Final Activity}}$$

* Gross Activity - Background

As shown in Fig. 9, a D. F. of 100 refers to 99 percent activity removed while a D. F. of 5 refers to 80 percent activity removed. However, a D. F. of either 5 or 100 may indicate satisfactory decontamination depending upon the initial activity.

TABLE 1 Comparison of Various Decontamination Factors

Case	D. F.	Net Initial Activity Units	Net Final Activity Units
1	5	5,000	1,000
2	5	500	100
3	100	100,000	1,000
4	100	10,000	100

The hypothetical D. F. values shown in Table 1 are designed to point out the limitation of reporting decontamination efficiency in terms of D. F. only. A D. F. of 5 was obtained in case 1 and 2, but the final activity of case 2 was one-tenth that of case 1. The D. F. in cases 3 and 4 was 100, and the final activity in case 4 was one-tenth that of case 3. Since the purpose of decontamination is to permit maintenance of a nuclear facility, the final activity measured is as important as D. F. Consequently, the final activity should be reported together with D. F. The initial activity should also be reported if there is considerable variation from sample to sample. In the present investigation, all contaminated metal surfaces used in decontamination tests were scrubbed with soap and water to remove all loose activity. As a result, only the tenacious film remained. The activity of all such tubing sections was approximately the same, i. e. 35,000 to 45,000 gamma counts per minute.

6.1.2 Background Factor

An additional expression of decontamination efficiency was used during loop tests. This expression, termed "background factor" is a measure of the activity remaining above background at the end of a decontamination treatment. It is defined as follows:

$$\text{Background Factor (B. F.)} = \frac{\text{Net Final Activity}}{\text{Background}}$$

This measurement is independent of initial activity but does depend very strongly on the background. To compare a series of runs using B. F. as a measurement, the background must be relatively constant for these runs. If the background varies greatly, the value of B. F. can be

misleading, as shown below:

Case	B. F.	Net Final Activity	Background
1	10	1000 cpm	100 cpm
2	5	1000 cpm	200 cpm

In both cases the final activity is the same but the value of B. F. is inconsistent. Consequently, for loop studies an average background was used. With the exception of two loop tests, all background values were within 20 percent of the average value. All values of net final activity were referred to this background, i. e.

$$\text{B. F.} = \frac{\text{Final Activity - Actual Background}}{\text{Average Background}}$$

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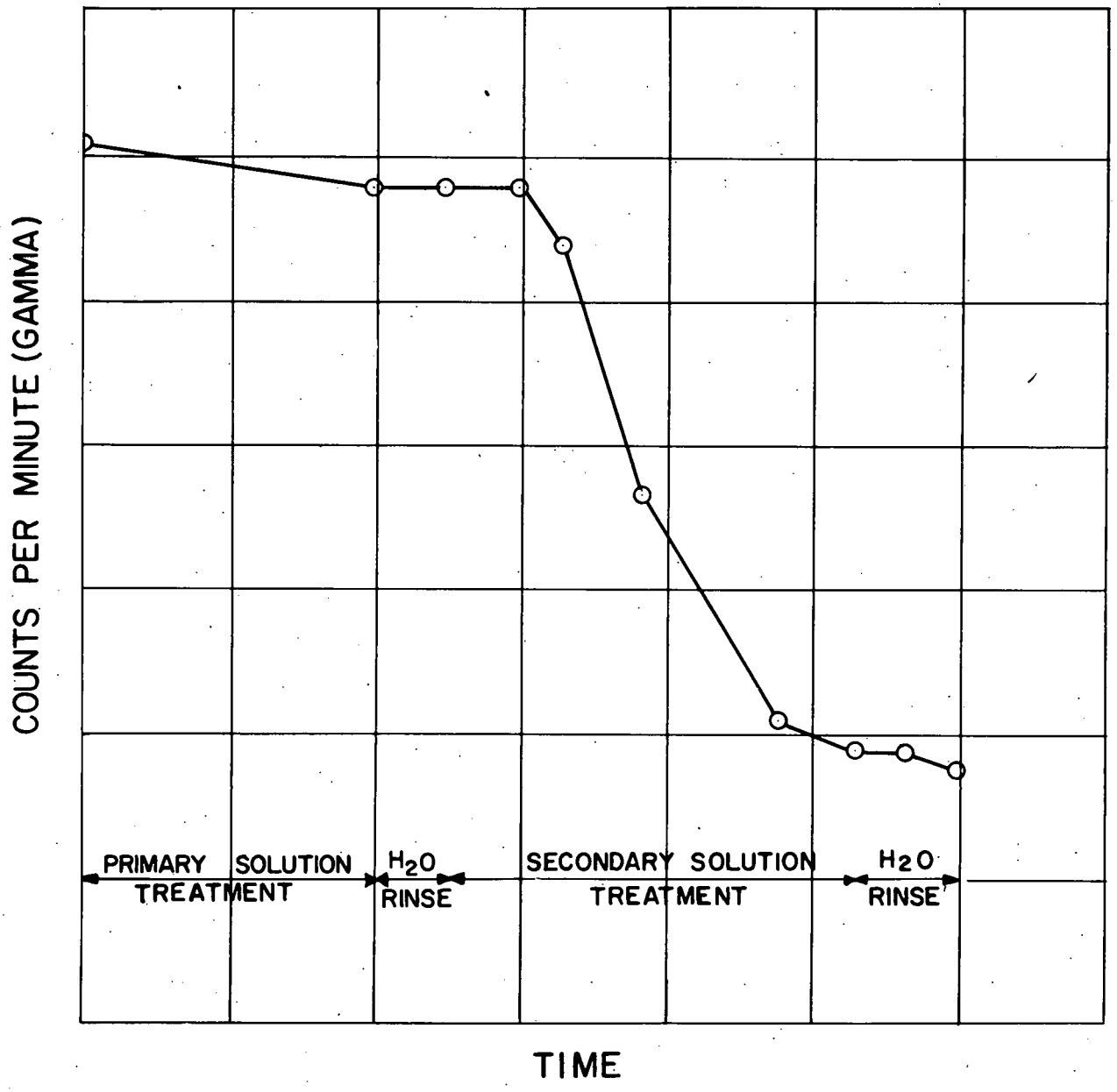

Fig. 8 Activity Profile of a Typical Loop Test Run Using the Caustic Permanganate-Rinse Decontamination Treatment

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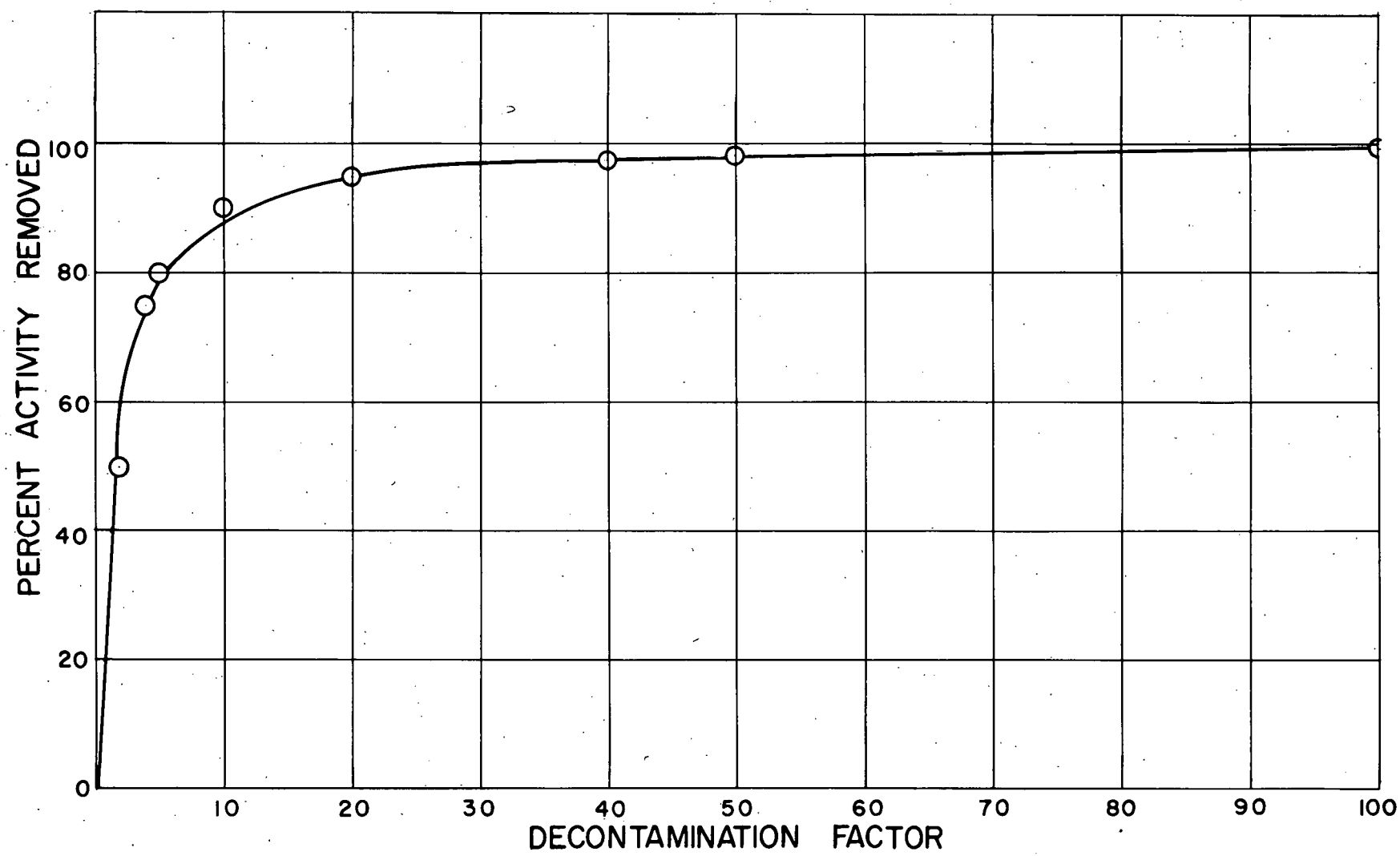

Fig. 9 Relationship Between Decontamination Factor and Percent Activity Removed

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6.2 Concentration of Chemical Agents

Previous data from Volume I of this report have shown that a caustic permanganate solution consisting of 10 percent sodium hydroxide and 5 percent potassium permanganate gave satisfactory decontamination results when followed by a rinse solution of either nitric acid, oxalic acid, citric acid, or ammonium citrate. The concentration of nitric acid varied from 5 percent to 10 percent by volume. However, due to the difficulty involved in the handling of this chemical, loop decontamination tests were performed using oxalic acid, citric acid, and ammonium citrate. A 5 percent oxalic acid rinse was used in two preliminary loop tests following an initial treatment with caustic permanganate. During the rinse phase of the treatments, considerable gas was evolved and resulted in some pump cavitation. This gas, probably carbon dioxide, was thought to be due to the reaction between the manganese dioxide in the loop and the oxalic acid. As a result, oxalic acid was not considered as a potential rinse in subsequent loop tests. The majority of the loop tests were performed using citric acid-Versene*, ammonium citrate or a combination of the two as secondary solution rinses.

6.2.1 Caustic Permanganate

The sodium hydroxide and potassium permanganate used in loop tests were reagent grade purity. This purity was chosen in order to avoid the introduction of any foreign materials, notably halides, into the loop. Three gallons of solution were used in the loop tests. The solution was prepared in a 15-gallon mixing tank provided with a high-speed mechanical stirrer. The required volume of demineralized water (resistivity of greater than 100,000 ohm - cm) was first added to the tank. While the water was being vigorously agitated by the stirrer, the required amount of sodium hydroxide (5 percent by weight) was added. The sodium hydroxide is quite soluble, and complete solution can be achieved within 15 minutes. After approximately 5 to 10 minutes, the required amount of potassium permanganate (5 percent by weight) was added. The delay in the addition of the potassium permanganate is made to take advantage of the greater solubility of the chemical at higher temperatures (due to the heat of solution of the sodium hydroxide). The solubility of potassium permanganate in water varies from 6.4 gms/100 cc at 20°C to 25 gms/100 cc at 65°C.[1] With vigorous agitation, complete solution of the permanganate was achieved within 15 minutes. At this stage the solution possesses a purple color and the pH is approximately 12.8.

During eight loop runs with the caustic permanganate - rinse (citric acid-Versene and/or ammonium citrate) treatment, samples of the caustic

* Versene is a trade name for products of the Dow Chemical Company, Midland, Michigan and is associated with the salts of ethylenediaminetetraacetic acid (EDTA).

permanganate were periodically removed and analyzed for percent caustic and permanganate. The caustic was determined by titration with standard acid using a pH meter to determine the end point. The permanganate was determined by first acidifying a known aliquot of solution with sulfuric acid. This solution was then heated to 80-90°C on a hot plate and titrated with standard sodium oxalate to a clear end point. The results indicated that the concentration of both caustic and permanganate did not decrease by more than 20 percent (10 percent to 8 percent and 5 percent to 4 percent by weight respectively) during this phase of the loop run. The average decrease in both cases was approximately 10 percent. This change may have been due to some preliminary decomposition of the potassium permanganate to form manganese dioxide.

6.2.2 Secondary Solutions

The citric acid and ammonium citrate used in loop tests were also of reagent grade purity. The concentration of the citric acid was 5 percent except for the citric acid-ammonium citrate combination solutions where the concentration varied from 2 percent to 5 percent. The ammonium citrate (dibasic) varied from 5 percent to 10 percent except for the combination solutions where the concentration varied from 2 percent to 5 percent. The concentration of the solutions was changed in order to vary the acidity (pH) and to determine its effect on decontamination and corrosion.

All secondary rinse solutions were prepared by addition of the required amounts (percent by weight) to 3 gallons of demineralized water. No waiting period was necessary and with vigorous stirring a clear solution was obtained within a matter of minutes. The measured initial pH of the various solutions used in loop tests is given below:

Solution	pH	Remarks
5% Citric Acid + 1/2% Versene ------	2.4-2.5	----
5% Citric Acid + 2% Ammonium Citrate + 1/2% Versene ----------	3.1	"Citric Acid" combination solution
2% Citric Acid + 5% Ammonium Citrate + 1/2% Versene ----------	4.2-4.3	"Citrate" combination solution
5%, 10% Ammonium Citrate ---------	5.1	----

Loop data presented in Table 2 indicate that an ammonium citrate concentration of 5 percent and 10 percent gave satisfactory decontamination results (D. F.'s of 23 and 12 respectively).

TABLE 2 Effect of Ammonium Citrate Concentration on Final Decontamination Factor

Run No.	Concentration	Flow Rate (fps)	Net Initial Activity (cpm)	Net Final Activity (cpm)	D. F.
11	3%	5	16,390	3,610	5
13	5%	5	32,770	1,400	23
14	10%	5	27,660	2,310	12

Corrosion data, presented in Section 7.1.1, indicate that the corrosion on Type 304 stainless steel by a 10 percent ammonium citrate solution was more than twice that at 5 percent. For this reason and based on the results given in Table 2, the optimum concentration for ammonium citrate was set at 5 percent.

Citric acid is an excellent complexing agent for iron and nickel. Lanford and Quinan have shown that ferric ion and citric acid exist as a 1:1 complex in strongly acid solution[2]. More recently, Warner and Weber have shown that the complex probably exists as an anionic species ($CiFe^-$)[3]. Evidence for this species is provided by the fact that ferric citrate can be removed from solution by means of an anion exchange resin in the chloride form at a pH as low as 2. It was also concluded that the 1:1 complexes are present in neutral solutions as long as sufficient citrate is present to prevent the formation of ferric hydroxide (about 5-fold excess over iron).

An additional complexing agent (Versene) was used in all runs where citric acid was used as a component in the secondary rinse. It was not known to what extent the citrate would be destroyed by reaction with residual caustic permanganate and/or manganese dioxide during the rinse step of the treatment. Consequently, it was desired to enhance the chelating power of the solution. A chelating agent was not used with the ammonium citrate because it was desired to take advantage of the greater chelating power of the Versene series for ferric ion under acidic conditions. The activated corrosion product scale is composed chiefly of magnetite (ferrosoferric oxide) and it is assumed that this is dissolved by the secondary solution rinse. However, if the iron were dissolved by the rinse solution as ferrite (FeO_2^-) or ferrate ($Fe_2O_4^=$), it would not be possible to chelate the iron with Versene under any conditions. Conclusive data is not available on the effect of adding the chelating agent, but initial screening data indicated that, when used in conjunction with an acidic rinse, the overall effectiveness of the decontamination treatment was increased. Three chelating agents were used in loop decontamination tests: Versene Acid, Versene Powder, and Versene Fe-3 Powder. Consequently, where Versene is used in this report, reference is made to one of

these three compounds.

Because of the limited solubility of the Versene Acid and the broad chelating power of the Versene Fe-3 Powder (chelates iron effectively up to pH 10.5), the tri-and tetra-sodium salts of Versene acid in powder form are recommended. This would include Versene Powder, or Versene 9. The use of either of these compounds would permit the precipitation of ferric ion as ferric hydroxide in a neutral or slightly alkaline medium. This would facilitate waste disposal in that the iron could be concentrated by precipitation with caustic. Ferric hydroxide is also an excellent scavenger and could adsorb other radioactive nuclides on its surface.

During three loop runs with the caustic permanganate-rinse (citric acid, ammonium citrate) treatment, samples of the rinse wereperiodically removed and analyzed for iron. The iron was determined by the orthophenanthroline colorimetric method. The results are given below:

Run No.	Rinse	PPM Iron Min.	Max.
9	5% Ammonium Citrate	30	50
10	5% Citric Acid 1/2% Versene	37	57
11	3% Ammonium Citrate	4	9

It requires 8.4 parts of Versene Powder and 7.4 parts of Versene 9 to chelate 1 part of metal in the pH range below 7.[4] A 1/2 percent solution of Versene (5,000 ppm) would adequately chelate the iron observed in loop samples and could be expected to chelate all the iron resulting from a large scale reactor decontamination.

6.2.3 Physical Properties

The densities and viscosities of the various rinse solutions and the caustic permanganate were determined in order to calculate Reynolds' Number for the investigation of flow rate. The densities and viscosities are given as a function of temperature in Fig. A-1 and Fig. A-2 of the Appendix. The densities were determined by means of a specific gravity bottle previously calibrated with water at various temperatures. The viscosities were determined with a Fisher-Irany Viscometer previously calibrated with water at various temperatures.

There is no data available on the susceptibility of the caustic permanganate and citric acid and/or ammonium citrate rinse solutions to decomposition by radiation. Normally, radiation of 10^8 to 10^9 roentgens is necessary to cause breakdown of similar compounds.[5] Insofar as the solution will be used in a steam generator isolated from the reactor core, the possibility of chemical decomposition by radiation is remote.

6.3 Temperature of Chemical Solutions

6.3.1 Caustic Permanganate

From the preliminary screening data presented in Volume I of the report, caustic permanganate solutions at temperatures between 185°F and 205°F appear to give satisfactory decontamination results. One test with the caustic permanganate at 75°F gave a poor decontamination factor.

An examination of the mechanism (Section 6.6) appears to show that it is necessary to have the caustic permanganate approximately at the boiling point. All loop runs were performed with the caustic permanganate solution slightly above this temperature. The temperature used was approximately 225°F. Sufficient pressure was used to prevent boiling.

6.3.2 Citric Acid - Versene

A series of runs were performed with a primary solution treatment of caustic permanganate and a 5 percent citric acid-1/2 percent Versene rinse. The rinse was circulated in the loop while being heated from 100°F to 250°F. A count of the residual activity of the contaminated sample was taken approximately every 2 minutes during the operation (Fig. 10). At various temperatures the slope of the activity-time curve was determined with a Gerber derivimeter. This value (Δ CPM/ Δ Time) was then plotted against its corresponding temperature (Fig. 11). The maximum slope (maximum change in activity with change in time) was then determined from the curve.

The temperature range corresponding to the maximum slope is shown as a broken line on each of the three curves. This temperature range (145° to 175°F) was taken as a minimum for decontamination with this rinse. A temperature of 175°F was used on all subsequent loop tests, with citric acid-Versene as a secondary rinse, to insure complete removal of activity.

6.3.3 Ammonium Citrate

The temperature for the ammonium citrate rinse was determined in the same manner as the citric acid-Versene rinse with one exception. For this rinse the concentration of the ammonium citrate was varied to determine its (concentration) effect on optimum temperature. Concentrations of 3 percent, 5 percent and 10 percent by weight of ammonium citrate were used. The caustic permanganate concentration was constant (10 percent sodium hydroxide, 5 percent potassium permanganate).

There was no point of maximum change in activity per change in time for the ammonium citrate rinse (Fig. 12). Examination of Fig. 13 shows the break for the 10 percent rinse curve to occur at approximately 200°F. For a 5 percent rinse the break occurs between 216°F to 225°F. The 3 percent rinse did not break until almost 230°F. Beyond these temperatures, the absolute value of the slope of the

curves continually increases showing a greater removal of activity with higher temperatures. These higher temperatures may also result in excessive corrosion of the base metal. Therefore, the above temperatures were chosen as an optimum for their respective concentrations.

The effect of activity removal with increasing temperatures is apparent for the 10 percent curve (Fig. 12). At 200°F, the curve starts to bend as if approaching a maximum point, but then commences to increase as the temperature increases. The curves of 3 and 5 percent ammonium citrate do not show this effect.

6.3.4 Combination Solutions

The operating temperature for the various combination solutions was chosen on the basis of the major constituent in the solution. A temperature of 220°F was established for the 5 percent ammonium citrate, 2 percent citric acid, 1/2 percent Versene rinse. A temperature of 175°F was established for the 5 percent citric acid, 2 percent ammonium citrate, 1/2 percent Versene rinse. The operating temperature of 220°F for the citrate combination solution would take advantage of both the major constituents in the solution.

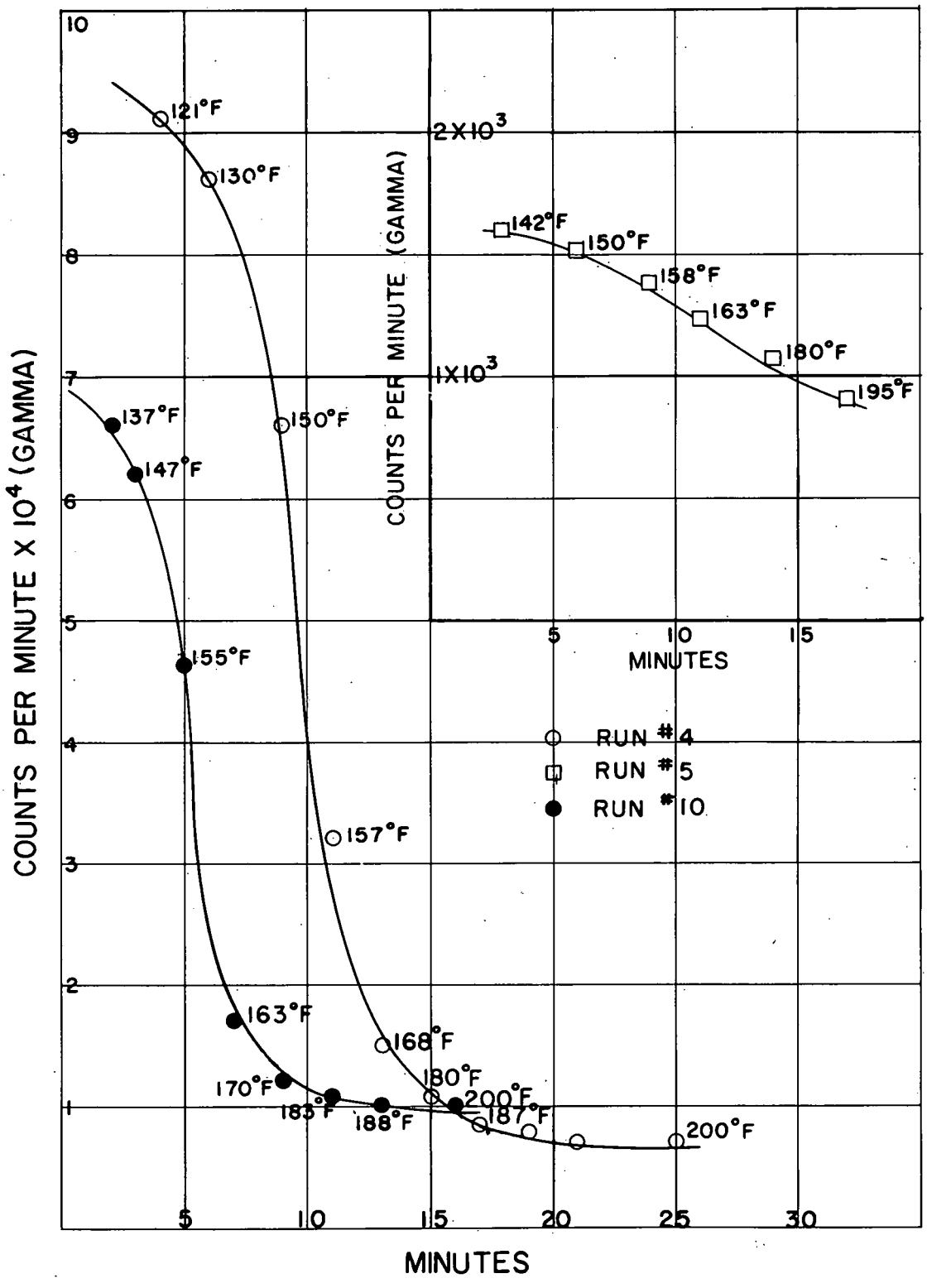

Fig. 10 Activity - Temperature Profile as a Function of Time for Citric Acid-Versene Rinse

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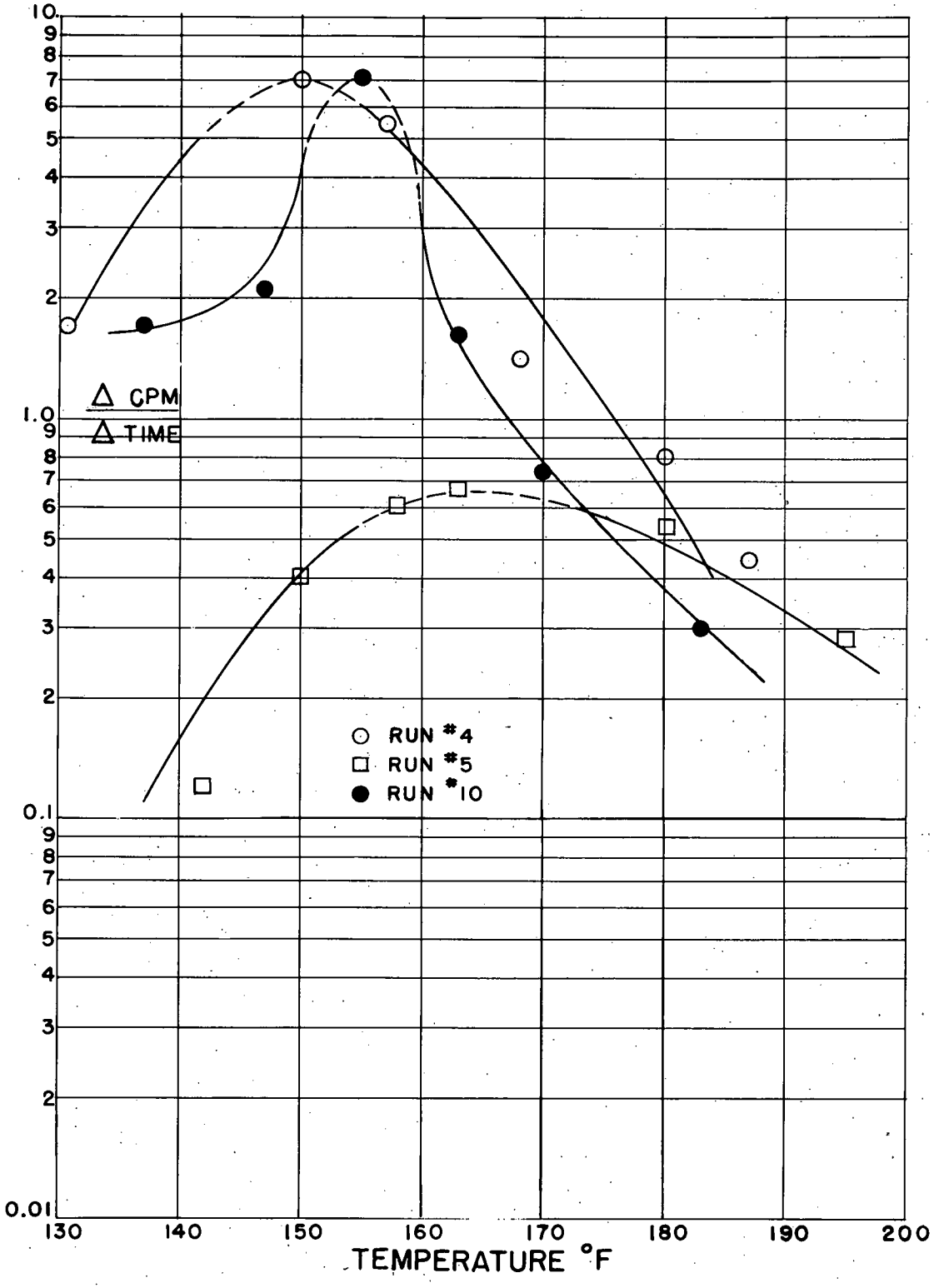

Fig. 11 Rate of Change of Activity as a Function of Temperature for Citric Acid-Versene Rinse

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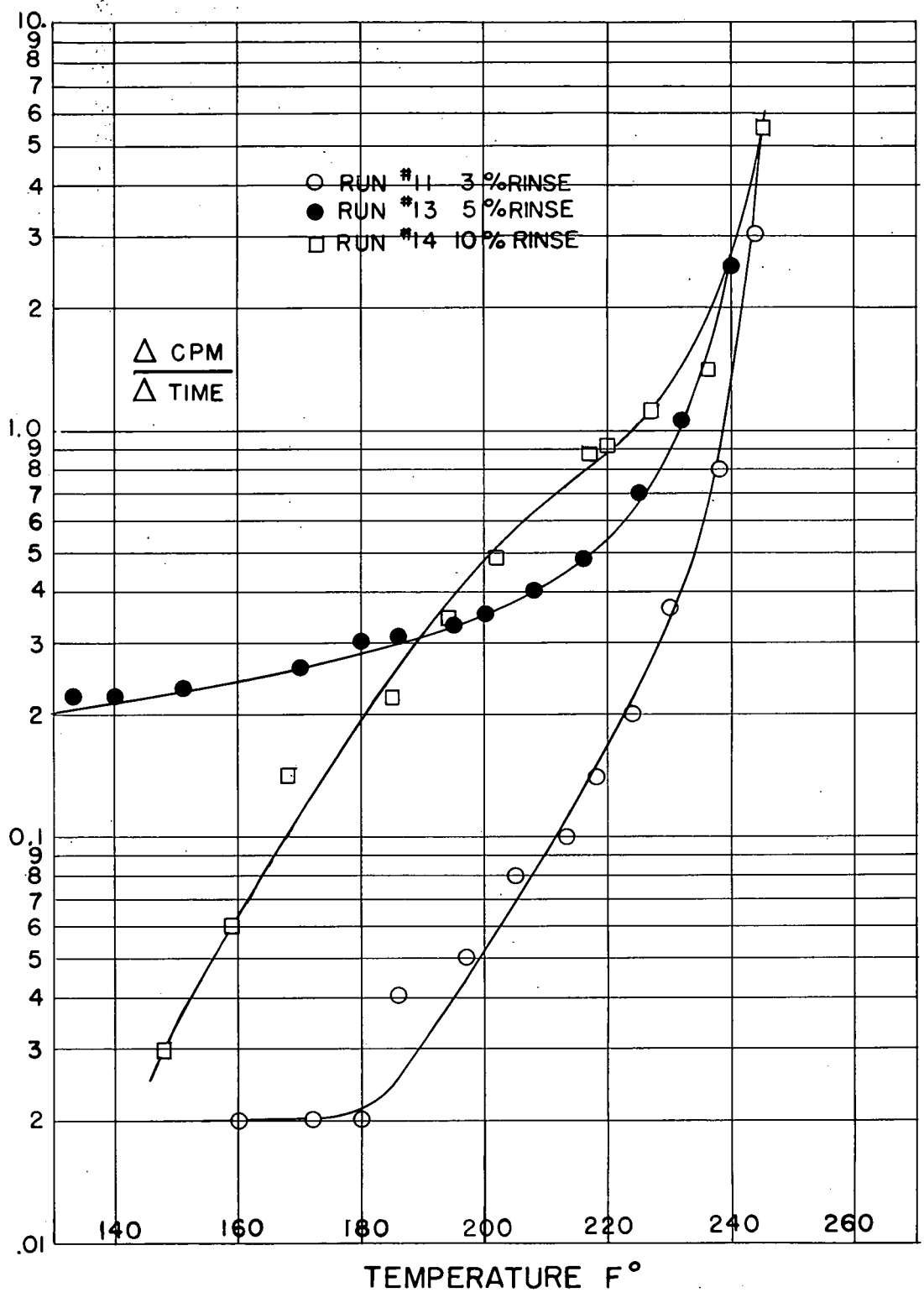

Fig. 12 Rate of Change of Activity as a Function of Temperature for Ammonium Citrate Rinse

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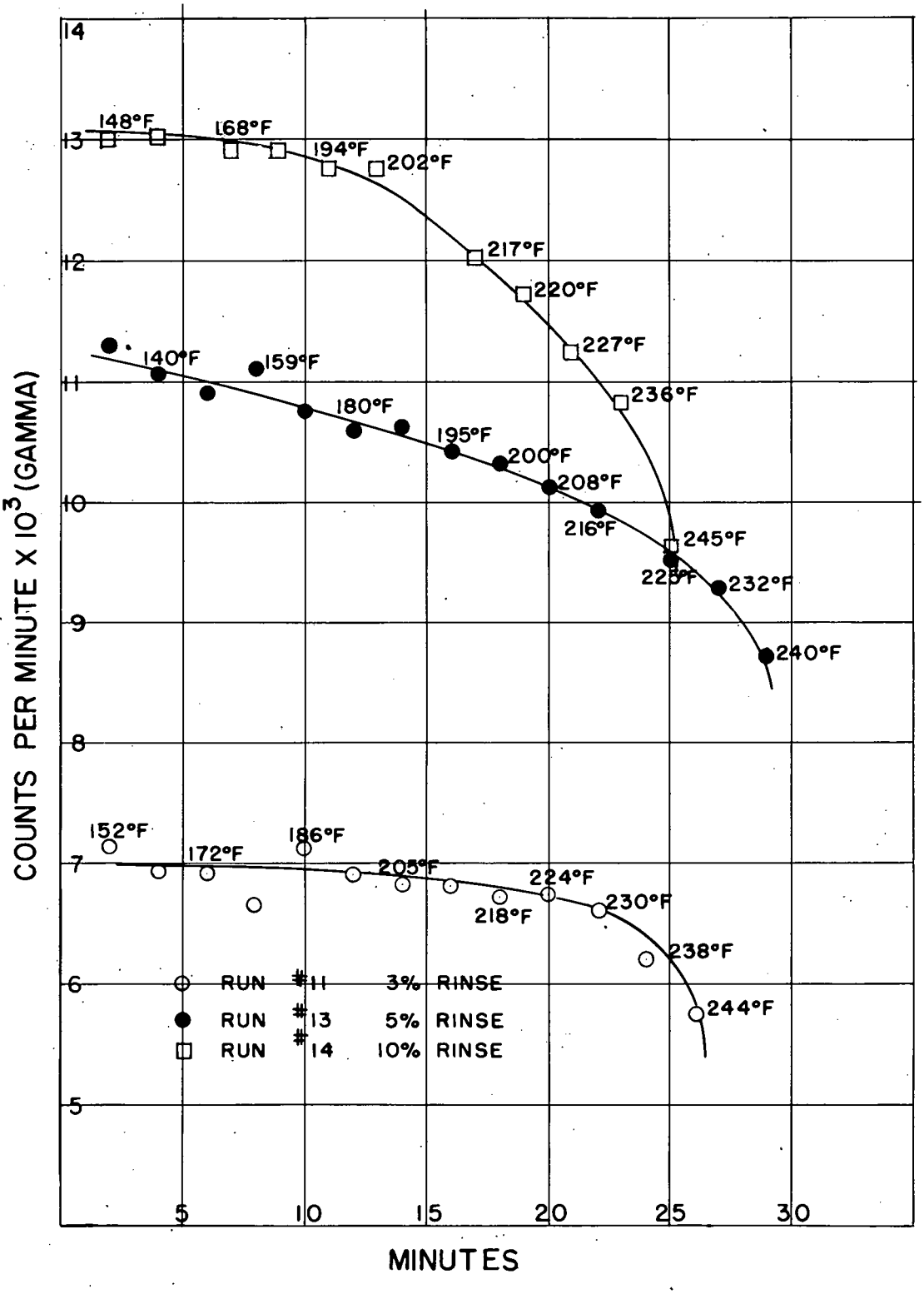

Fig. 13 Activity-Temperature Profile as a Function of Time for Ammonium Citrate Rinse

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6.4 Decontamination Flow Rate

6.4.1 Loop Flow Modification

Prior to evaluating the effect of flow rate on decontamination, it was necessary to modify the sample section of the loop. This was required because the Reynolds' Number, which is a measure of the turbulence of the fluid, would not be constant in the length of contaminated tubing. The fluid would not recover sufficiently from entrance disturbances before leaving the contaminated tubing section. This would cause a serious discrepancy in using a value of flow velocity derived from experimental data. In a large steam generator, the tubes would be long enough to allow complete recovery of the fluid.

The modification involved installing an 18-inch length of identical but uncontaminated tubing upstream of the sample section. A Swagelok union was used to join the contaminated sample to this additional tube length. With this union, there was a minimum disturbance to the fluid in passing from the flow levelling section to the contaminated section. With the Reynolds' Number nearly constant for the length of the contaminated section, the calculated velocity would then be a true indication of the average turbulence inside the tubing.

It was only possible to determine a minimum Reynolds' Number for the fluid in the sample holder due to the complicated geometry. However, for most cases the minimum value was in the turbulent region.

6.4.2 Determination of Optimum Flow Conditions

The variation of final decontamination obtained at various flow rates is shown in Run No. 22 where ammonium citrate was used as a rinse solution (Fig. 14). The caustic permanganate treatment and first water rinse were performed at 2 ft/sec. The ammonium citrate rinse was first circulated at 2 ft/sec. After 12 minutes at 220°F at this flow rate, the residual activity was constant. When the flow was increased to 4 ft/sec , a noticeable drop in activity was observed; 14 minutes later the flow rate was increased to 6 ft/sec , and a further drop in residual activity was observed.

To determine an optimum flow for the secondary solution rinse, a series of loop decontamination tests were performed with Type 304 3/4-inch 16-Gage BWG stainless steel tubing. The tests were performed with ammonium citrate and citric acid-Versene encompassing a flow range of 2 to 12 ft/sec. The velocity of the caustic permanganate solution was the same as that of the water and secondary solution rinses. The decontamination factor and background factor were determined for each loop run.

A definite flow dependence was found with the 5 percent ammonium citrate rinse. It was observed that an increase in flow rate tended to increase the removal of activity (Fig. 15). With citric acid there was no apparent effect of flow rate on the removal of activity (Fig. 16). This flow dependence of the ammonium

citrate rinse may be due to the difference in pH between ammonium citrate and citric acid-Versene. The ammonium citrate rinse (pH = 5.1) may require a turbulent action for effective removal and chelation of the contamination. Citric acid-Versene (pH = 2.4-2.5) probably removes the activity by chemical reaction as well as chelation.

It is believed that there is no dependence of flow with caustic permanganate. During Run No. 22 (Fig. 14) the flow of the caustic permanganate was kept constant while the flow rate for the ammonium citrate was varied. In later tests, the flow rate of the permanganate solution was the same as the ammonium citrate. The data from Run No. 22 fall on the curve of the data obtained from later ammonium citrate runs. The discussion of the decontamination mechanism (Section 6.6) will present a clearer understanding of the caustic permanganate treatment.

If ammonium citrate is used as a secondary solution rinse, high flow rates would be necessary to achieve good decontamination. It was found that the addition of citric acid to the ammonium citrate rinse reduced the background factor with no change in velocity. This is shown by the data in Table 3. This would permit lowering the flow rate to a value below that which would be necessary for ammonium citrate.

TABLE 3 Effect of Citric Acid-Versene on The Flow Dependency of Ammonium Citrate

Run No.	Flow Velocity ft./sec.	Secondary Solution	Background Factor
23	5	5% Ammonium Citrate	10.8
43	5	Citrate Combination Solution	7.7
46	5	Citrate Combination Solution	7.2

It would also avoid using the citric acid-Versene rinse which has a lower pH and would be expected to result in a higher corrosion rate. This would also be true for the citric acid combination solution. Consequently, a flow velocity of 5-feet per second was chosen for the citrate combination solution. This value represents a minimum flow velocity. Higher flow velocities will result in better decontamination but pumping and piping costs would be higher.

6.4.3 "Aeration" Effect

It was observed that greater decontamination was achieved when the loop was exposed to the atmosphere between the end of the first water rinse and the addition of the citric acid-Versene solution (Table 4). This effect was not found with the ammonium citrate rinse.

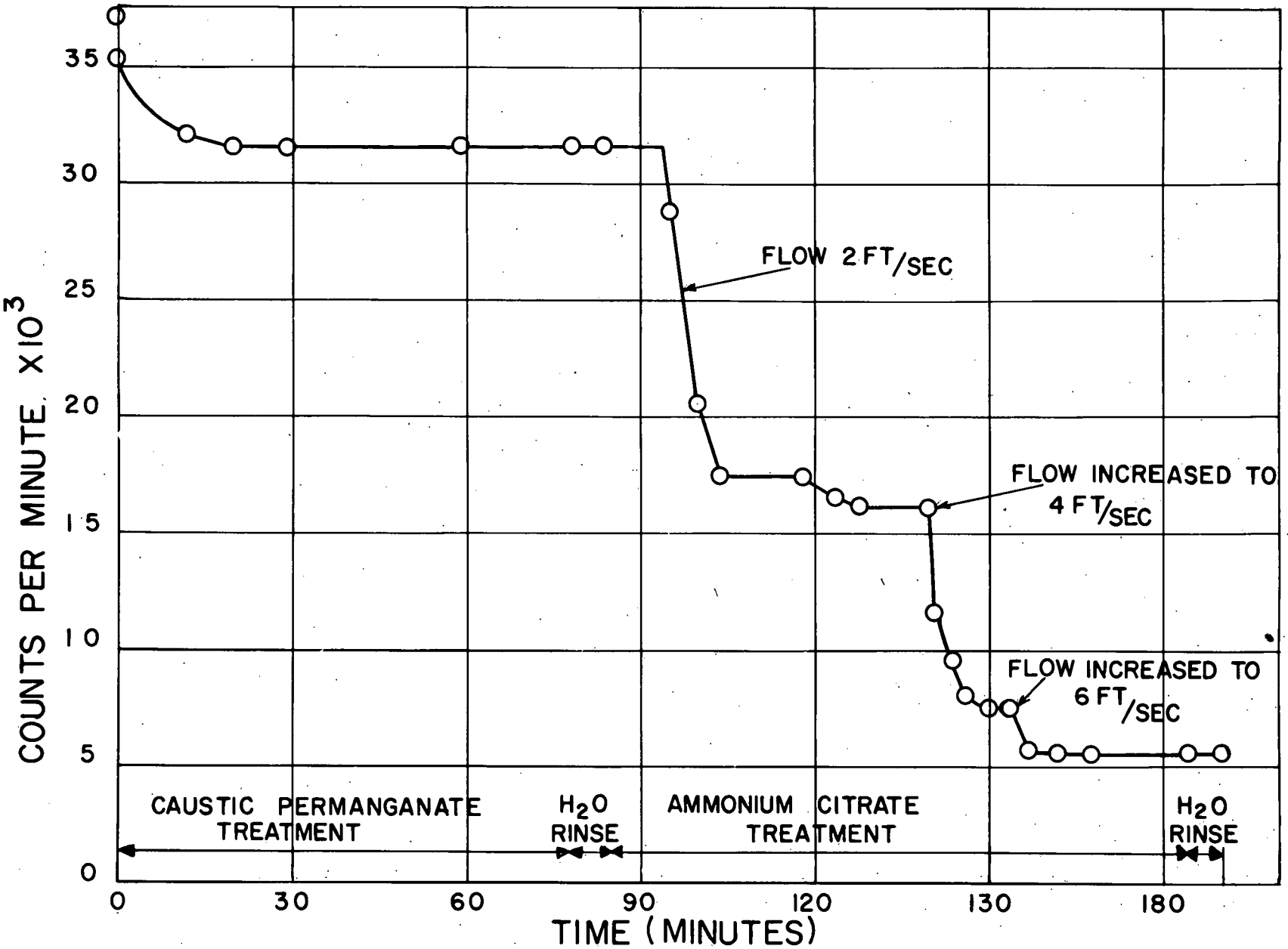

Fig. 14 Variation of Decontamination with Flow Rate - Loop-Test Run No. 22

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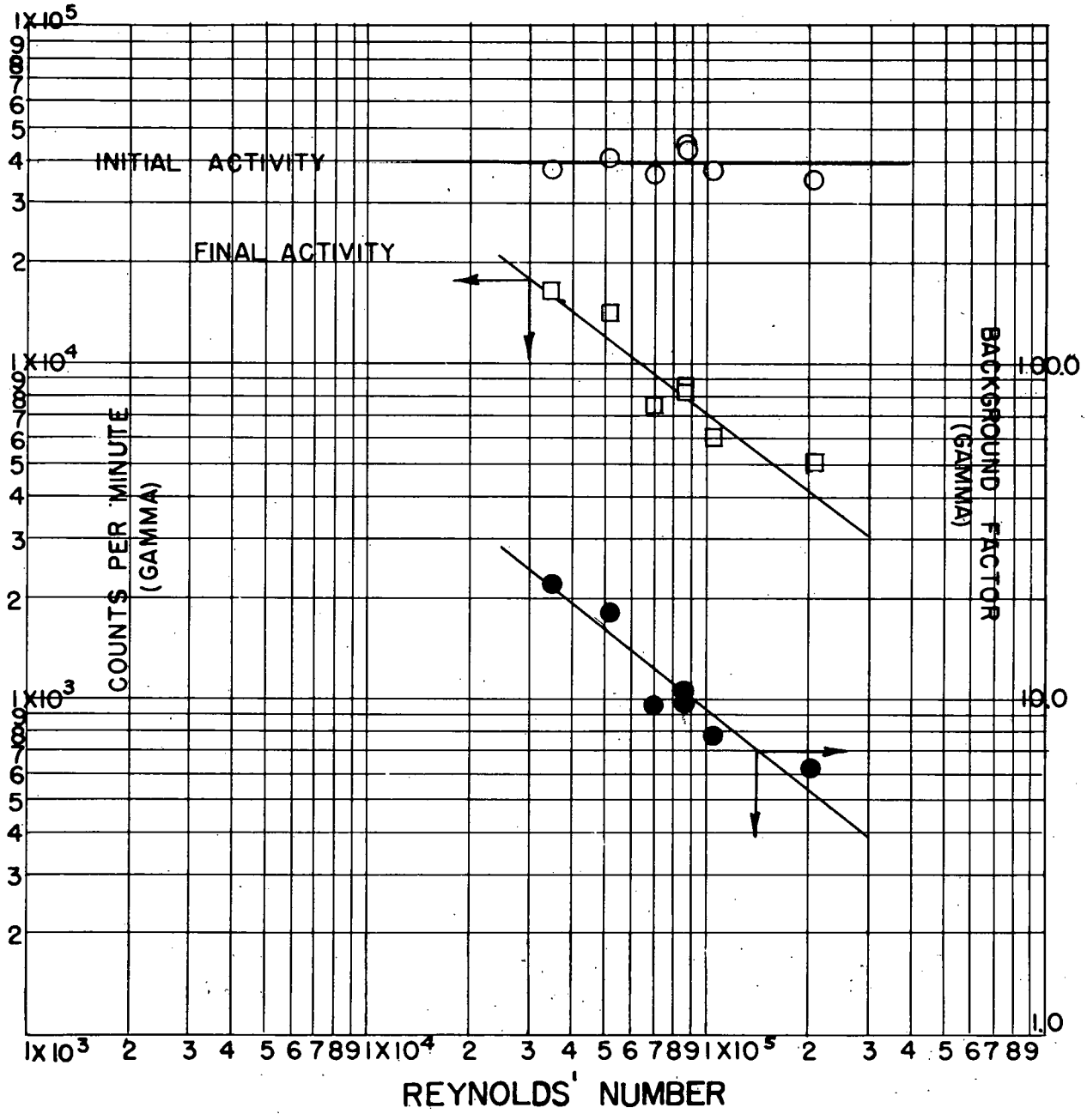

Fig. 15 Relationship Between Flow Velocity and Decontamination using an Ammonium Citrate Rinse

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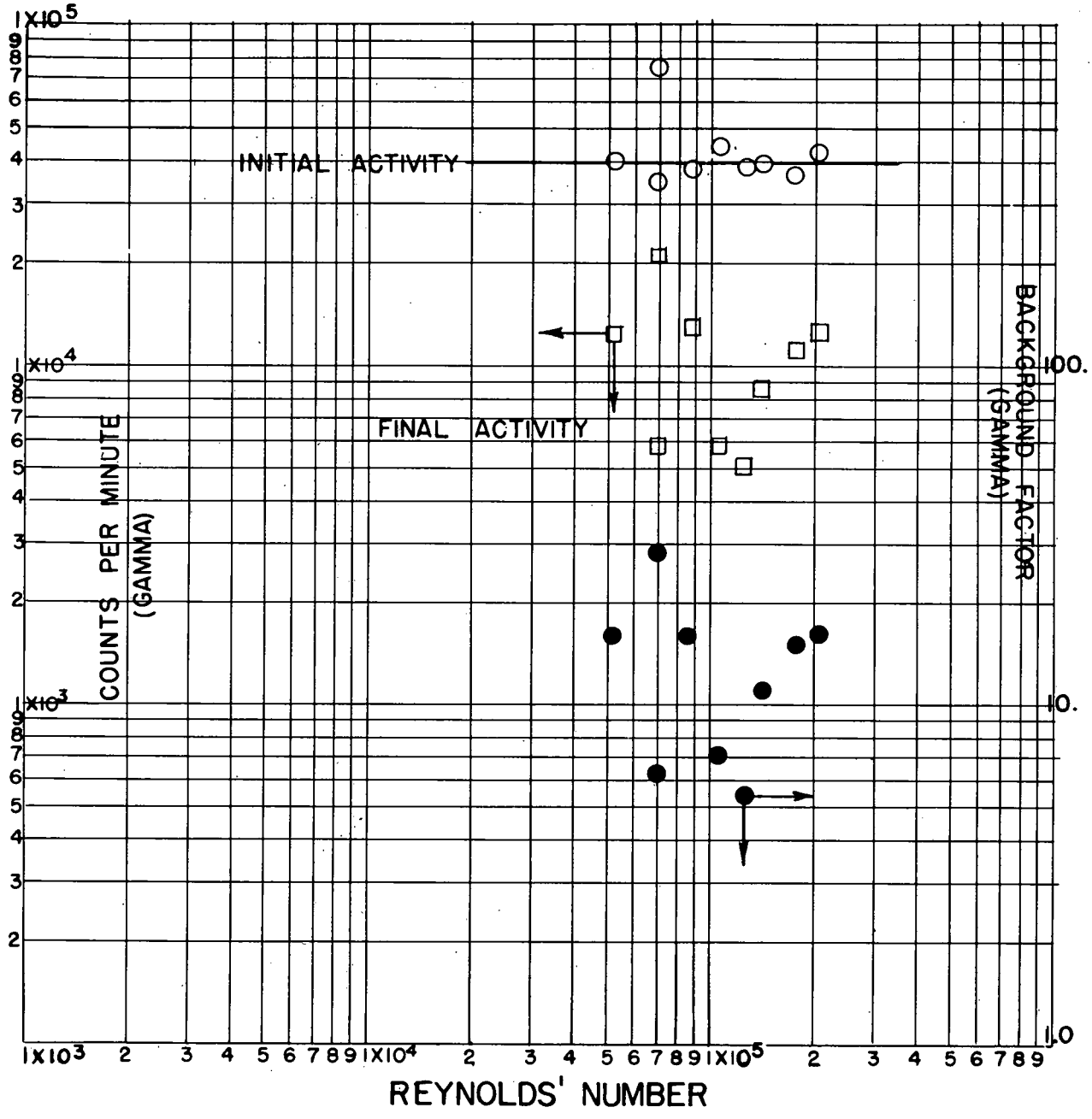

Fig. 16 Relationship Between Flow Velocity and Decontamination using a Citric Acid-Versene Rinse

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TABLE 4 Effect of Citric Acid-Versene Aeration Period on Final Background Factor

Run No.	Flow Rate fps	Net Residual Activity cpm	Aeration Time Minutes	Background Factor (Background = 735 cpm)
32	5	11,920	3	16.2
29	4	20,660	6	28.1
28	8	8,070	11	11.0
30	12	12,040	11	16.4
27	6	5,200	12	7.1
26	10	10,850	12	14.8
31	3	12,150	12	16.5
15	5	1,840	28	2.5
20	1	4,750	38	6.5
33	4	4,780	56	6.5
34	7	4,170	61	5.7

The data of Table 4 are shown graphically in Figure 17 where background factor is plotted against the "aeration" or air exposure time. The curve indicates that an aeration period of 20 minutes or more reduced the background factor more than three-fold over that when no aeration period was used. The cause of the aeration effect is not known at this time. It may be due to a further oxidation of the activated corrosion product scale by the manganese dioxide in the presence of air. The lower pH (2.4-2.5) of the citric acid solution may have a greater tendency to remove the resulting scale than the ammonium citrate rinse (pH = 5.1).

An "aeration" period of at least one hour was used in subsequent loop tests involving the combination solutions since citric acid is a constituent in both the citric acid combination and the citrate combination solutions.

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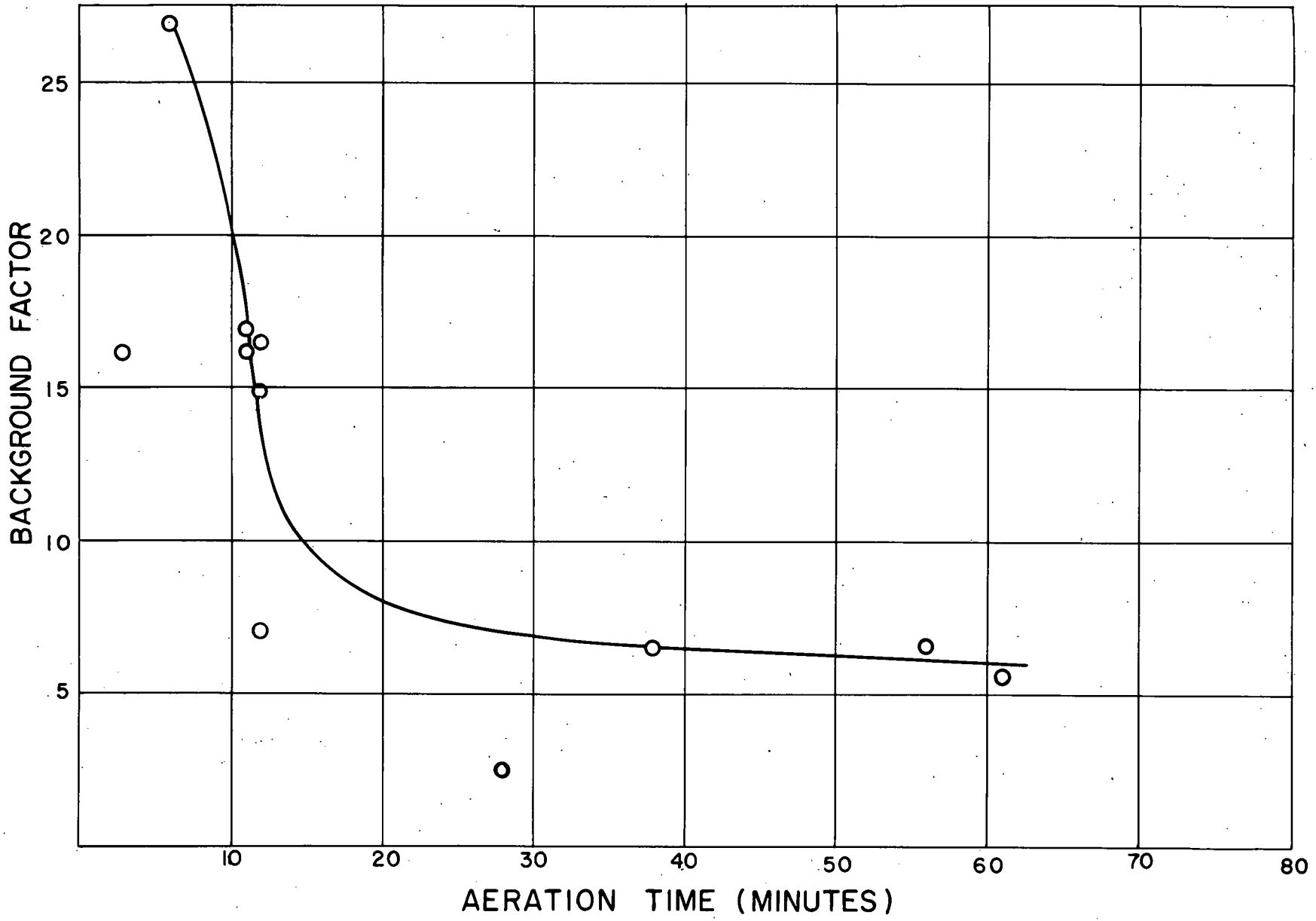

Fig. 17 Effect of Aeration Time on Decontamination

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6.5 Residence Time of Decontamination Solutions

In this report, residence time is defined as the time during which a particular solution is in contact with the contaminated surface at the desired flow and temperature. It does not include the time during which the solution is circulated and brought to temperature.

The selection of a residence time is similar to that of concentration in that it requires a compromise between corrosion rate and ability to decontaminate. When the activity has reached a constant value, it can be assumed that further exposure will remove little if any additional activity. This is important for the secondary solution rinses where corrosion rates are higher than for the caustic permanganate.

Generally, preliminary screening tests were performed with a caustic permanganate residence time of 30 minutes. In one case where the residence time was increased to 60 minutes, a higher degree of decontamination was achieved for the same secondary rinse conditions. However, in loop experiments, the contact or exposure time for the caustic permanganate varied from 70 to 80 minutes. This included a heat up time of 30 to 35 minutes, a residence time of 30 minutes, and a cooling time of 10 to 15 minutes.

The residence time for the secondary solution rinses was determined from the results of 20 loop tests. These runs were performed using caustic permanganate followed by various secondary solution rinses, i.e. 5 percent citric acid - 1/2 percent Versene, 5 percent ammonium citrate, or the citrate combination rinse. The data were shown in bar graph form (Fig. 18); the time required for the activity to reach a constant value $\left(\frac{\Delta \text{cpm}}{\Delta \text{time}} = 0\right)$ is shown as a frequency distribution. The graph indicates that constant activity was generally reached between 18 and 22 minutes after reaching the recommended temperature. There were no loop runs where a residence time longer than 27 minutes was necessary, nor was there any evidence that a particular rinse favored a specific residence time. On the basis of these results, a residence time of 30 minutes is recommended. Any additional time beyond 30 minutes would only increase the corrosion rate while removing only negligible activity.

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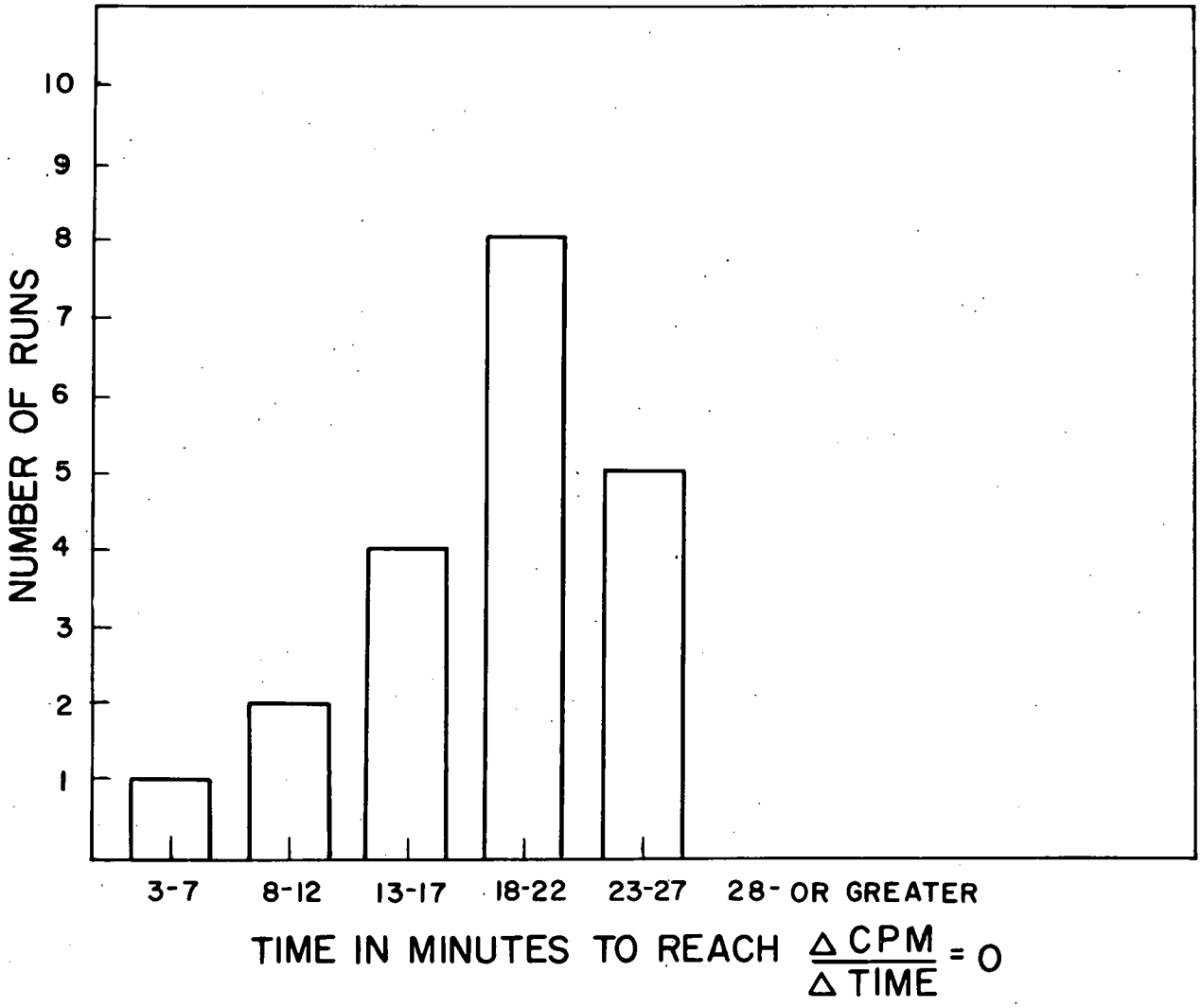

Fig. 18 Evaluation of Residence Time for Secondary Solution Rinses

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6.6 A Mechanism for Caustic Permanganate, Citric Acid, Ammonium Citrate Decontamination

It was stated in Volume I of this report that nitric acid, oxalic acid, citric acid, and ammonium citrate were equally effective as secondary solution rinses. This may indicate that these rinses removed the activated corrosion product scale by the same mechanism. Any attempt to improve on the effectiveness of the decontamination treatment must be made with some idea of the overall mechanism involved. Therefore, a possible mechanism is presented which may account for some of the observations noted during the course of this work. The mechanism involves four steps:

A. Oxidation
B. Formation of Manganese Dioxide
C. "Aeration" or Air Oxidation (when citric acid is employed in the secondary solution rinse)
D. Removal of Activity

The first step in the decontamination treatment is the formation and reaction of the oxidizing solution. When a mixture of caustic and permanganate is heated near the boiling point, oxygen is liberated according to the reaction[6]

$$\underset{\text{Purple}}{4KMnO_4} + 4\ NaOH \rightleftharpoons \underset{\text{Green}}{4\ NaKMnO_4} + 2\ H_2O + O_2 \qquad (1)$$

The combination of the permanganate and oxygen provides a strong oxidizing media to convert the corrosion product scale to a form that can be readily removed by the secondary solution rinse. The oxygen is probably responsible for the sharp increase in the corrosion rate of Type 304 stainless steel in caustic permanganate at 95°C (Section 7.3.2).

Radiochemical analyses of the permanganate and citrate solutions, following decontamination of a section of the APPR-1 steam generator dividing plate, revealed that 75 percent of the Mn^{54} activity was removed in the permanganate solution (Section 8.1.2). The Mn^{54} has been found associated with the primary system reactor water rather than the insoluble corrosion products[7]. This activity may be merely adsorbed on the oxide scale and subsequently removed by exchange during the caustic permanganate step.

The second step in the decontamination mechanism is the formation of a brown film which is assumed to be manganese dioxide. This is an excellent scavenger for radioactive nuclides whether they are present in solution or associated with particulate matter. The MnO_2 is formed as the result of a disproportionation reaction of the green manganate solution in an excess of water or in the presence of acid:[6]

$$3\ NaKMnO_4 + 2H_2O \longrightarrow 2KMnO_4 + 3NaOH + KOH + MnO_2 \qquad (2)$$

The reaction does not take place in an excess of alkali; however, it will take place if the alkali is removed by the addition of acid, even a weak acid such as carbonic acid. Contaminated pipe samples, used in bench screening tests, were invariably covered with a brown film, after brief rinsing with water following the caustic permanganate step. Metal test specimens removed from the sample section of the loop after the completion of the first water rinse were also found to possess this same film. However, as the pH of the first water rinse was basic (pH of 12.5 to 12.8) in all loop runs, it is possible that not all the manganese dioxide was formed until the addition of the ammonium citrate and/or citric acid-Versene rinse.

The third step involves an "aeration" time of the contaminated specimen following the first water rinse. As previously stated in Section 6.4.3, the reason for increased decontamination as a result of the aeration period is not known at this time.

The final step in the decontamination is the removal of the activated corrosion product scale. It has been shown that the major part of the activity (approximately 80 percent) is removed by the secondary solution rinse. The rinse must accomplish the dissolution of the manganese dioxide as well as the removal of the corrosion product scale. The former is accomplished by chemical reaction with citrate and/or citric acid-Versene by reducing the manganese to the manganous ion form. The citrate and/or citric acid is probably converted to a degradation product such as itaconic or aconitic acid with a minimum of gas evolution. The scale removal may be accomplished by a loosening and solublizing action of the citrate and/or citric acid-Versene solution. All rinse solutions removed during the secondary solution phase of the decontamination were found to be clear. Citrate is an excellent complexing agent for ferric ion, forming mole to mole complexes in the pH range from 1.5 to 7.[3] Versene is also an excellent complexing agent for ferric ion, particularly in the acidic range and for other polyvalent ions in both the acid and basic ranges.

PART II METALLURGICAL ASPECTS

7.0 DISCUSSION OF RESULTS

The metallurgical aspects of the decontamination program involved loop, dynamic autoclave, and static autoclave testing of metals exposed to the caustic permanganate and the citric acid-Versene ammonium citrate rinse solutions. Corrosion rates were determined for Type 304 stainless steel (annealed and sensitized), Babcock and Wilcox Croloy 16-1, and carbon steel (AISI C1010). Metallurgical testing involved checking metal test specimens, welds, and "U" bends for evidence of intergranular corrosion, cracking, contact corrosion, and pitting. The program outline is given below:

A. Loop Studies

1. Corrosion Rate in Decontaminating Solutions
   a. Type 304 stainless steel (annealed and sensitized)
   b. Babcock & Wilcox, Croloy 16-1
   c. Carbon Steel (AISI C1010)
   d. Inconel(Simulated APPR-1 run only)

B. Dynamic Autoclave Testing (15-16 hours)

1. Corrosion Rate in Caustic Permanganate
   a. Type 304 stainless steel (annealed and sensitized) coupons, "U" bends and weld samples

2. Corrosion Rate in Rinse Solutions same as B1a

C. Long Term Static Autoclave Testing (4-8 weeks)

1. Corrosion Rate in Caustic Permanganate:same as A1a, c

2. Corrosion Rate in Rinse Solution:same as A1a, c

7.1 Loop Decontamination Corrosion Results

The sample section previously described in Section 4.2.4 of this volume was used to determine corrosion rates for various metals exposed to the decontamination treatment. Metallurgical analysis was performed on these coupons and also on sections of tubing that had been exposed in the APPR-1 purification blowdown line and subsequently decontaminated.

Corrosion test specimens were exposed for the entire loop decontamination; consequently, only total weight loss results are reported. As a number of different rinse solutions were evaluated with some variation in total exposure time, loop corrosion results have been tabulated as weight loss per decontamination

hour (mgs/dm^2-hr). The decontamination exposure time varied from 2.5 to 3.0 hours; one loop run was 4.25 hours. The loop exposure time included the following:

		Minutes
A.	Caustic Permanganate Step	
	1. Filling loop and heating solution to temperature (225-250°F)	30-40
	2. At temperature	30
	3. Cooling prior to draining	10-15
B.	Water Rinse Step	10
C.	Citrate Rinse Step	
	1. Filling loop and heating solution to temperature (175-220°F)	30-35
	2. At temperature	30
	3. Cooling prior to draining	0-10
D.	Water Flush Step (First)	10
	Total	2.5 to 3.0 hours

The water rinse and water flush steps were included in the total exposure time because it was felt that the residual chemical solution in the loop during these steps might cause additional corrosion and add to the total weight loss.

7.1.1 Metal Coupon and Tubing Results

Figure 19 is a graphical summary of 13 loop runs where metal specimens were exposed to various solution treatments. The data have been grouped so as to permit a comparison of the rinse solutions under approximately the same conditions (Appendix Table B-1, 2).

There does not appear to be a significant difference in the weight loss results between the ammonium citrate rinse and the citric acid-Versene rinse with the exception of the Babcock and Wilcox Croloy 16-1. However, the Croloy 16-1 results show considerable variation, ranging from 2.4 to 81.0 mgs/dm^2-hr , which may account for the higher results. There does appear to be a significant difference in the weight loss between the annealed and sensitized Type 304 stainless steel. The relative difference is shown in Table 5 where the weight loss for the different metals tested are compared to annealed Type 304 stainless steel. The average weight loss of the sensitized steel resulting from the decontamination treatment using 5 percent ammonium citrate as a rinse was 3.1 times greater

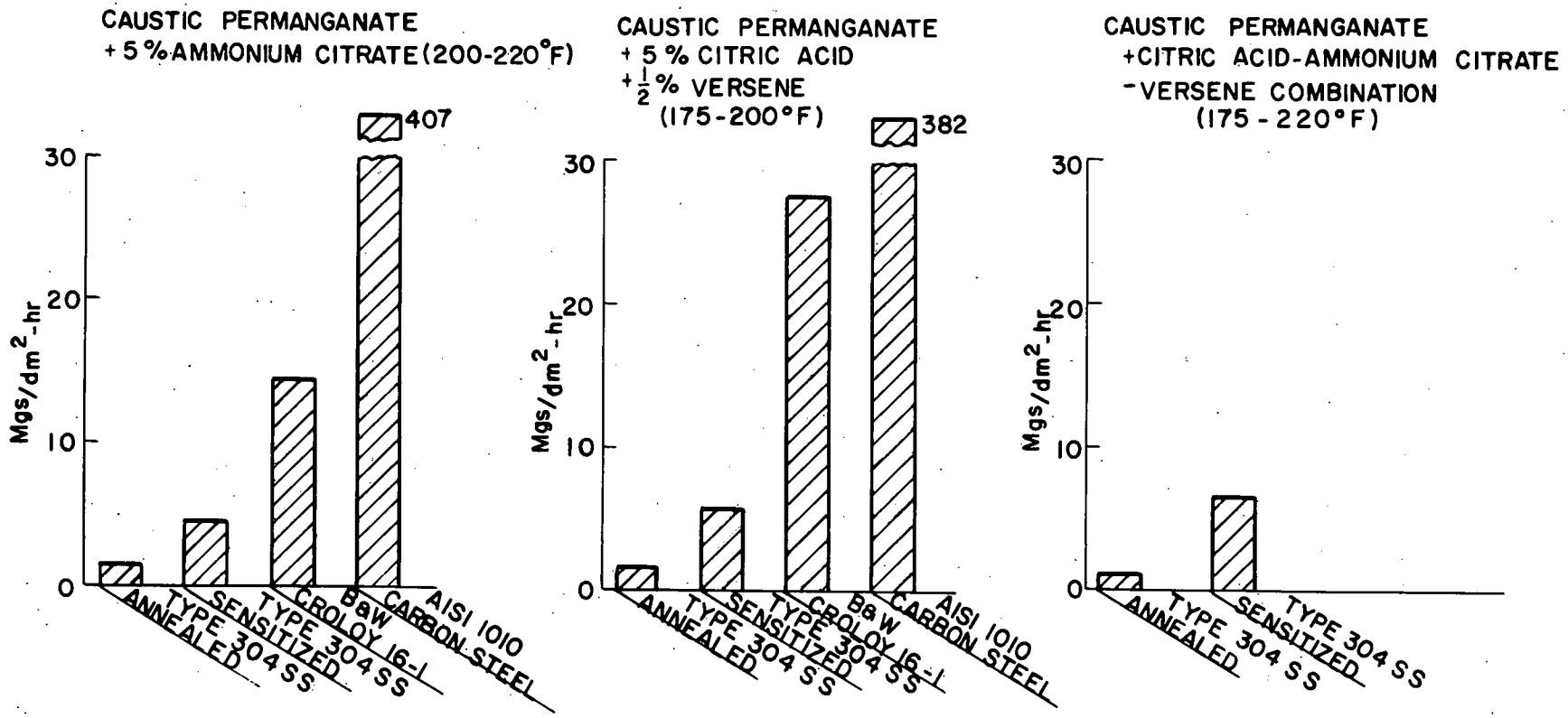

Fig. 19 Effect of Different Rinses on Weight Loss of Various Metals Following the Caustic Permanganate Solution (225-250°F)

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than that of the annealed steel. The weight losses on the sensitized steel were even higher in the case of the citric acid-Versene (3.6) and the citrate combination rinses (6.7). The Babcock and Wilcox Croloy 16-1 and carbon steel weight losses were significantly higher in the order mentioned.

TABLE 5 Ratio of Weight Losses for Various Materials to Annealed Type 304 Stainless Steel - Caustic Permanganate - Rinse Treatment

Material	5% Ammonium Citrate	5% Citric Acid + 1/2% Versene	Citric Acid-Versene, Ammonium Citrate Combination
Type 304 Stainless Steel (Sensitized)	3.1	3.6	6.7
Babcock and Wilcox Croloy 16-1	10.3	17.2	-
Carbon Steel (AISI C1010)	291	239	-

A number of contaminated sections of Type 304 stainless steel tubing decontaminated in loop tests were examined for metallurgical effects. Photomicrographs of the tubing exposed to the various solution treatments revealed no evidence of any deleterious effects (Fig. 20, Fig. 21).

A number of stainless steel coupons were exposed to more than one decontamination treatment in order to determine the corrosion effect as a result of successive treatments. The results for Type 304 stainless steel are presented in Fig. 22 where the weight loss results (mgs/dm^2-hr) are given as a function of the number of decontamination cycles. The previous treatments for each point were not necessarily performed with the same chemical solution. As would be expected, the corrosion rate is the same if not lower for succeeding decontamination cycles. The decrease in corrosion rate is more apparent in the case of the sensitized metal than in the case of the annealed metal. The corrosion results for the citrate combination solution were not included in Fig. 22 as only coupon data exposed to two decontamination cycles were available (Appendix Table B-3, 4). However, the results indicate the same pattern of decreasing weight loss with successive decontamination cycles. Photomicrographs of stainless steel coupons (Type 304 annealed and sensitized, Babcock and Wilcox Croloy 16-1) revealed no evidence of intergranular corrosion, cracking, or localized attack (Fig. 23, Fig. 24, and Fig. 25).

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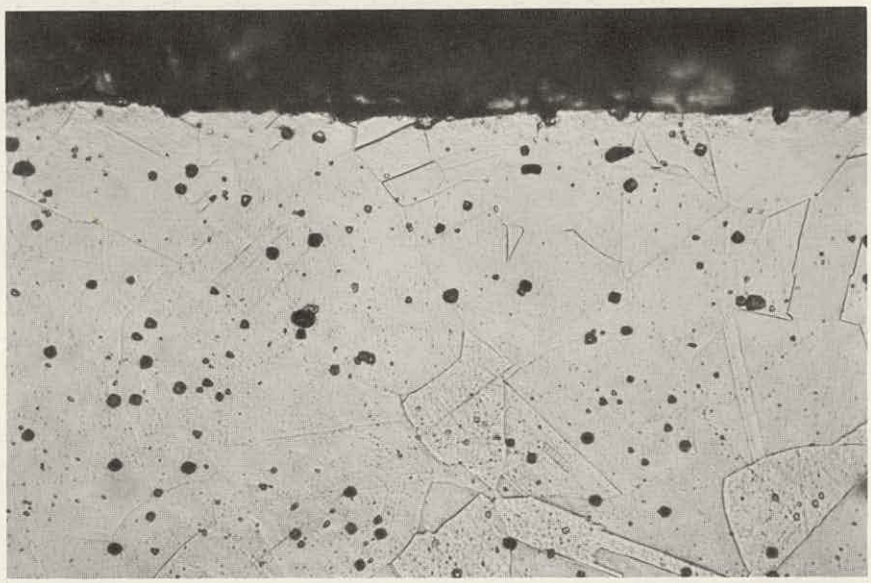
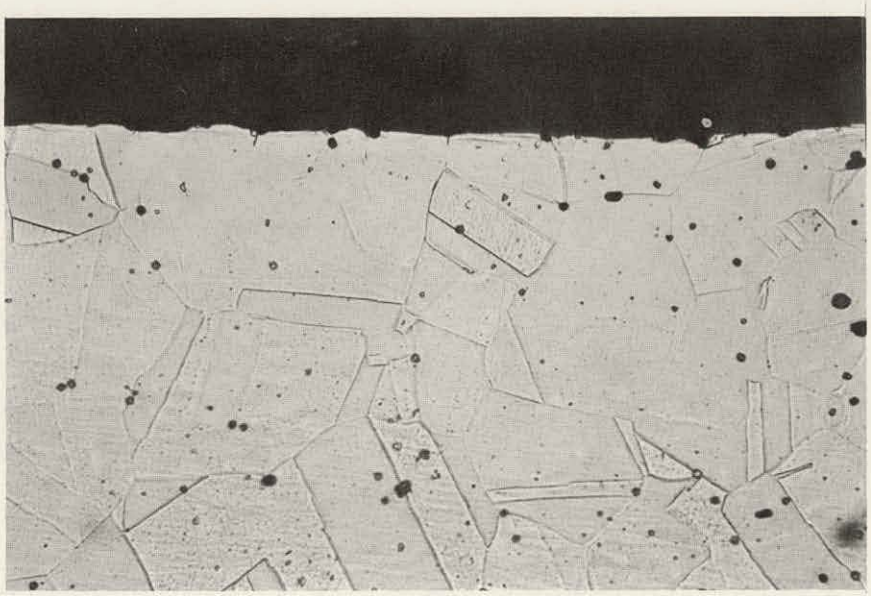


500 X Oxalic Acid Etch

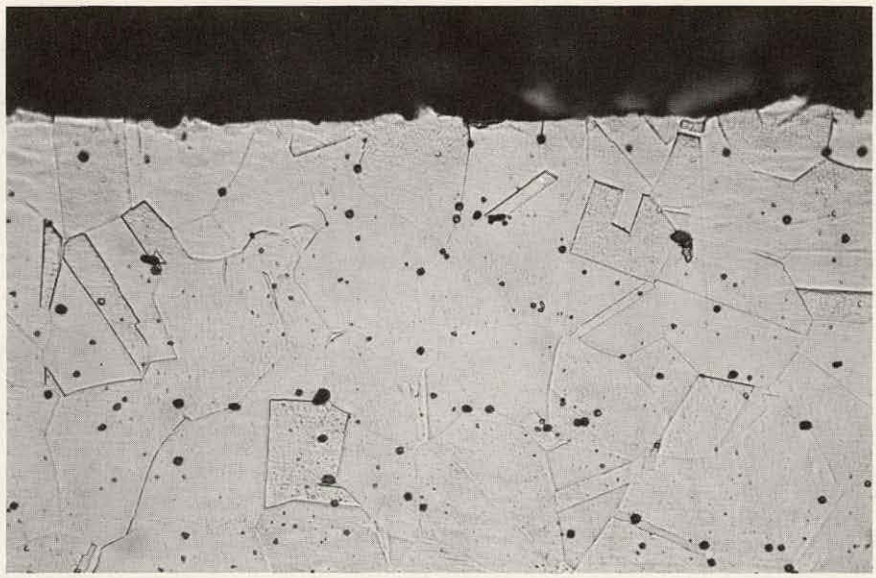
Sample Untreated



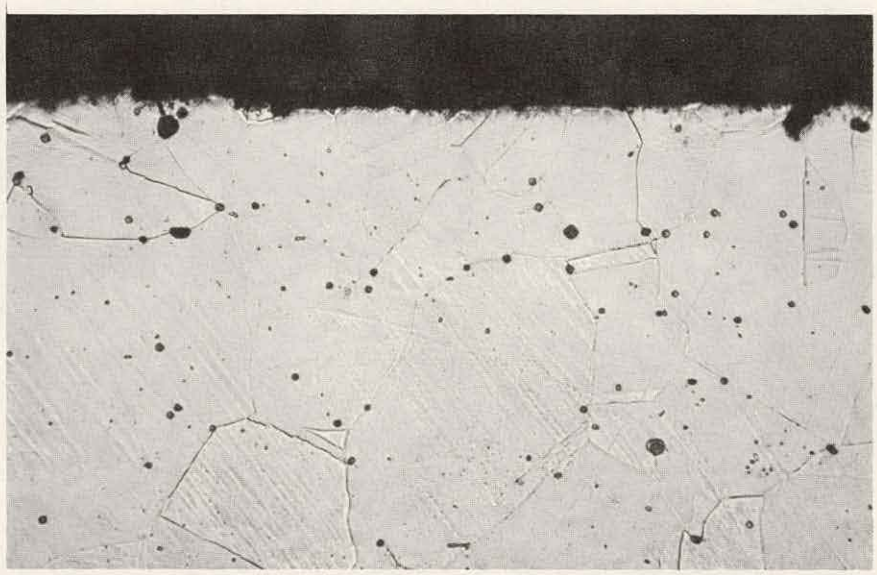
500 X Oxalic Acid Etch

Sample Exposed to Caustic Permanganate-5% Ammonium Citrate Decontamination Treatment-Loop Test No. 25

Fig. 20 - Photomicrograph of Type 304 Stainless Steel Tubing Exposed to to a Decontamination Treatment



500 X Oxalic Acid Etch
Sample Exposed to Caustic Permanganate-5% Citric Acid, 1/2% Versene Decontamination Treatment-Loop Test No. 34



500 X Oxalic Acid Etch
Sample exposed to Caustic Permanganate-Citrate Combination Solution Decontamination Treatment-Loop Test No. 43

Fig. 21 - Photomicrograph of Type 304 Stainless Steel Tubing Exposed to a Decontamination Treatment

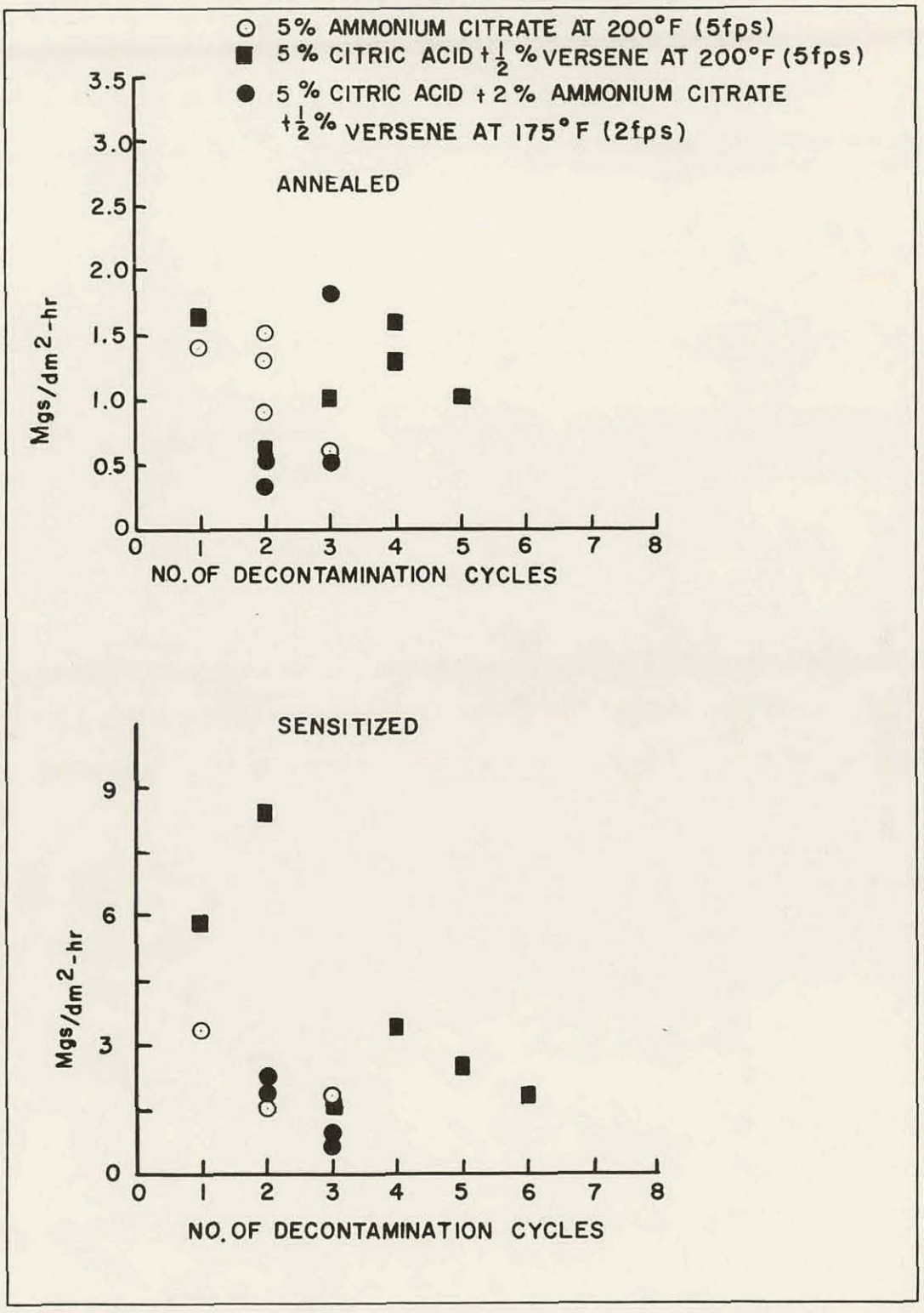


Fig. 22 Effect of Decontamination Cycles on Weight Loss of Type 304 Stainless Steel

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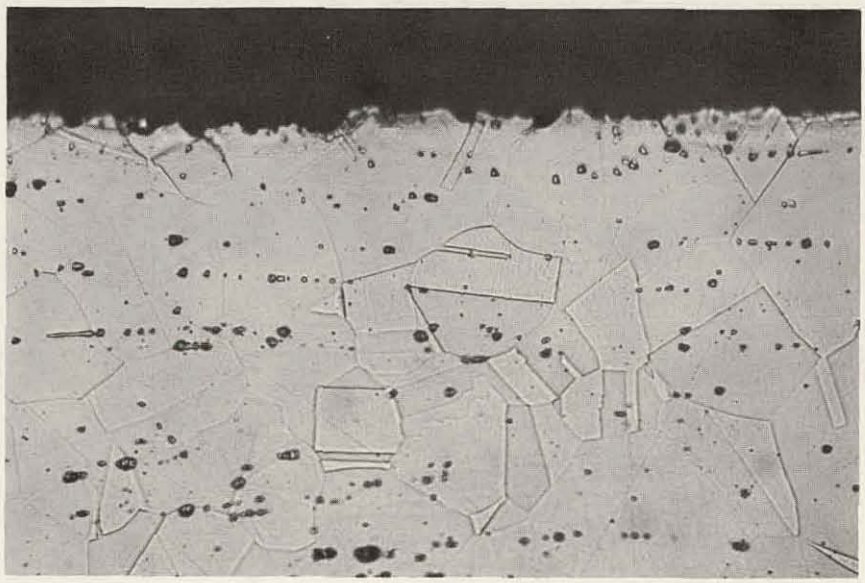
500 X Oxalic Acid Etch

Sample Untreated



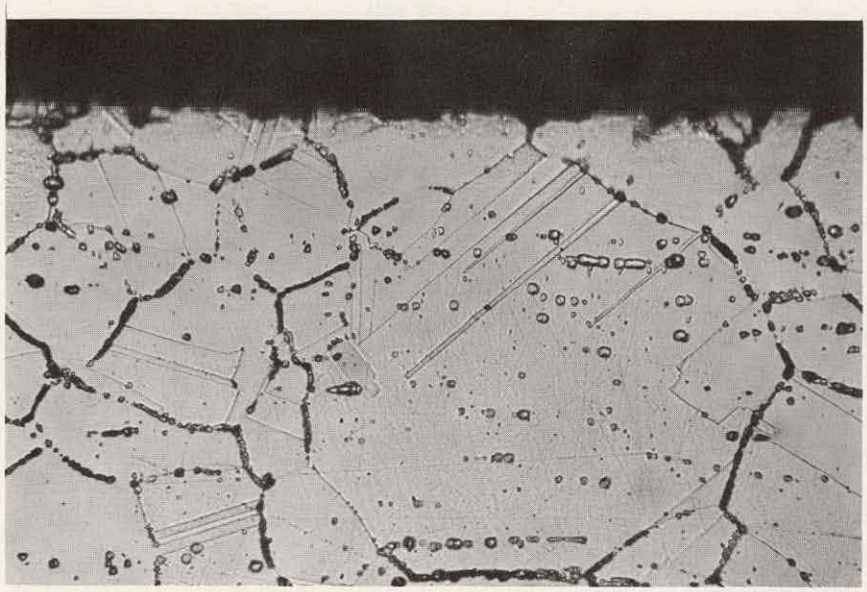
500 X Oxalic Acid Etch

Sample Exposed to Caustic Permanganate-Citrate Combination Solution and Caustic Permanganate-Citric Acid Combination Solution-Loop Tests No. 38, 39

Fig. 23 - Photomicrograph of Annealed Type 304 Stainless Steel Coupon Exposed to Two Decontamination Treatments

500 X Oxalic Acid Etch

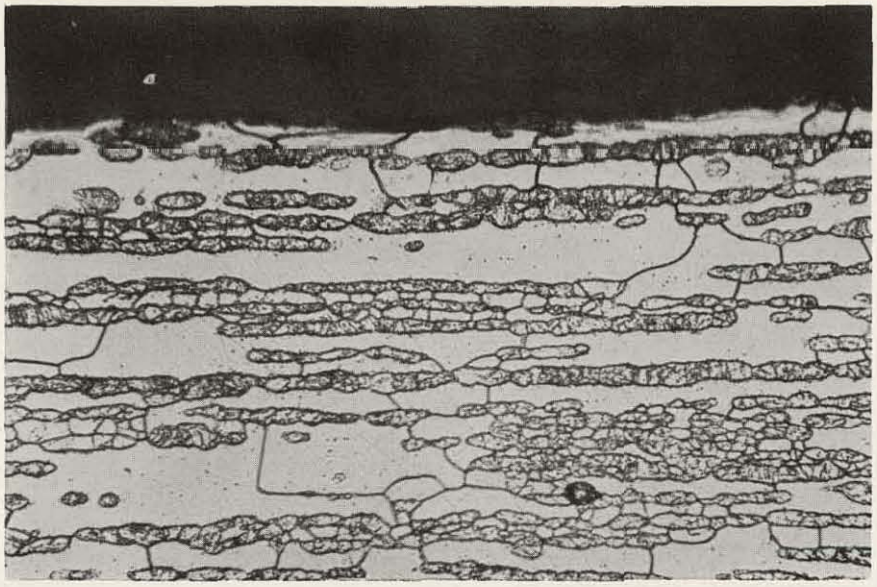
Sample Untreated



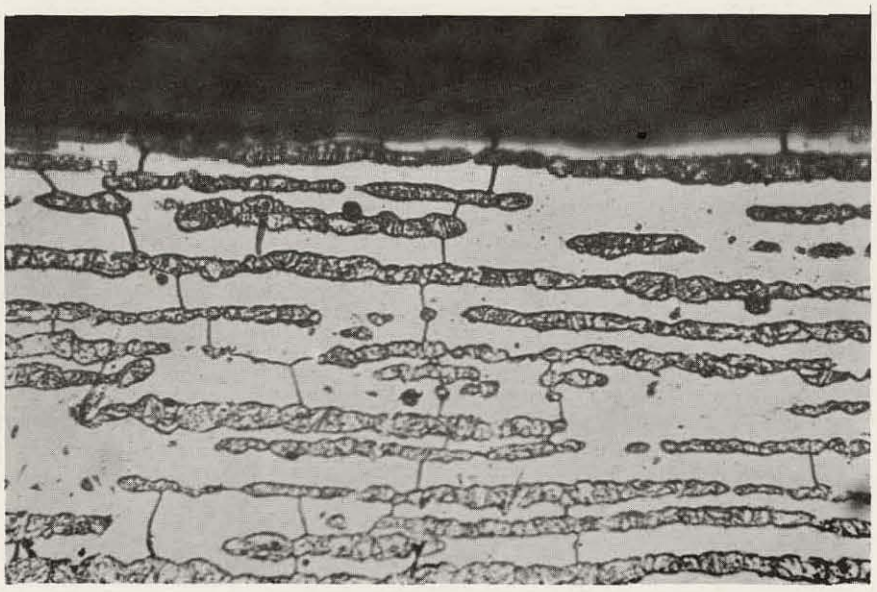
500 X Oxalic Acid Etch

Sample Exposed to Caustic Permanganate-Citrate Combination Solution and Caustic Permanganate-Citric Acid Combination Solution - Loop Tests No. 38, 39

Fig. 24 - Photomicrograph of Sensitized Type 304 Stainless Steel Coupon Exposed to Two Decontamination Treatments



500 X Chromic Acid Etch
Sample Untreated



500 X Chromic Acid Etch
Sample Exposed to Caustic Permanganate-Rinse Decontamination Treatments

Fig. 25 - Photomicrograph of Babcock and Wilcox Croloy 16-1 Coupon Exposed to Two Decontamination Treatments

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7.1.2 Relationship Between Corrosion Rate and Decontamination with the Caustic Permanganate-Rinse Decontamination Method

A number of metal coupons, contaminated in the APPR-1 purification system were decontaminated by the caustic permanganate-rinse decontamination method. The purpose of these loop tests was to determine the relative decontamination ability of the treatment on various metals. The metal coupons (3-1/2 x 1/2 x 1/16-inch) were exposed for various periods of time in the APPR-1 primary purification system. These coupons were subsequently washed, counted, and then weighed prior to loop decontamination. The activity of the coupons was determined by means of a thin mica end window G-M tube connected to a Model 1091 Atomic Associates Scaler. Suitable corrections were made for coincidence and background. The background factor was based on an average background value.

The results of the loop decontamination tests are presented in Table 6. The results for the Type 304 stainless steel coupons indicate a relationship between the descaled weight loss (due to the decontamination treatment) and the extent of decontamination (Fig. 26). An increase in weight loss results in an increased decontamination factor with a corresponding decrease in background factor. The results for the Croloy 16-1 and the carbon steel have not been included in Fig. 26 because of an insufficient number of samples. However, it is interesting to note from the Croloy 16-1 results in Table 6 that excellent decontamination was achieved at the expense of corrosion. There is no apparent relationship between the carbon steel weight loss results and the extent of decontamination. The activity on carbon steel specimens exposed to the APPR-1 primary coolant is known to be loose and easily removed.[8]

It should be emphasized that the descaled weight loss results reported in Table 6 include both the activated corrosion product scale and the base metal. This is the weight loss that would result from the decontamination of a reactor system.

TABLE 6 Relationship Between Decontamination Factor, Background Factor, and Weight Loss on Various Metals using the Caustic Permanganate-Rinse Decontamination Treatment

Sample	Initial Activity (beta-gamma) cpm	Final Activity (beta-gamma) cpm	D. F.	B. F.	Total Weight Loss mgs/dm^2
		Type 304 Stainless Steel (Annealed)			
C-88	58,536	1666	35	5.1	3.7
C-93	59,132	1399	42	4.3	4.3
C-94	62,206	1589	39	4.9	4.3
C-90	69,894	1714	41	5.3	5.2
C-87	53,891	1450	37	4.4	5.8
C-34	82,131	1135	72	3.5	8.3
C-92	73,003	1217	60	3.7	8.5
C-91	50,758	1093	46	3.4	8.7
C-86	63,161	1097	58	3.4	16.7
		Type 304 Stainless Steel (Sensitized)			
S-16	123,991	1727	71	5.3	16.7
S-20	120,019	1832	66	5.6	16.9
S-13	125,799	1543	82	4.7	19.4
S-18	127,285	1848	69	5.7	20.7
S-15	104,430	766	136	2.3	51.0
S-21	108,993	552	197	1.7	73.8
		Babcock and Wilcox Croloy 16-1			
F-1-29	131,307	169	777	0.52	57
F-1-28	105,778	205	516	0.63	518
F-1-27	129,024	179	720	0.55	602
		Carbon Steel			
I-25	36,059	109	331	0.33	672
I-21	70,627	783	90	2.4	829
I-23	48,659	1212	40	3.7	988
I-24	33,865	381	89	1.2	2731

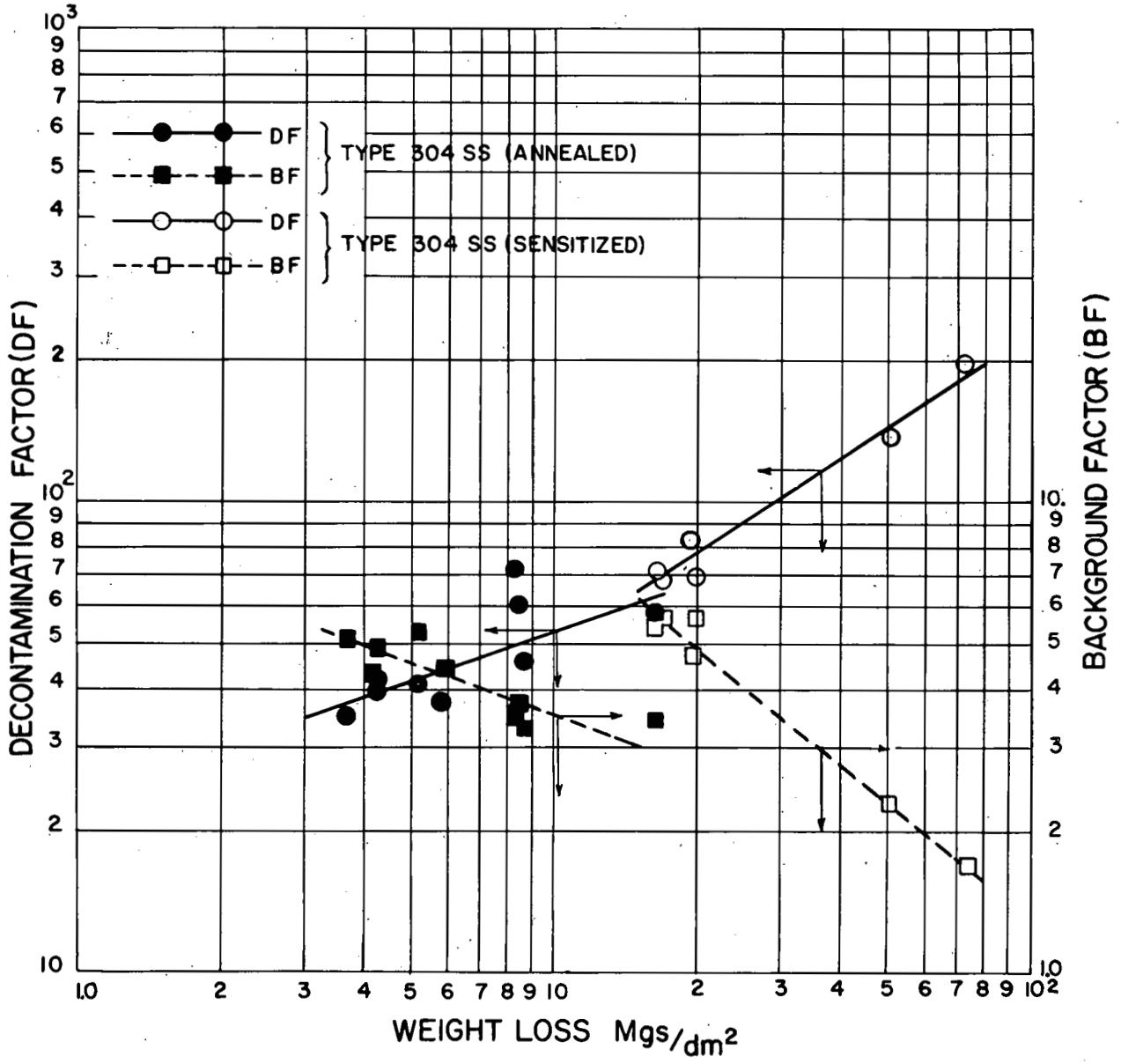

Fig. 26 Relationship of Decontamination Factor and Background Factor to Corrosion Rate of Type 304 Stainless Steel

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7.2 Dynamic Autoclave Test Results

The design of the sample section of the loop did not permit the metallurgical evaluation of Type 304 stainless steel stressed and welded samples. Dynamic autoclave corrosion studies were therefore performed with these specimens as well as Type 304 stainless steel coupons (annealed and sensitized). Corrosion and metallographic information were obtained on the various metal samples exposed to solutions of 5 percent citric acid -1/2 percent Versene, 5 percent ammonium citrate, citrate rinse (5 percent ammonium citrate, 2 percent citric acid, 1/2 percent Versene) at 175°F, and caustic permanganate (10 percent sodium hydroxide, 5 percent potassium permanganate) at 195°F. An evaluation of the relative effects of each solution on the various specimens could then be obtained. With the exception of the citric acid-Versene, it was not possible to obtain the temperatures previously established in Section 6.3 for the decontamination solutions because of the experimental arrangement.

A stressed specimen was prepared by bending a coupon (3-1/2 x 1/2 x 1/16-inch) into the shape of a "U". The sensitized stressed specimens were sensitized before bending to avoid any possibility of stress relief.

Weld specimens were prepared in such a manner as to duplicate the tube to tube sheet weld in the APPR-1 steam generator. This included the use of a Type 308L stainless steel welding rod filler wire (Fig. 27). The sensitized and weld metal areas of the weld specimens were examined metallurgically because the decontamination solution will come in contact with these areas during an actual decontamination of a steam generator. The root area of the weld would not be exposed to the decontamination solutions.

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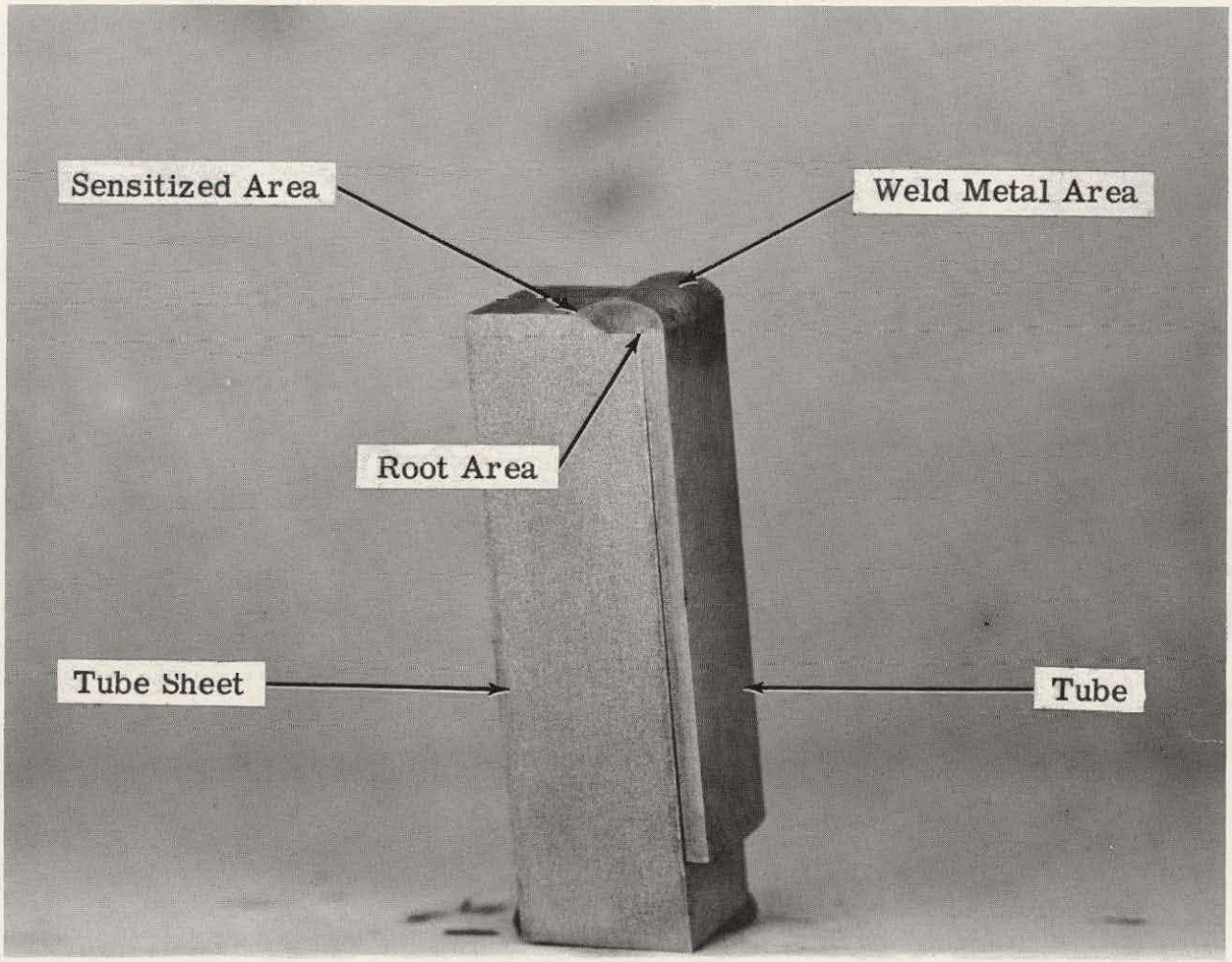

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Fig. 27 - Photograph of Simulated Tube to Tube Sheet Weld Specimens

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7.2.1 Test Equipment and Procedure

The inlet of a Type 304 stainless steel autoclave of 1.2 liter capacity was connected to the discharge of a small centrifugal pump. The discharge of the autoclave was piped to a 3 liter glass beaker open to the atmosphere. The suction side of the pump was also connected to this glass beaker. All piping was made with 1/4-inch Type 304 stainless steel tubing. The test specimens were suspended in the autoclave on a thin length of Type 304 stainless steel wire. The specimens were separated from each other by sections of glass tubing. Metal to metal contact was therefore restricted as much as possible.

For a typical test, the specimens were placed in the autoclave and the solution under investigation was heated in the beaker by a hot plate. A heating mantle was wrapped around the autoclave for an additional heat source. When the solution was at the proper temperature, the pump was started and the solution circulated through the autoclave for the desired period of time. The temperature of the solution was maintained within $\pm 5^{o}F$ by proper use of the heating mantle and hot plate. In all tests a flow rate of one gpm (0.025 ft/sec) was maintained by controlling pump speed with a powerstat.

Prior to exposure, the specimens were washed in water and acetone to remove any foreign matter and then weighed on an analytical balance. The specimens were exposed for fixed periods of time (0.5, 0.5, 1, 2, 4 and 8 hours), removed from the autoclave at these intervals, washed in water and acetone, and reweighed on the analytical balance.

7.2.2 Metal Coupons

The weight loss of the coupons due to exposure in the four solutions are presented in Appendix Table C-1-4. The weight loss results as a function of exposure time are presented in Fig. 28 and Fig. 29. The annealed metal samples showed only a small weight loss in each of the three rinse solutions after 15 to 16 hours exposure, i.e. 2.5, 3.0 and 3.5 mgs/dm^2 for the citric acid-Versene, ammonium citrate, and the citrate combination solutions respectively. These weight losses represent a total penetration of approximately 0.001 mils. Metallurgical examination of the coupons revealed no evidence of intergranular corrosion or cracking (Fig. 30 top).

Weight losses for the sensitized coupons were significantly higher than the annealed coupons. It appears that lower pH resulted in a greater initial corrosion rate. This can be seen from the weight loss after four hours exposure in the respective rinses (Table 7). After approximately fifteen hours exposure, the values approach a point where the total weight losses have nearly the same values, but are higher for lower pH solutions.

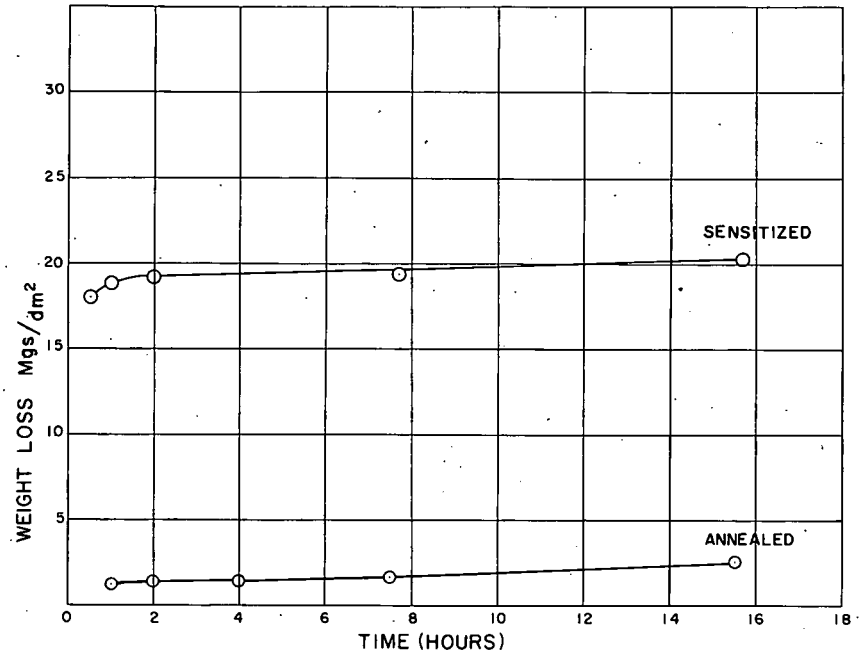
TABLE - 7 Comparison of Weight Loss Results for Type 304 Stainless Steel (Sensitized) after 4 and 15 Hours in Various Decontamination Solution Rinses at 175°F

Solution	pH	Total Weight Loss mgs/dm^2		Total Penetration (mils)
		4 hours	15 hours	15 hours
Citric Acid Citrate Combination rinse	2.5	19.3	20.2	0.010
	4.3	14.1	17.3	0.009
Ammonium Citrate	5.1	10.5	16.6	0.008

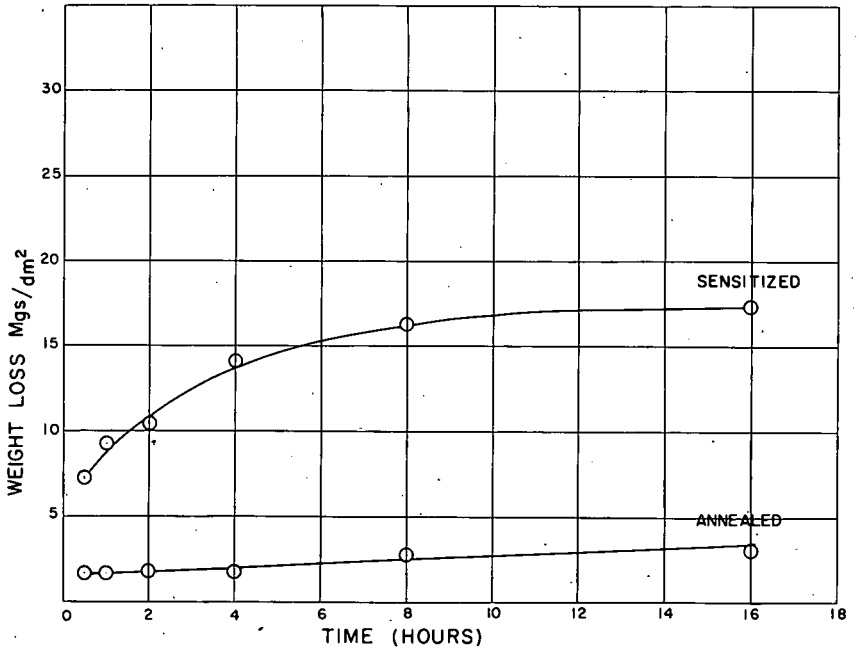
It would be expected that the lower pH solutions would tend to cause more attack. Since the coupons appear to approach a steady state corrosion rate, there may not be any significant attack after the initial contact period.

Photomicrographic examination of the sensitized coupons revealed no evidence of any significant amount of intergranular corrosion (Fig. 30 bottom).

For the primary treatment solution (caustic permanganate), the final weight losses were higher than in the rinse solutions for both the annealed and sensitized coupons. This may be a result of the higher temperature of this test (195°F as compared to 175°F for the rinse), and the effect of the oxygen evolved from the caustic permanganate at high temperatures. The difference between the sensitized and annealed weight loss results is not as large as observed in the case of the secondary solution rinses. This is due to the greater attack of the caustic permanganate on annealed Type 304 stainless steel.



5% Citric Acid, 1/2% Versene at 175°F and 1 gpm



Citrate Combination Solution at 175°F and 1 gpm

Fig. 28 - Dynamic Autoclave Weight Loss Results of Type 304 Stainless Steel for Citric Acid-Versene and Citrate Combination Solution Rinse

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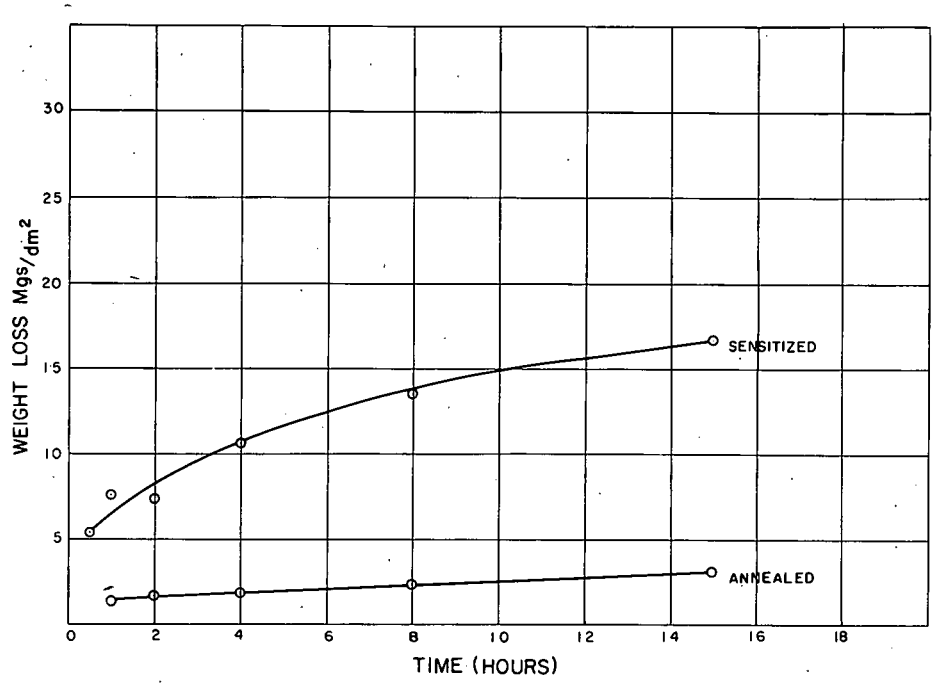
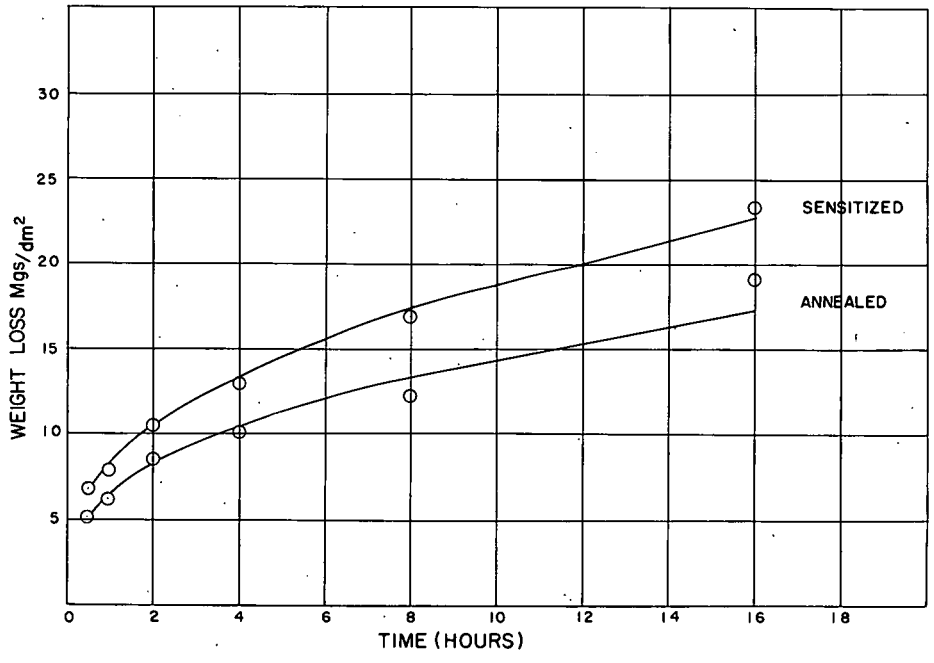


5% Ammonium Citrate at 175°F and 1 gpm



Caustic Permanganate at 195°F and 1 gpm

Fig. 29 - Dynamic Autoclave Weight Loss Results of Type 304 Stainless Steel for Ammonium Citrate Rinse and Caustic Permanganate Solution

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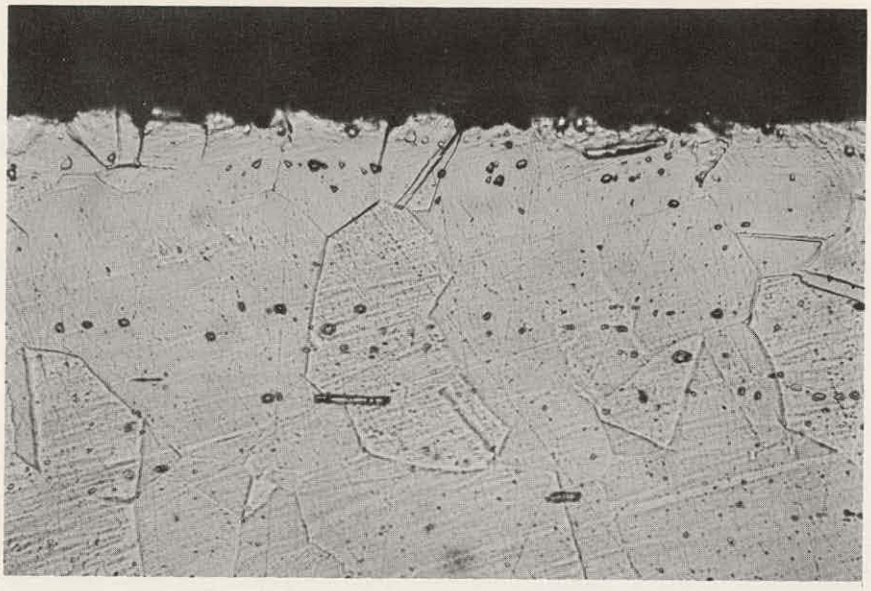
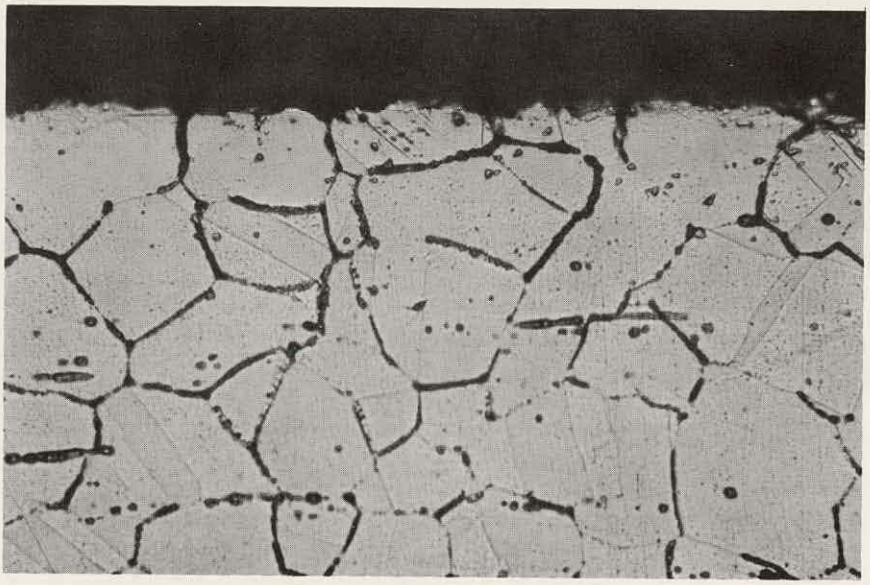


500 X Oxalic Acid Etch
Annealed Sample Exposed for 16 Hours at 175°F and 1 gpm



500 X Oxalic Acid Etch
Sensitized Sample Exposed for 16 Hours at 175°F and 1 gpm

Fig. 30 - Photomicrographs of Type 304 Stainless Steel Coupons Exposed to the Citrate Combination Rinse Solution

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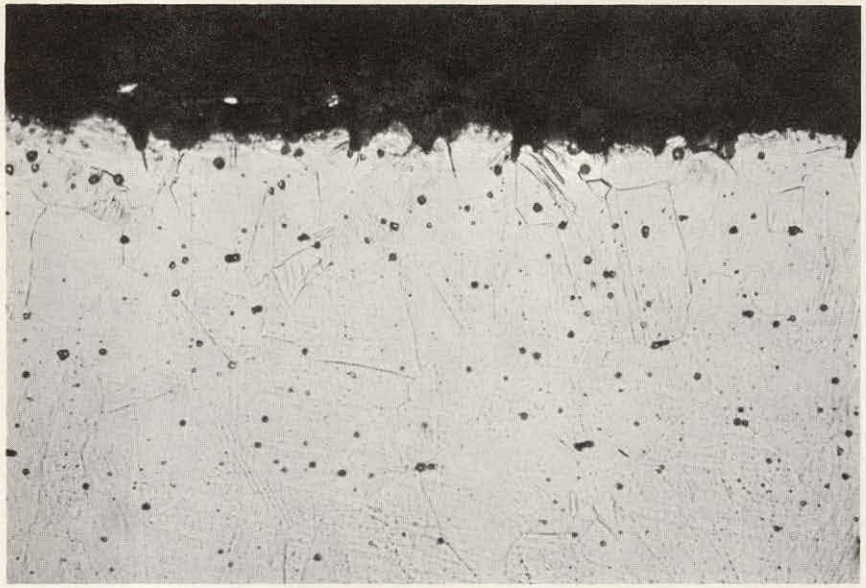
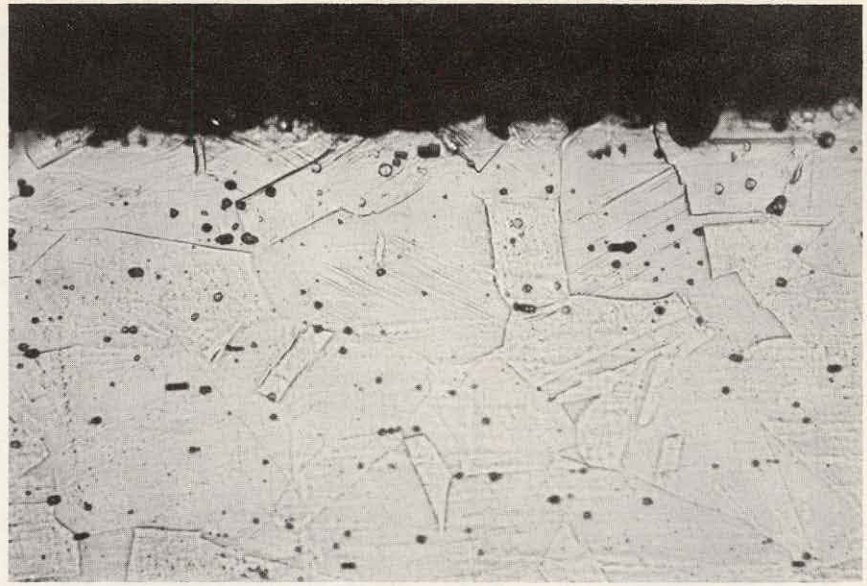
7. 2. 3 "U" Bends and Weld Samples

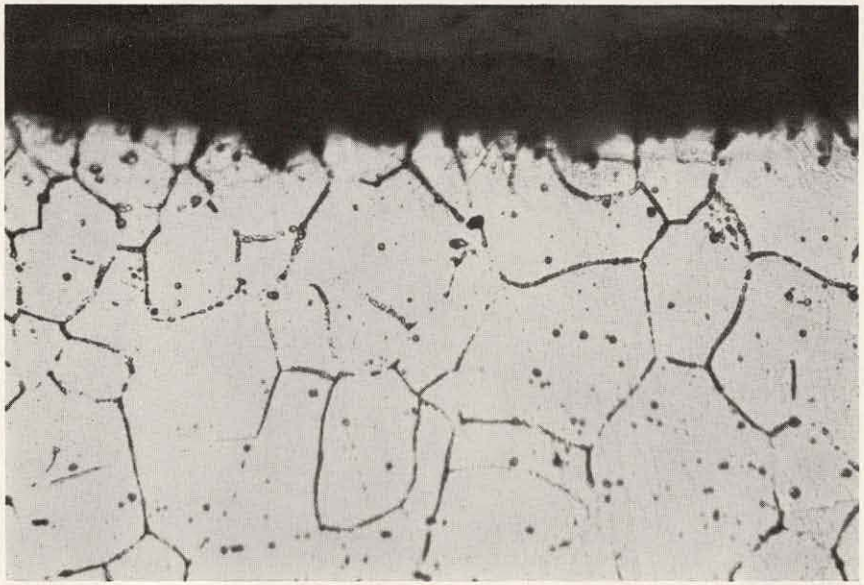
The Type 304 stainless steel annealed and sensitized "U" bends, exposed to the various decontamination solutions, were examined for stress corrosion cracking. The sensitized and weld metal area of the tube to tube sheet weld specimens were examined for intergranular corrosion, cracking,and localized attack. Photomicrographs of the "U" bends revealed no stress corrosion cracking on the inside or outside edges (Fig. 31 and Fig. 32). They also revealed no cracking nor evidence of any significant amount of localized attack or intergranular corrosion of the weld specimens.



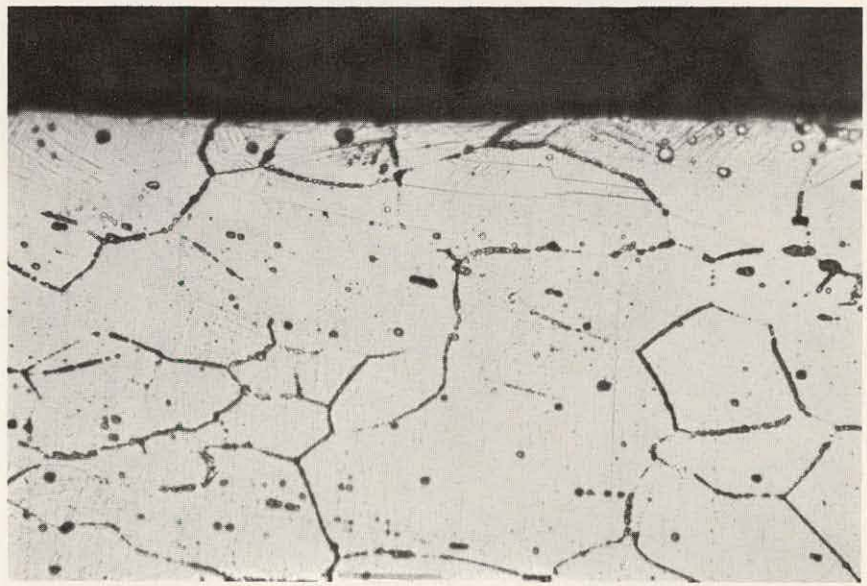
500 X Oxalic Acid Etch
Annealed Specimen Inside Edge



500 X Oxalic Acid Etch
Annealed Specimen Outside Edge

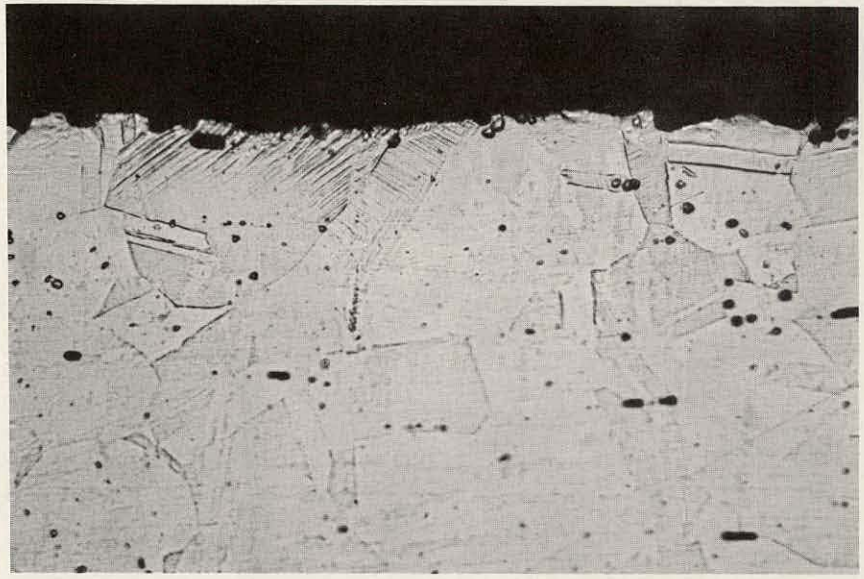


500 X Oxalic Acid Etch
Sensitized Specimen Inside Edge

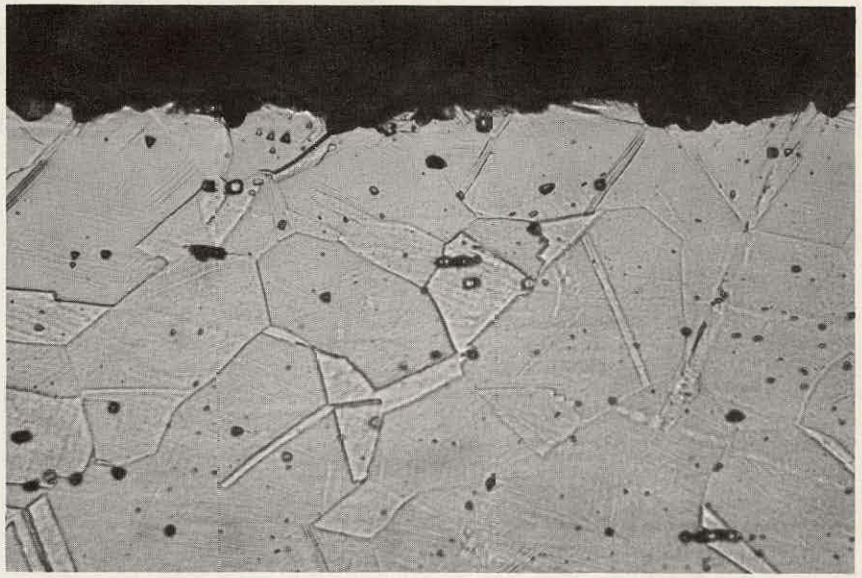


500 X Oxalic Acid Etch
Sensitized Specimen Outside Edge

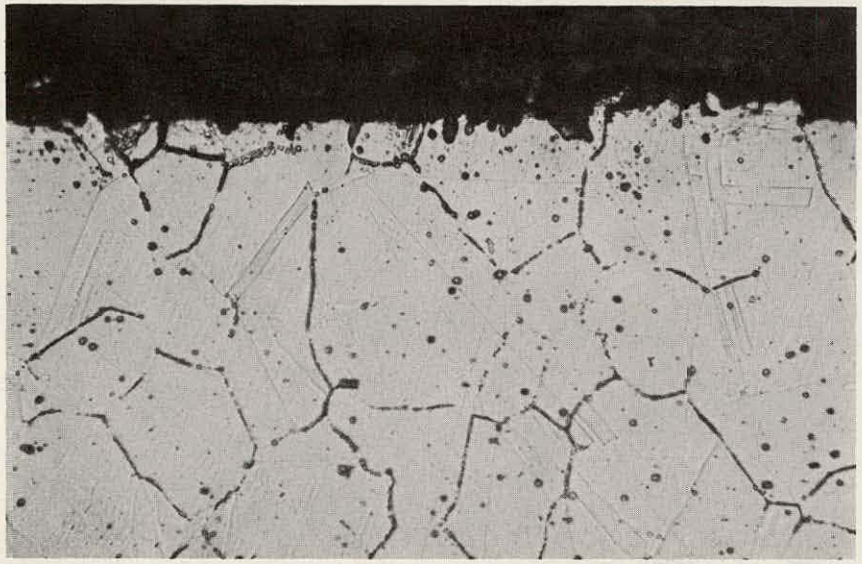
Fig. 31 -Photomicrographs of "U" Bend Control Specimens



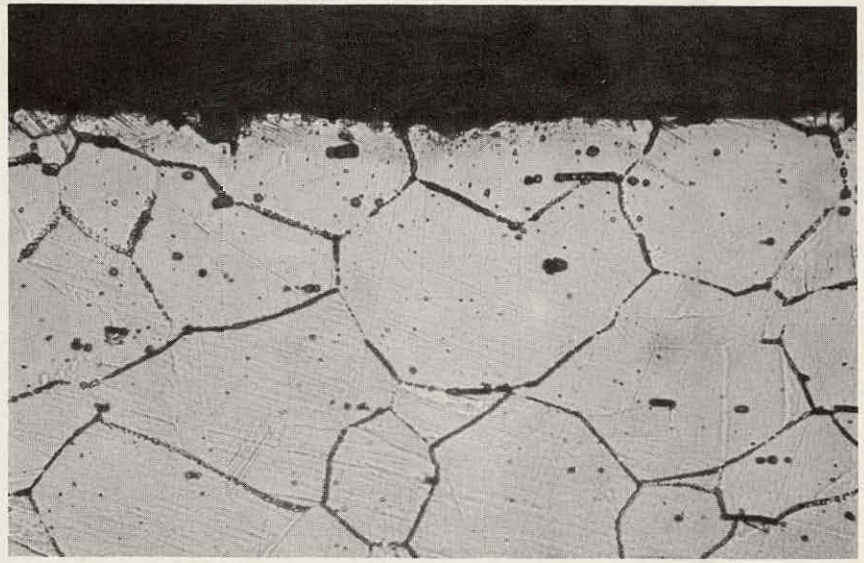
500 X Oxalic Acid Etch
Annealed specimen inside Edge Exposed for 16 Hours at 175°F and 1 gpm



500 X Oxalic Acid Etch
Annealed Specimen Outside Edge Exposed for 16 Hours at 175°F and 1 gpm



500 X Oxalic Acid Etch
Sensitized Specimen Inside Edge Exposed for 16 Hours at 175°F and 1 gpm



500 X Oxalic Acid Etch
Sensitized Specimen Outside Edge Exposed for 16 Hours at 175°F and 1gpm

Fig. 32-Photomicrographs of "U" Bend Specimens Exposed to the Citrate Combination Solution Rinse

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7.3 Long Term Static Autoclave Test Results

The purpose of the long term static tests was to determine the magnitude of the corrosion rate which could be expected during storage of the caustic permanganate and the citrate combination waste solutions. It was also of interest to determine the relative effect of temperature of the various decontamination solutions on Type 304 stainless steel and AISI C1010 carbon steel specimens. The specimens used in these tests were the same size and shape and had received the same heat treatment as those used in the dynamic autoclave tests (Section 7.2).

7.3.1 Test Equipment and Procedure

The long term static corrosion tests were performed in 1.2 liter stainless steel autoclaves. The metal test specimens were suspended in the autoclaves by the same method as that employed in the dynamic autoclave tests (Section 7.1.2).

The caustic permanganate tests were performed at room temperature or 77°F (25°C), 122°F (50°C), 167°F (75°C), and 203°F (95°C). The last three temperatures were maintained within ± 1°F by placing the autoclaves in a constant temperature oven. At seven day intervals the autoclaves were removed from the oven and room temperature storage area. They were opened and the samples removed, washed in water and acetone, weighed on an analytical balance and reinserted into the autoclaves. The solutions were analyzed for caustic and permanganate and the concentrations adjusted if necessary. This procedure was repeated for the duration of the test. The same procedure was employed for the citrate combination solution at temperatures of 77°F and 203°F.

7.3.2 Metal Coupons

The weight losses for Type 304 stainless steel (annealed and sensitized) and carbon steel (AISI C1010) in caustic permanganate are tabulated in Appendix Table D-1-5 and are shown in Fig. 33, Fig. 34, and Fig. 35 respectively. The weight loss is given as a function of time (days) at various temperatures. These curves were used to determine the effect of temperature on the corrosion rate of stainless steel in caustic permanganate. The curves in Fig. 36 were plotted in terms of the Arrhenius equation:

$$\ln k = -E_a/RT + \text{Const.}$$

where

- k = Corrosion rate
- E_a = Activation energy
- R = Gas constant
- T = Absolute temperature

The curve indicates an increased corrosion rate at higher temperatures. Between 75°C and 95°C a rapid increase in corrosion rate is observed. This may be due to the liberation of oxygen as a consequence of the reaction between caustic and permanganate (Section 6.6 - equation (1)). The liberated oxygen is probably increasing the corrosion rate by depolarizing the metal surface. (9)

Photomicrographs of the Type 304 stainless steel and AISI C1010 carbon steel show no evidence of any harmful metallurgical effects (Fig. 37 and Fig. 38).

The weight loss results for Type 304 stainless steel (annealed and sensitized) and carbon steel (AISI C1010) in citrate combination rinse at 77°F are shown in Fig. 39. It was not possible to obtain data at 203°F because of decomposition of the solution when exposed to the atmosphere at this temperature for long periods of time. This effect did not occur at anytime during the loop and dynamic corrosion tests. Photomicrographs revealed no harmful metallurgical effects at 77°F (Fig. 40).

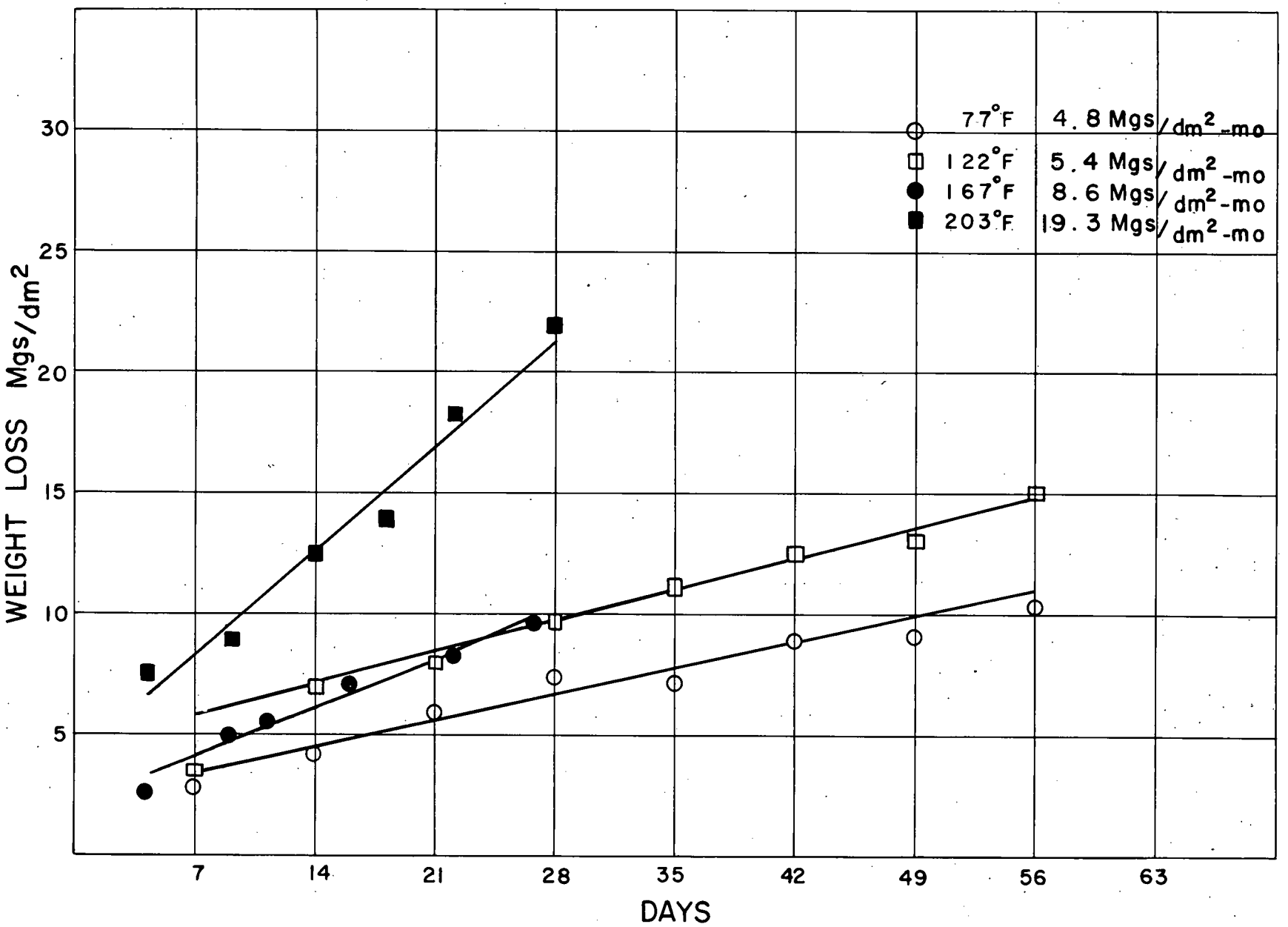

Fig. 33 Static Autoclave Weight Loss Results for Annealed Type 304 Stainless Steel in Caustic Permanganate

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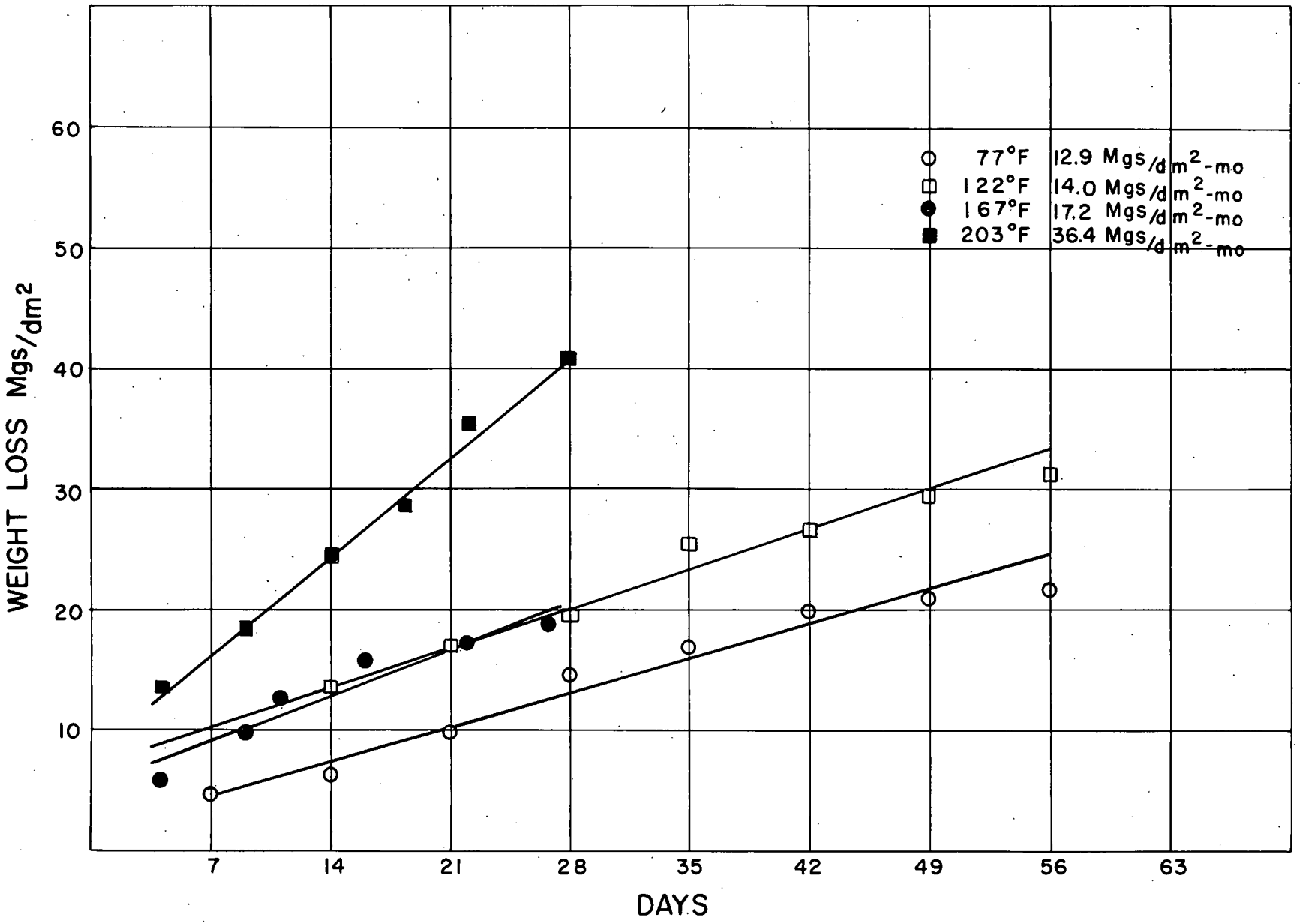

Fig. 34 Static Autoclave Weight Loss Results for Sensitized Type 304 Stainless Steel in Caustic Permanganate

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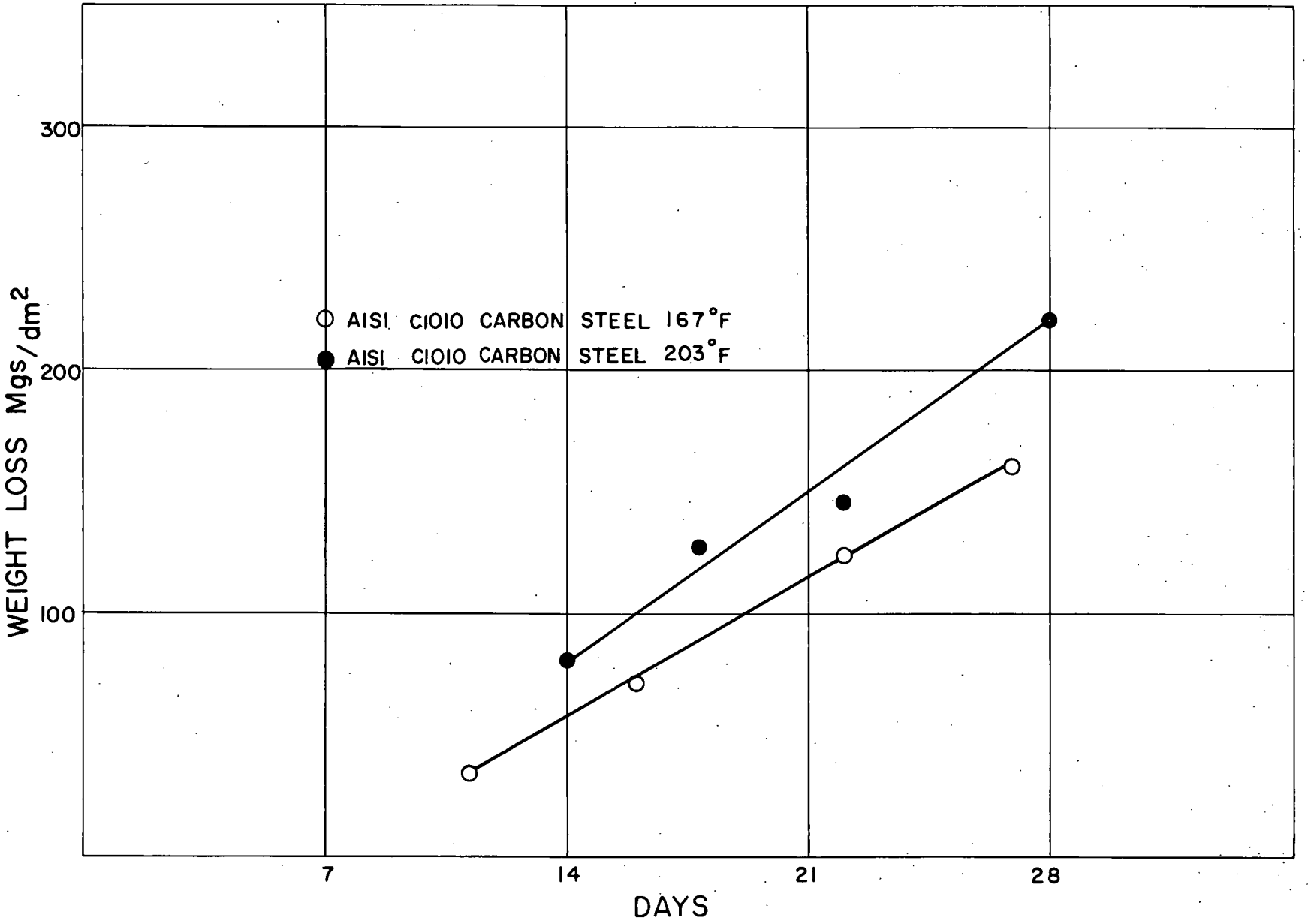

Fig. 35 Static Autoclave Weight Loss Results for Carbon Steel in Caustic Permanganate

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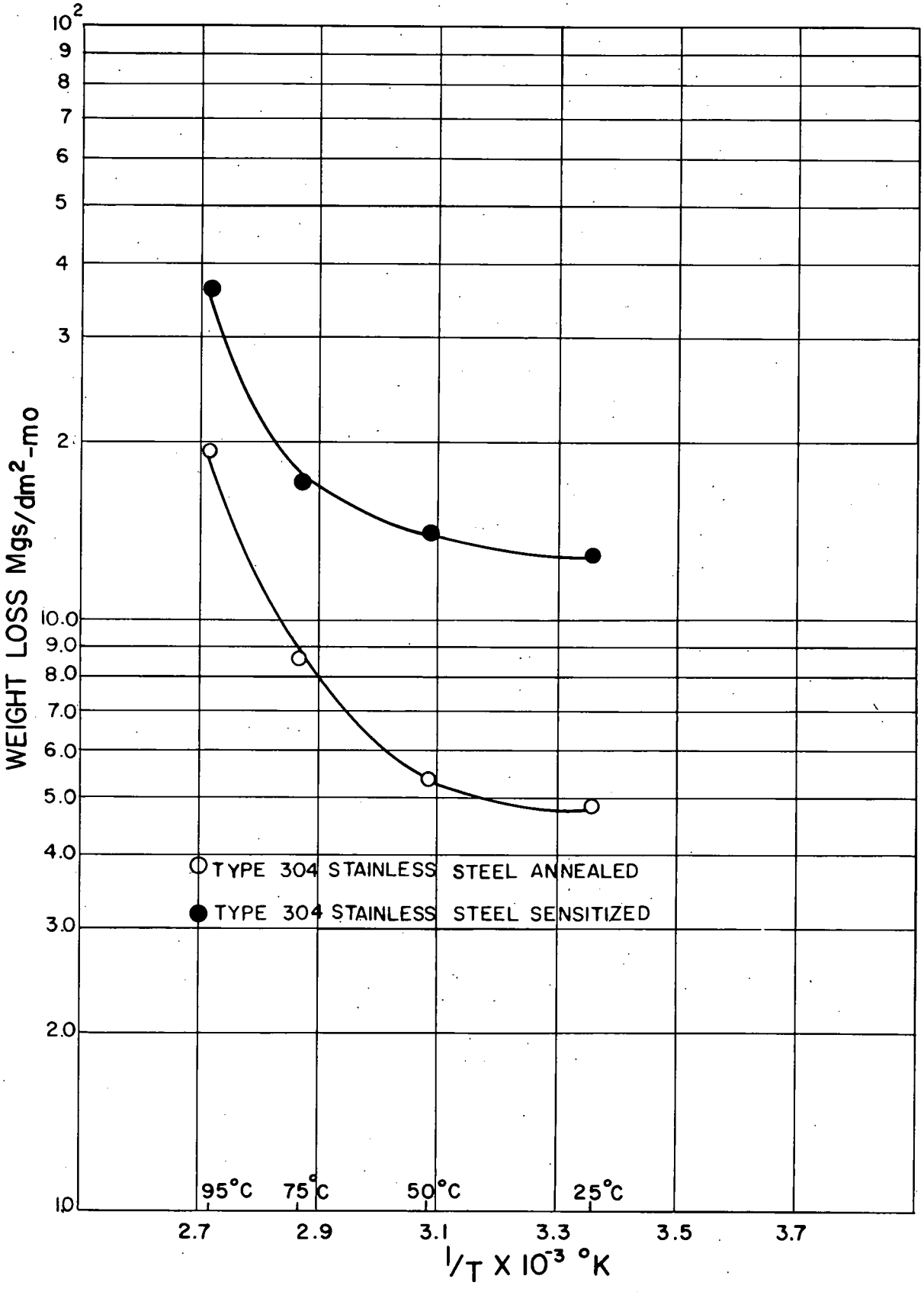

Fig. 36 Effect of Temperature on Weight Loss Results for Type 304 Stainless Steel in Caustic Permanganate

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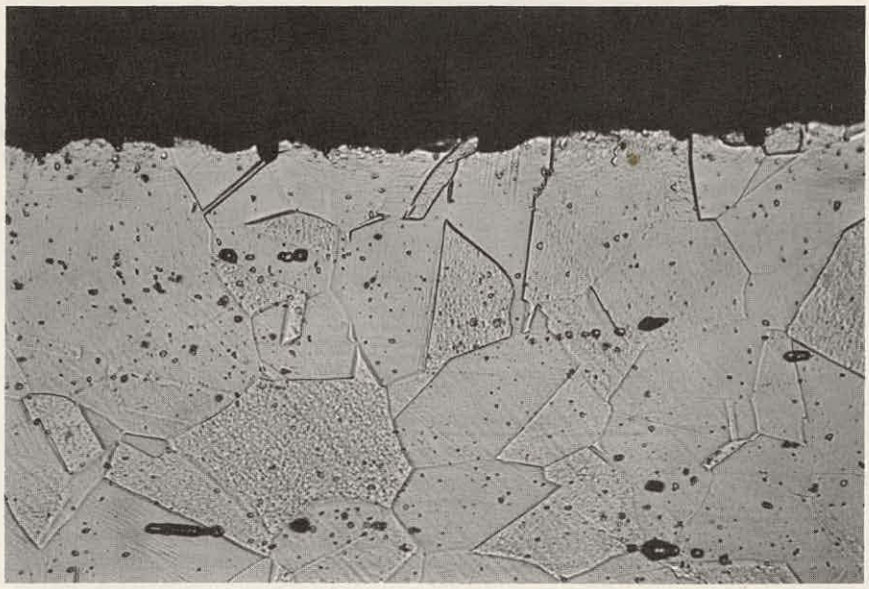
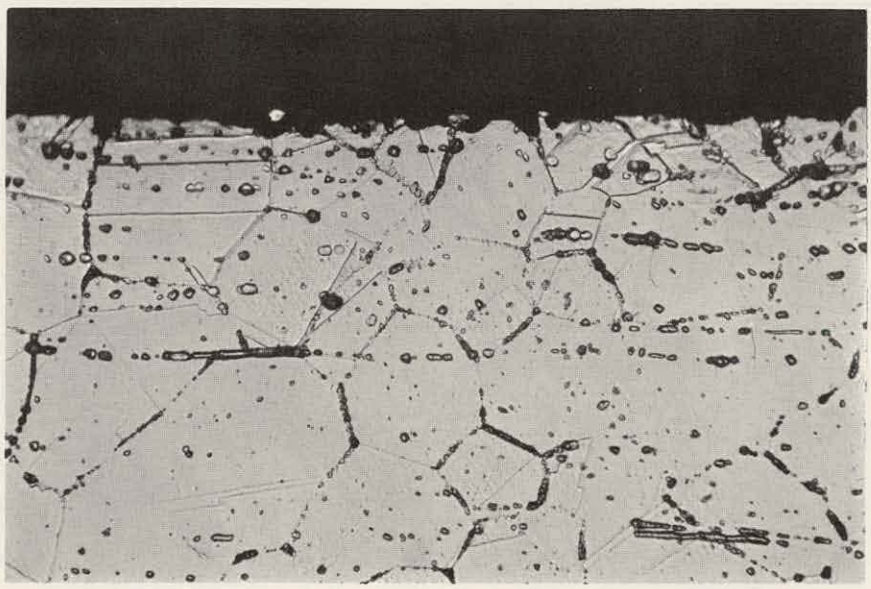
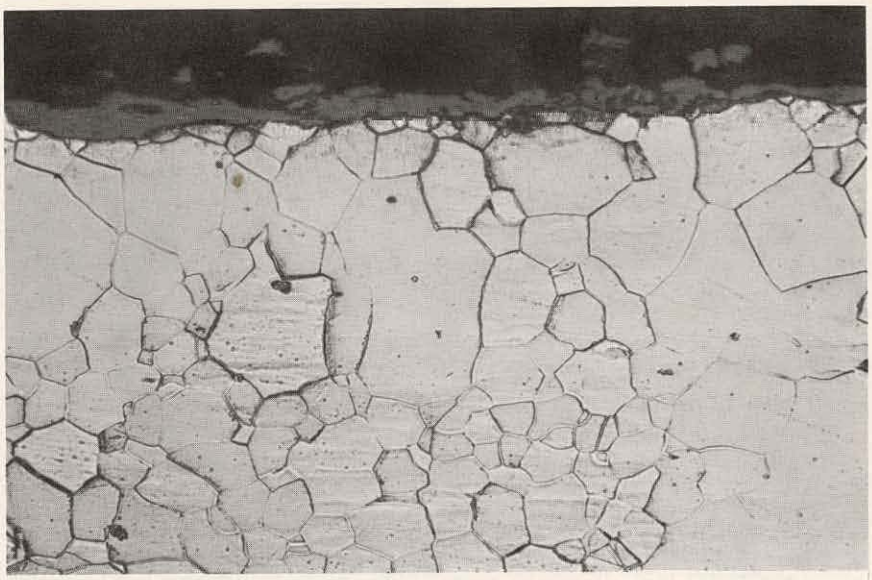


500 X Oxalic Acid Etch
Annealed Sample Exposed for 28 Days at 203°F



500 X Oxalic Acid Etch
Sensitized Sample Exposed for 28 Days at 203°F

Fig. 37 - Photomicrographs of Type 304 Stainless Steel Coupons Exposed to the Caustic Permanganate Solution



500 X 2%Nital Etch

Sample Untreated

500 X 2%Nital Etch

Sample Exposed for 28 Days at 203°F

Fig. 38 - Photomicrograph of Carbon Steel Coupon Exposed to the Caustic Permanganate Solution

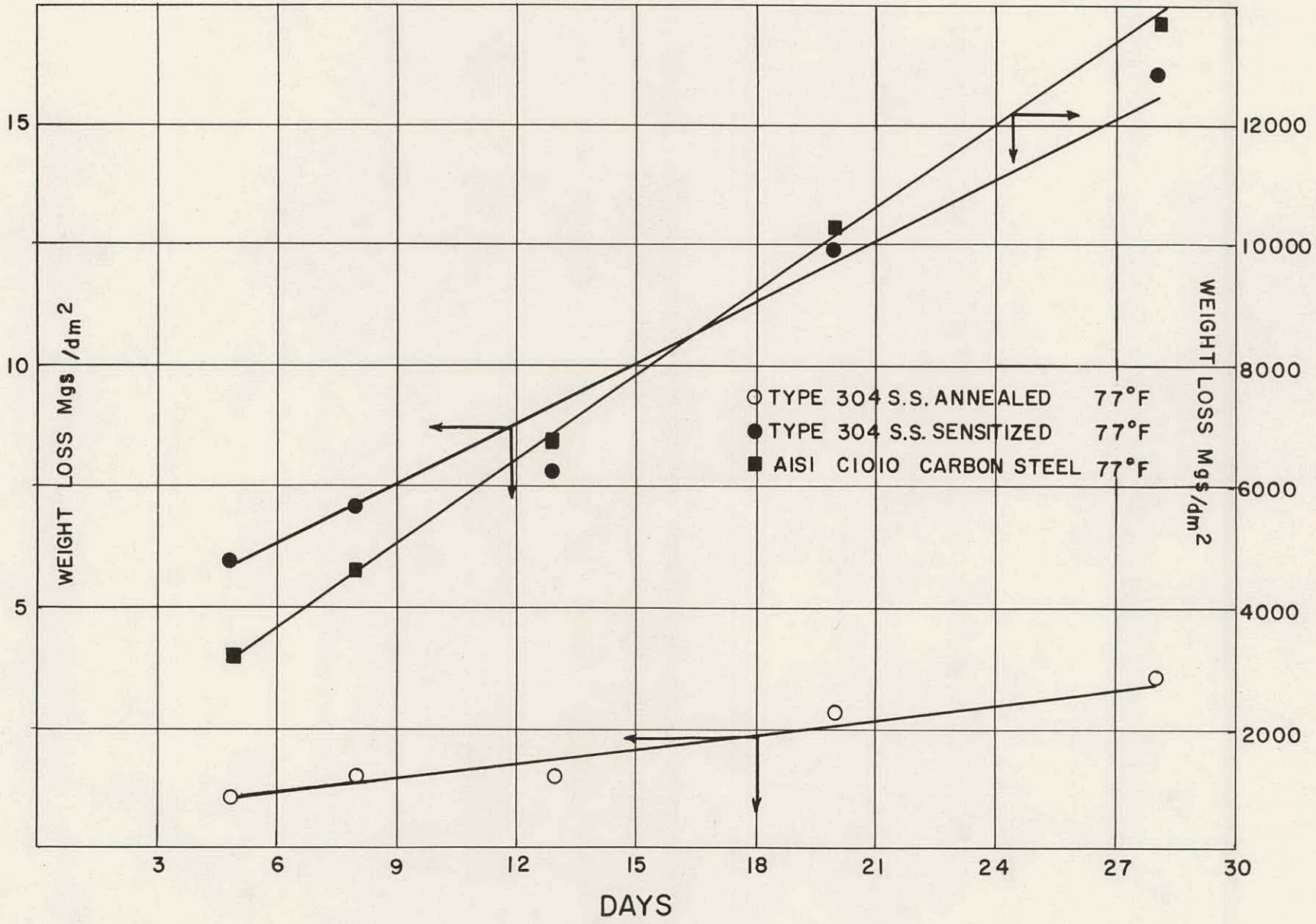


Fig. 39 Static Autoclave Weight Loss Results for Type 304 Stainless Steel and Carbon Steel in Citrate Combination Solution Rinse

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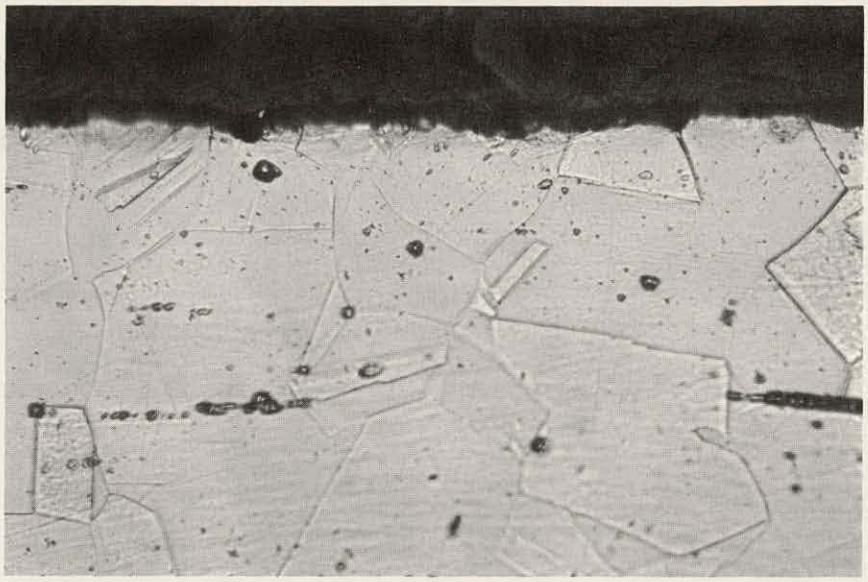
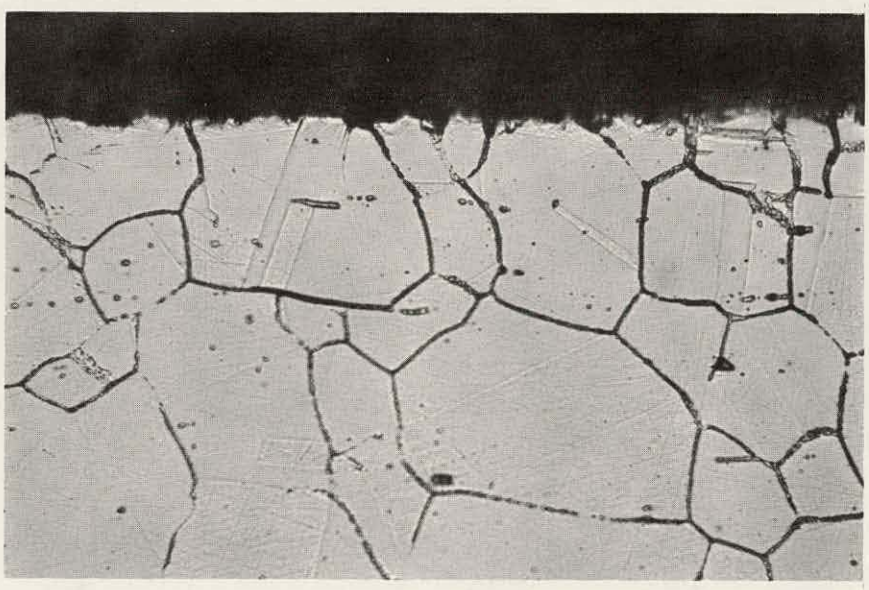


500 X Oxalic Acid Etch
Annealed Sample Exposed for 28 Days at 77°F



500 X Oxalic Acid Etch
Sensitized Sample Exposed for 28 Days at 77°F

Fig. 40 - Photomicrographs of Type 304 Stainless Steel Coupons Exposed to the Citrate Combination Solution Rinse

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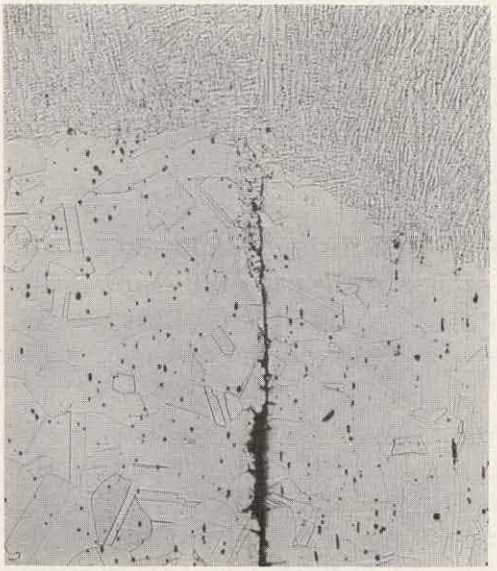
7.3.3 "U" Bend and Weld Samples

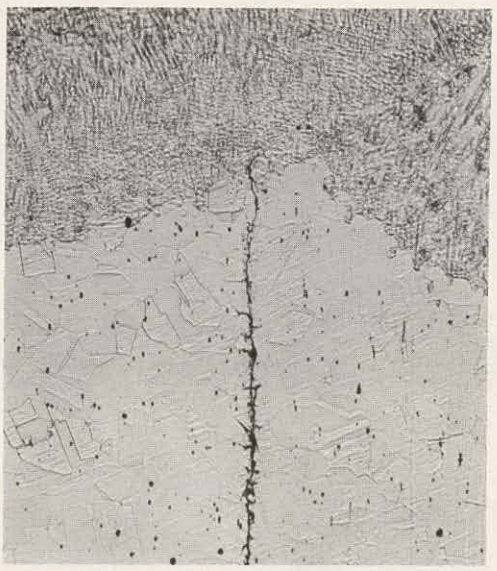
A metallurgical examination of the weld specimens exposed to the caustic permanganate revealed evidence of possible crevice corrosion in the root area. This was observed in samples exposed for eight weeks at 77°F and 122°F, but was not observed in samples exposed for four weeks at 203°F (Fig. 41).

No evidence of crevice corrosion was found in the root area of the samples exposed to the rinse solution for four weeks at 77°F. During a decontamination treatment, the root area of the weld will not be exposed to the solutions. There was no evidence of any harmful metallurgical effects on any of the sensitized and weld metal areas of the weld specimens or the bend areas of the "U" bend specimens.

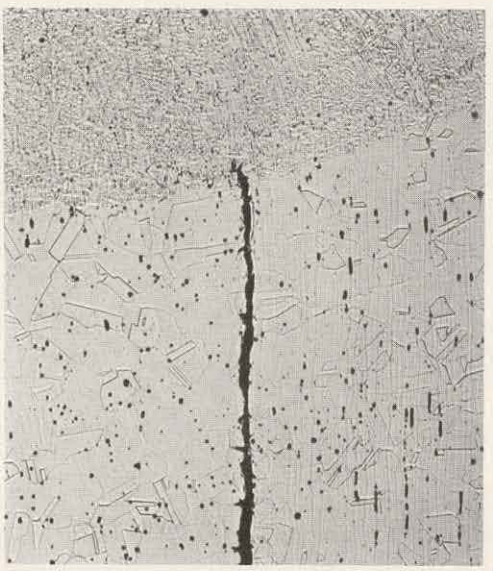


100 X Oxalic Acid Etch
Specimen Untreated

100 X Oxalic Acid Etch
Specimen Exposed 56 days at 77°F (Note penetration into weld Metal)



100 X Oxalic Acid Etch
Specimen Exposed 56 Days at 122°F (Note penetration into Weld Metal)



100 X Oxalic Acid Etch
Specimen Exposed 28 days at 203°F (Note Absence of Penetration into Weld Metal)

Fig. 41 - Photomicrographs of Weld Root Area on Specimens Exposed to Caustic Permanganate Solution

PART III RECOMMENDED CHEMICAL DECONTAMINATION SOLUTION AND APPLICATION

8.0 DISCUSSION OF RESULTS

On the basis of the data presented in the preceding sections, a caustic permanganate solution followed by a citrate combination solution rinse was chosen as a decontamination treatment for a stainless steel steam generator. This choice was based upon preliminary screening results, presented in Volume I of this report, loop parameter studies, corrosion, and metallurgical evaluation presented in this volume. Flow velocity and corrosion were the most important factors in this discision.

A fill-flush decontamination method is most applicable with the caustic permanganate-citrate combination rinse treatment. Results indicate that the solutions can be applied without additional feed during a decontamination treatment. Furthermore, this method of application is simpler to control and easier to perform.

8.1 Caustic Permanganate-Citrate Combination Decontamination Treatment

The recommended conditions and procedure for the caustic permanganate-citrate combination rinse decontamination method are given in Table 8.

TABLE 8 Recommended Solutions and Procedure for Stainless Steel Decontamination

Step	Solution and Concentration (by weight)	Residence Time (minutes)	Flow Rate (ft/sec)	Temperature (^{O}F)
1	10% Sodium Hydroxide 5% Potassium Permanganate	30	5	225
2	Demineralized Water	5-10	5	Room Temperature
3	60 Minute "Aeration"			
4	5% Ammonium Citrate 2% Citric Acid 1/2% Versene	30	5	220
5	Demineralized Water	5-10	5	Room Temperature

A typical loop test with the recommended decontamination treatment is shown in Fig. 42. The activity profile of the test is shown as a function of time. There is an initial drop in activity during the caustic permanganate treatment (Points 1 through 4). As will be shown in Section 8.1.2, this is probably due to the removal of Mn^{54} from the activated corrosion product scale. There is a rapid decrease in activity with the addition of the citrate combination solution to the loop (Points 8 to 9). During the heat up and circulation period of the rinse, the effect of the citric acid is probably predominant (Point 9 to 180°F). Beyond this temperature, the effect of the ammonium citrate is predominant. There is only a small decrease of activity during the latter part of the 30 minute residence period. Radiochemical analyses indicate that almost all of the activity in the rinse is due to Co^{58}, Co^{60}, Fe^{59} and Cr^{51}.

8.1.1 Decontamination of the Steam Generator Dividing Plate

During the APPR-1 November 1958 shutdown, a section was removed from the steam generator inlet and outlet dividing plate. This section is probably the most representative sample that can be obtained of the type of scale that may be encountered in the tubes of the steam generator. It possessed a tight, black, lustrous, radioactive film similar to that shown in Fig. 43 top left. A piece of this section was decontaminated using the caustic permanganate-citrate combination treatment. The procedure used for the decontamination was similar to that used for the screening evaluation. The contaminated piece was placed in a beaker of 10 percent sodium hydroxide and 5 percent potassium permanganate at 210°F for 30 minutes. It was then removed, washed with demineralized water, and allowed to dry in air for approximately one hour. This was followed by the citrate rinse (5 percent ammonium citrate, 2 percent citric acid, 1/2 percent Versene) at 210°F for 30 minutes. At the completion of the secondary solution rinse, the sample was covered with a light brown film. A short jet of demineralized water from a wash bottle completely removed this film and the sample appeared clean (Fig. 43 top right). Because of the ease with which the film slipped from the sample with the wash stream, it is believed that a thin layer of liquid was between the film and base metal. There was virtually no agitation during the treatment to aid in removing the film. The activity of the sample was reduced from 300 mr/hr to 2.5 mr/hr as a result of the decontamination. A photomicrograph of the sample revealed no adverse metallurgical effects (Fig. 43 bottom). While an excellent D. F. was achieved, it must be remembered that this was a bench scale test under ideal conditions. The D. F. may not be as high on a full scale test. However, for a nuclear facility, higher temperatures and greater turbulence would be obtained which would aid in the decontamination.

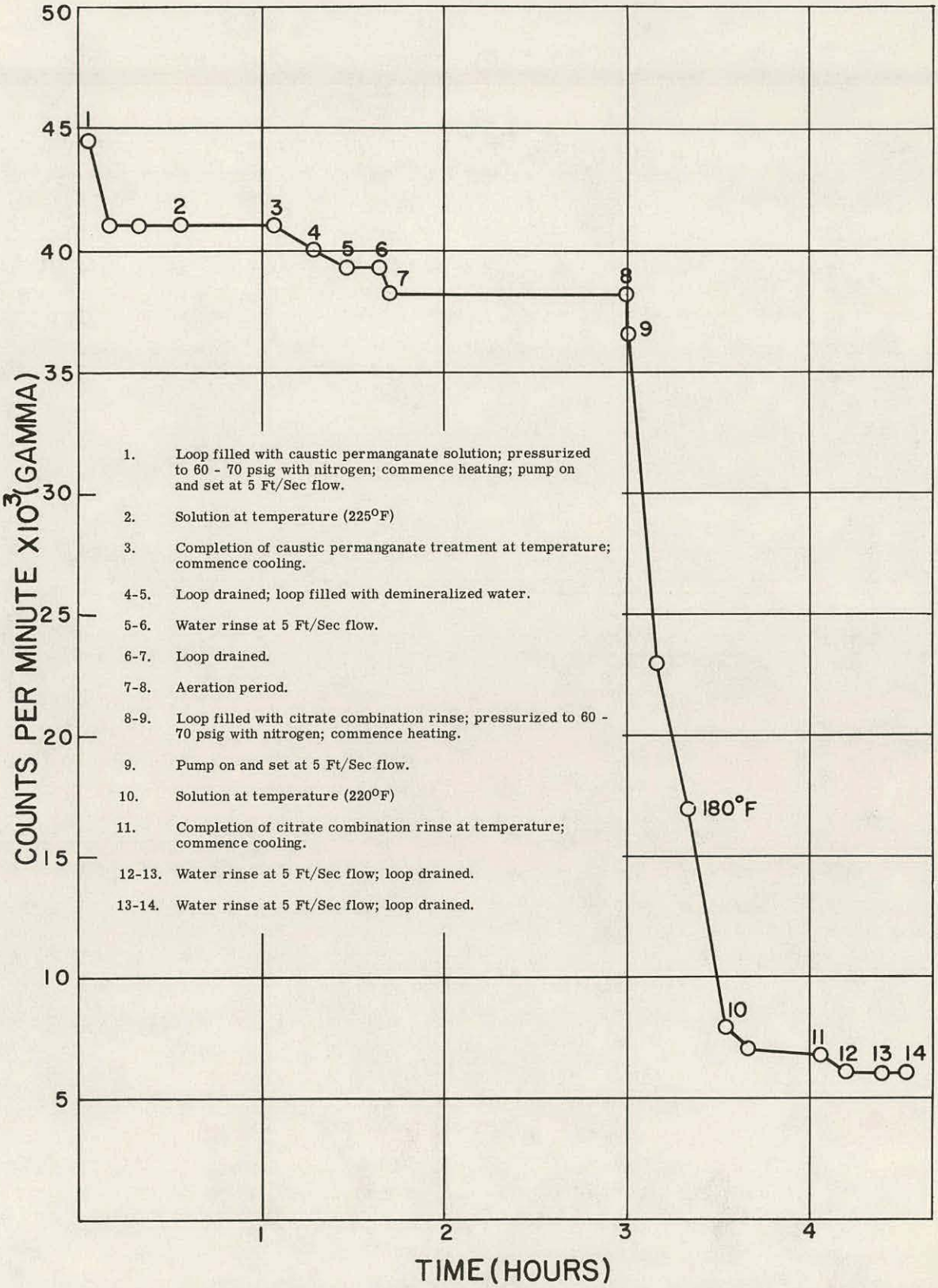


Fig. 42 Decontamination with the Caustic Permanganate-Citrate Combination Solution Treatment-Loop Test No. 46

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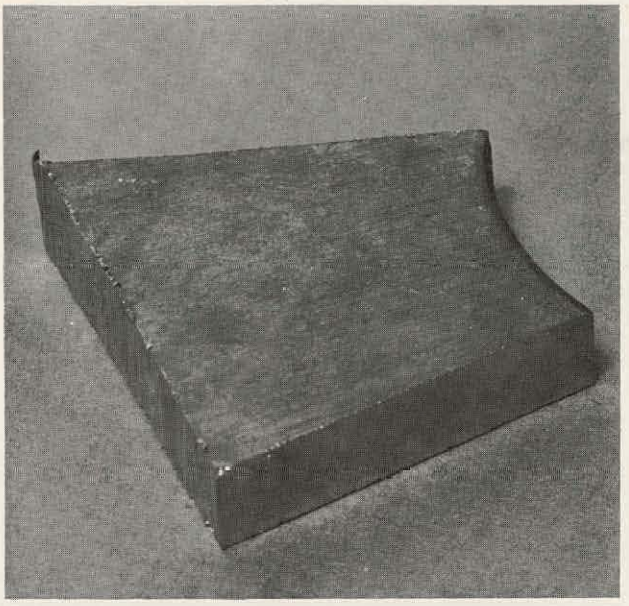
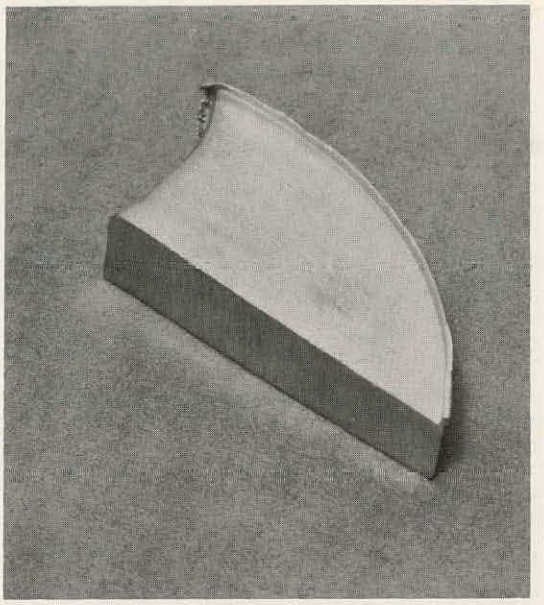
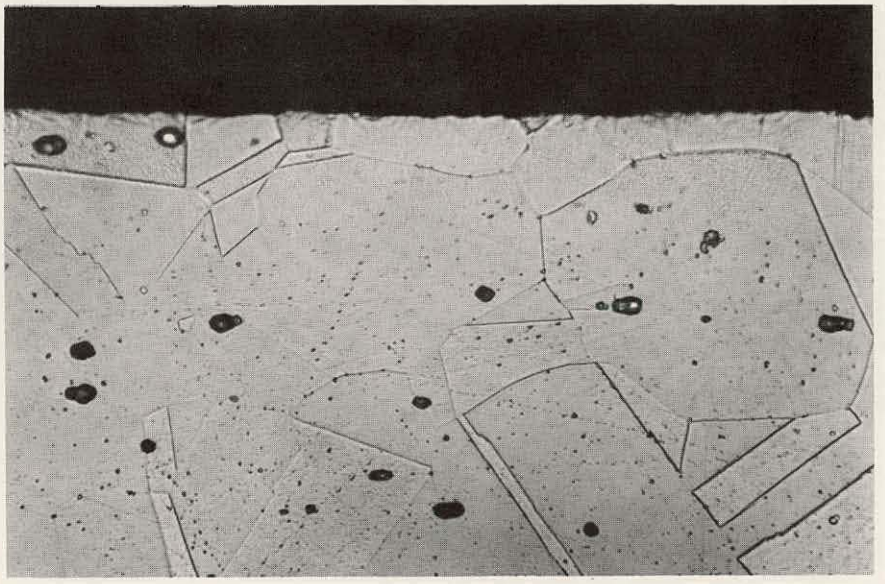


A Section Before Decontamination



A Section After Decontamination



500 X Oxalic Acid Etch
Photomicrograph of Dividing Plate Section After Decontamination

Fig. 43 - Photograph of Steam Generator Dividing Plate Section Before and After Decontamination with the Caustic Permanganate-Citrate Combination Solution Treatment

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8.1.2 Radiochemical Results

The remainder of the original section removed from the steam generator was cut into approximately twelve pieces. These were used in conjunction with an Activity Buildup Program (Task I), and were decontaminated by the same method described above. The decontamination solutions were analyzed for Co^{58}, Co^{60}, Mn^{54}, Fe^{59} and Cr^{51}. The results of the radiochemical analyses indicated that approximately 75 percent of the Mn^{54} is removed during the caustic permanganate treatment and the remainder in the citrate combination rinse. The Co^{58} and Co^{60} were removed almost entirely during the citrate rinse (Table 9). Iron 59 and Cr^{51} were not detected

TABLE 9 Radiochemical Analysis of the Caustic Permanganate and Citrate Combination Solution for Mn^{54}, Co^{58}, and Co^{60}

C. P. dpm x 10^5	Citrate dpm x 10^5	Total dpm x 10^5	% Nuclide in Citrate to Total
		Mn^{54}	
25.6	8.0	33.6	23.8
23.9	8.8	32.7	26.9
11.9	3.2	15.1	21.2
4.8	1.8	6.6	27.3
82.1	22.1	104.2	21.2
20.0	5.4	25.4	21.2
60.9	27.7	88.6	31.3
42.1	13.6	55.7	24.4
			24.7 average
		Co^{58}	
9.6	380	389.6	97.5
7.9	410	417.9	98.1
10.0	830	840.0	98.8
14.0	622	636.0	97.8
9.5	258	267.5	96.4
21.0	964	985.0	97.9
			97.8 average
		Co^{60}	
3.7	174	177.7	97.9
3.1	188	191.1	98.4
6.0	70	76.0	92.1
5.0	424	429.0	98.8
4.4	114	118.4	96.3
4.2	360	364.2	98.8
			97.0 average

in either of the solutions. A chemical analysis for iron in both solutions indicated that most of the inactive iron was present in the caustic permanganate solution. Both Fe^{59} and Cr^{51} have been identified in the deposits on metal coupons exposed in the APPR-1 primary purification blowdown system. Chemical decontamination of these coupons indicates that the major part of the Fe^{59} (approximately 60 percent) and Cr^{51} (approximately 85 percent) is removed by the caustic permanganate solution. The failure to detect these nuclides in the deposits removed from the dividing plate is not clear at this time since both Fe^{59} and Cr^{51} were detected in wipe samples.

With the exception of one sample, the decontamination factors resulting from the decontamination treatment were all greater than 70. One sample had zero activity at the completion of the treatment. The initial and final activity as well as the DFs obtained are tabulated in Table 10.

TABLE 10 Decontamination Results of Steam Generator Dividing Plate Using the Caustic Permanganate-Citrate Combination Solution Treatment

Net Initial Activity Counts Per Minute (Gamma)	Net Final Activity Counts Per Minute (Gamma)	Decontamination Factor (Gamma)
2,195	0	-
8,208	11	746
3,174	17	187
6,894	18	383
5,591	29	193
22,770	40	569
17,160	41	419
15,180	78	195
12,960	124	105
10,900	147	74
27,090	279	97
13,760	372	37

The differences in initial activity of the samples are due to differences in size and location. The surface of the section exposed to primary coolant on the inlet side of the steam generator was higher in activity than that exposed to primary coolant on the outlet side.

In all but two cases the final activity was below 200 cpm. The inference is drawn that there is probably no selective removal of any one nuclide for the entire treatment because of the very low final activities.

8.2 Decontamination Treatment with the Turco "4501" Process

A commercial decontamination product, manufactured by Turco Products, Inc., was also evaluated. This decontamination treatment called the Turco "4501" Process involves the use of three solutions. The first solution is a conditioning solution to prepare the corrosion product scale for the subsequent treatment with caustic permanganate and nitric acid.

A thorough discussion of the treatment together with results of its application in the field of decontamination can be found in Volume I of this report. Briefly, it is a three step process involving the following:[10]

1. 45 minute treatment (conditioning cycle) with Turco 4501 solution at 275°F.

2. High pressure water rinse.

3. 45 minute treatment with Turco 4502 solution at 215 to 220°F (3.8 lbs/gal).

4. High pressure water rinse.

5. 30 minute treatment with 25 percent nitric acid at room temp. (75° to 90°F).

6. High pressure water rinse.

A concentration of 2 lbs/gal was used in the loop decontamination and corrosion tests. It was not possible to obtain complete solution with the recommended concentration (3.8 lbs/gal) at room temperature. Three loop tests were performed using the Turco "4501" Process; two were performed with contaminated sections of tubing for decontamination evaluation and one test was performed with metal test coupons for corrosion evaluation. The activity profiles for the two decontamination tests are shown in Fig. 44. One test was performed at 3 ft/sec and the other test at 8 ft/sec.

An initial drop in activity was noted during the Turco 4501 treatment (Points 1 to 4). A further reduction in activity was observed during the addition of the Turco 4502 solution (Points 7 to 8). The major part of the activity was removed during the nitric acid treatment (Points 15 to 16).

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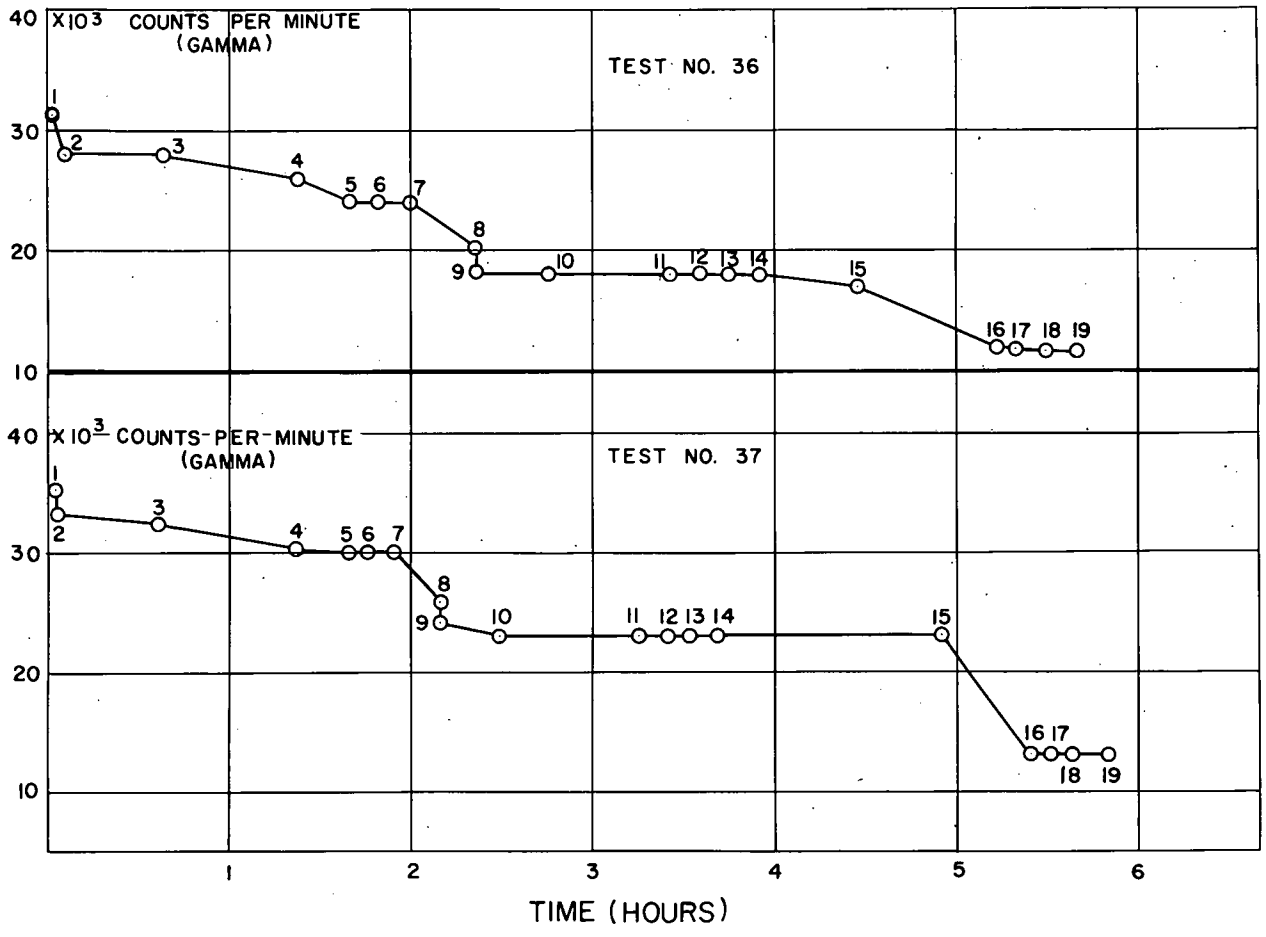

1-2. Loop filled with Turco 4501 solution; pressurized to 70-80 psig with nitrogen; commenced heating.

2. Pump on and set at designated flow rate (3 ft/sec for test no. 36 and 8 ft/sec for test no. 37).

3. Solution at temperature (275°F).

4. Completion of Turco 4501 treatment at temperature; commenced cooling.

5-6. Loop drained; loop filled with demineralized water.

6-7. Water rinse at designated flow rate.

7-8. Loop drained; loop filled with Turco 4502 solution; pressurized to 60-70 psig with nitrogen; commenced heating.

9. Pump on and set at designated flow rate.

10. Solution at temperature (220°F).

11. Completion of Turco 4502 treatment at temperature; commenced cooling.

12-13. Loop drained; loop filled with demineralized water.

13-14. Water rinse at designated flow rate; loop drained.

14-15. Loop filled with 25 percent nitric acid; pressurized to 60-70 psig with nitrogen.

15. Pump on and set at designated flow rate; temperature maintained at 100°F.

16. Completion of nitric acid rinse.

16-17. Loop drained.

17-18. Loop filled with demineralized water.

18-19. Water rinse at designated flow rate; loop drained.

Fig. 44 - Decontamination with Turco "4501" Process-Loop Test No. 36 and 37

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8.3 Comparison of the Caustic Permanganate-Citrate Combination Treatment and the Turco "4501" Process

The results of loop tests involving the evaluation of the caustic permanganate-citrate combination treatment and the Turco "4501" Process are given below:

	Caustic Permanganate-Citrate Combination Treatment.	Turco "4501" Process	
DECONTAMINATION RESULTS			
Loop Test No.	46	36	37
Flow Velocity (ft/sec)	5	3	8
Net Initial Activity (gamma cpm)	44, 260	29, 370	34, 210
Net Final Activity (gamma cpm)	5, 250	10, 200	12, 550
D. F.	8.4	2.9	2.7
B. F.	7.1	13.9	17.1
CORROSION RESULTS			
Loop Test No.	39	12	
Flow Velocity (ft/sec)	5	5	
Weight Loss (mgs/dm^2)			
Type 304 Stainless Steel			
Annealed	3.5	5.6	
	3.1	4.5	
	3.9		
	3.5		
Avg.	3.5	5.1	
Sensitized	19.0	9.1	
	15.7	14.9	
	14.9		
Avg.	16.5	12.0	

The results of the decontamination loop tests indicate that the caustic permanganate-citrate combination treatment was more effective in removing the activated corrosion product scale. The weight loss results on Type 304 stainless steel (annealed) were approximately the same for both treatments. The weight loss results for the sensitized material

were higher in the case of the caustic permanganate-citrate combination treatment. This would be expected because the citrate combination solution has a more corrosive effect on Type 304 stainless steel than 25 percent nitric acid.

At the completion of the Turco "4501" Process, an excessive amount of manganese dioxide was found in the loop. This may have been due to insufficient water flushing after the 4501 treatment. It was necessary to remove this material before additional loop studies could be performed.

A 5 percent solution of oxalic acid, circulated at 160°F, was used to insure complete removal of manganese dioxide. This operation was performed after all test specimens had been removed from the loop sample section.

8.4 Simulated APPR-1 Loop Test Results

The decontamination of a nuclear facility would require a longer solution exposure time than that used in loop studies, i.e., time for filling, heating, cooling, and draining would be longer. Two loop tests were performed to determine the effect of longer exposure time on decontamination and corrosion. The APPR-1 steam generator was used as a reference design for this evaluation. The chemical decontamination treatment was identical to that given in Table 8. The exposure times for the various solutions are given below:

A. Caustic Permanganate Step

Operation	Time Required (Hours)
1. Fill system	2.00
2. Commence circulation (5 fps) heat system (85°F/hr)	2.00
3. Residence time at temperature (225°F)	0.50
4. Cool system below boiling of solution	1.00
5. Drain system	0.50
Total	6.00

B. Water Rinse Step

1. Repeat A1	2.00
2. Circulate at 5 fps	0.08
3. Drain system	0.50
Total	2.58

C. "Aeration" Period	2.00
Total	2.00

D. Citrate Combination Step

Repeat Steps A 1-5 except solution is heated to 220°F	6.00
Total	6.00

E. Water Rinse Step

Repeat Steps B 1-3 Except circulate for 15 minutes		2.75
	Total	2.75
F. Repeat E 4 times		11.00
	Total	11.00

Grand Total Decontamination Time. . . 30.33 hours

The filling operation could not be extended over the two hour period; therefore the loop was filled within a few minutes and allowed to remain idle for the duration of the filling period. To simulate draining, the loop was allowed to remain idle for approximately 30 minutes at which time the loop was drained.

8.4.1 Decontamination Evaluation - Tubing

The activity versus time curve for the simulated APPR-1 decontamination loop test with a contaminated section of Type 304 stainless steel tubing is shown in Figure 45. Prior to evaluation, the tubing was scrubbed to remove loose activity. It was then decontaminated in the loop as outlined in the previous section. The results of the evaluation are given in Table 11.

TABLE 11 Results of Simulated APPR-1 Decontamination Evaluation(Test No. 47)

Initial Activity (Before Scrubbing)	40 mr/hr
Initial Activity (After Scrubbing)	4 mr/hr
Initial D. F.	10
Net Initial Activity before Decontamination	54, 237 cpm (4 mr/hr)
Net Final Activity	6, 149 cpm
Final D. F.	8.8
Total D. F.	88

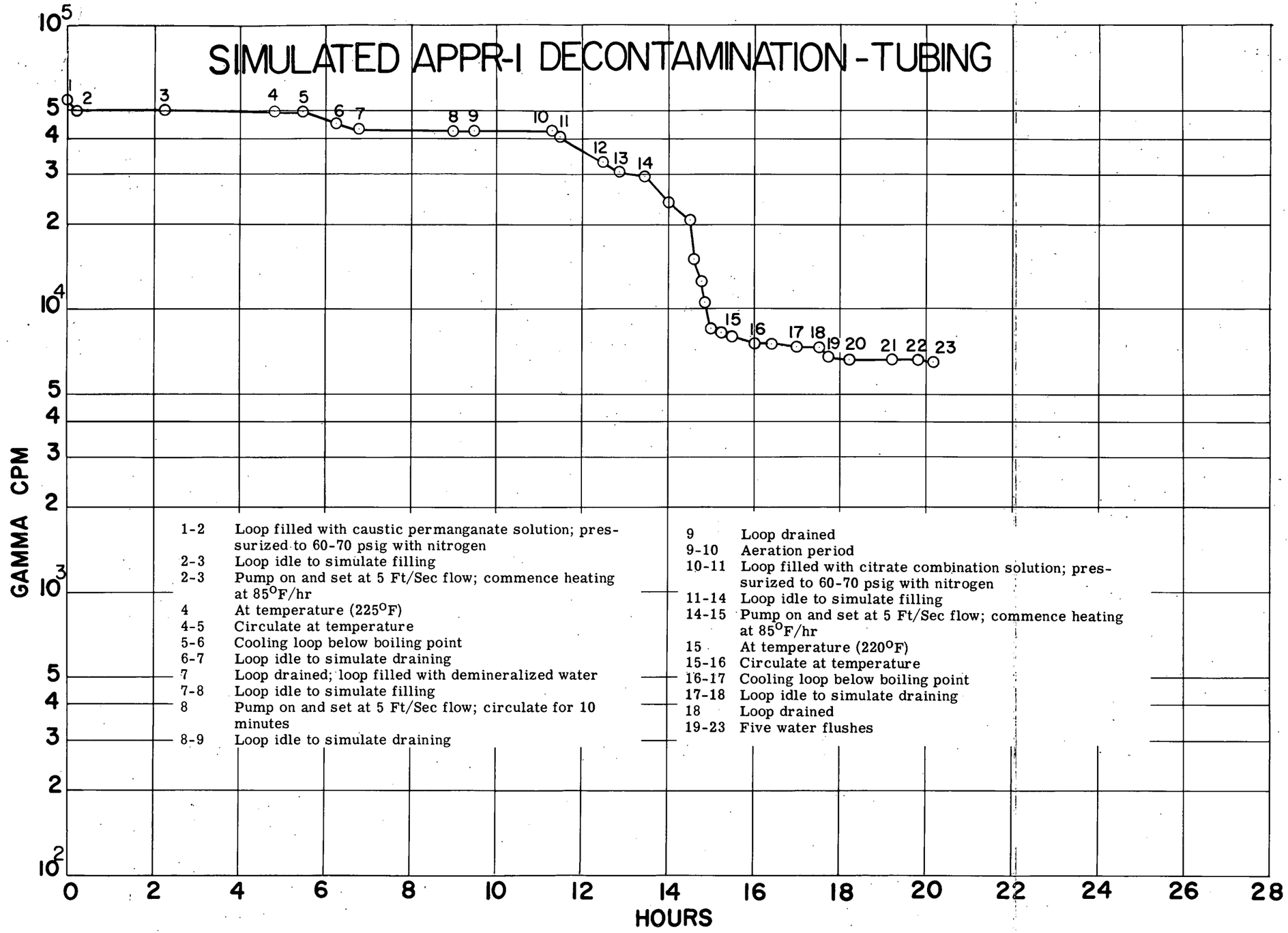

Fig. 45 Simulated APPR-1 Decontamination on Type 304 Stainless Steel Tubing-Loop Test No. 47

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The exposure time for the final water flushes did not include a simulated 2 hour fill and 0.5 hour drain time. It was felt that this would have little effect on the final decontamination factor. Fig. 46 shows the relationship between the number of water rinses and purity level (pH and resistivity). Five water rinses appear sufficient to bring the resistivity and pH to a constant level. Metallurgical examination of the tubing revealed no pitting, intergranular corrosion, or other harmful effects (Fig. 47).

The final D. F. for the simulated run is in close agreement with a previous run performed to determine if the loose activity would be removed by the recommended treatment. The result of that run where the tubing was not scrubbed prior to decontamination is given below:

Net Initial Activity	474,000 cpm
Net Final Activity	5,629 cpm
Total D. F.	84

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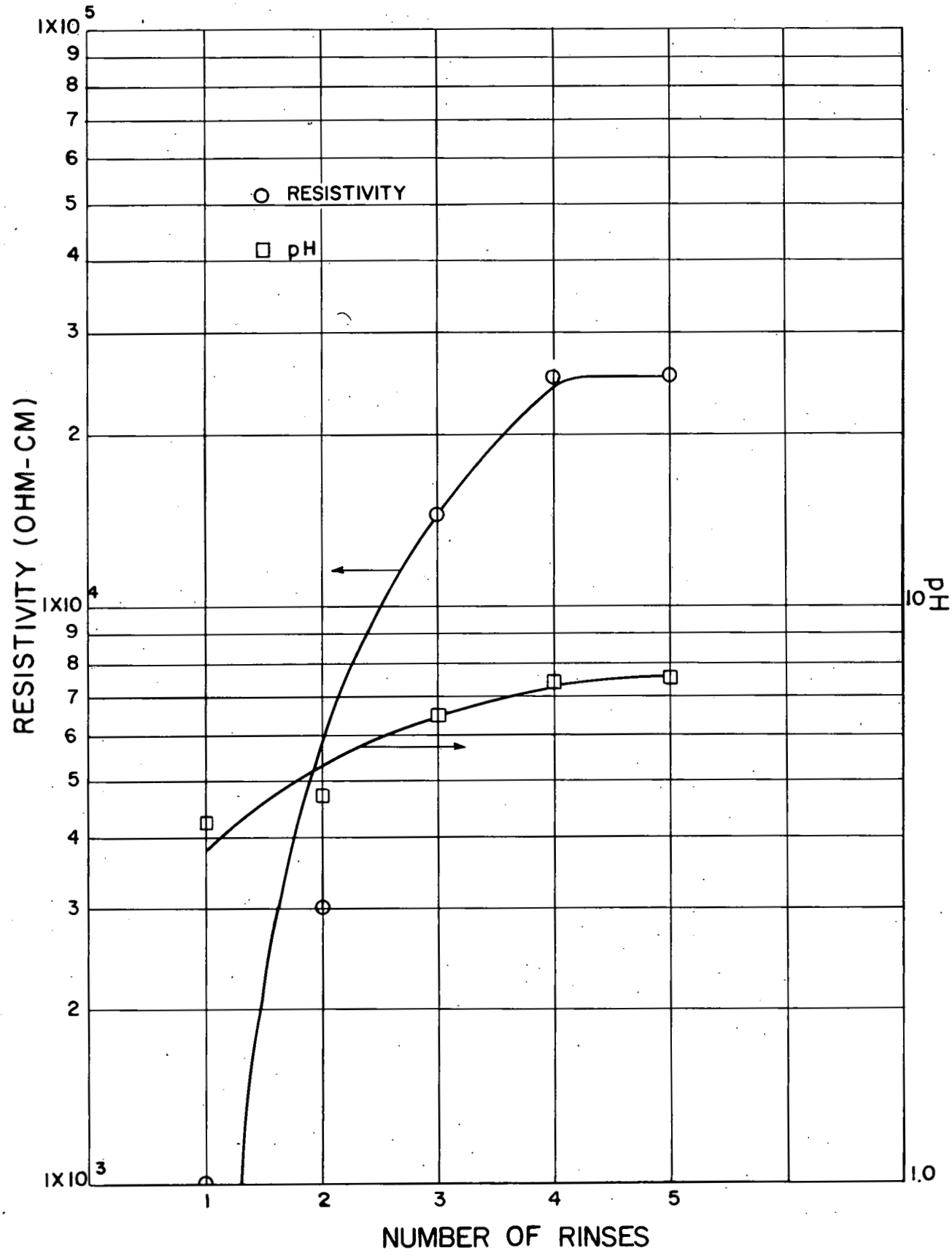

Fig. 46 Variation of Resistivity and pH with Number of Water Rinses-Loop Test No. 47

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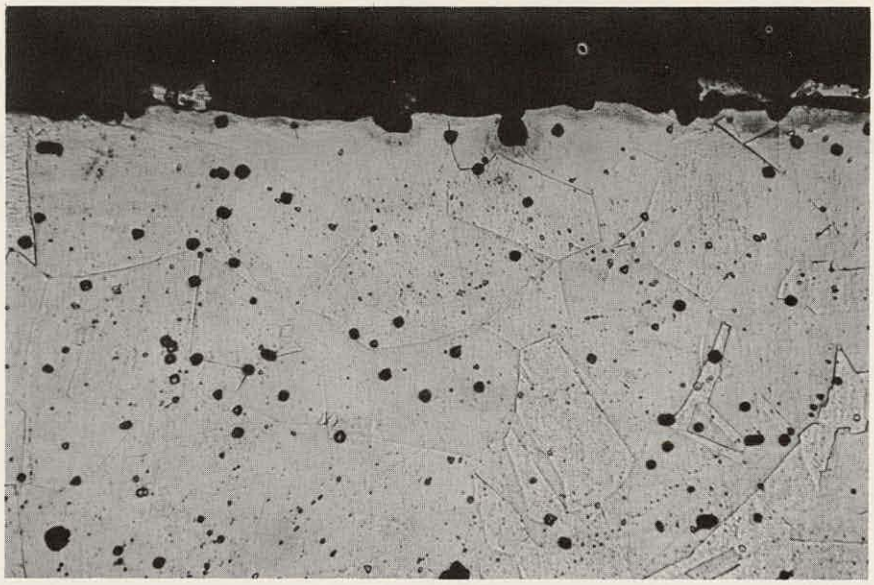
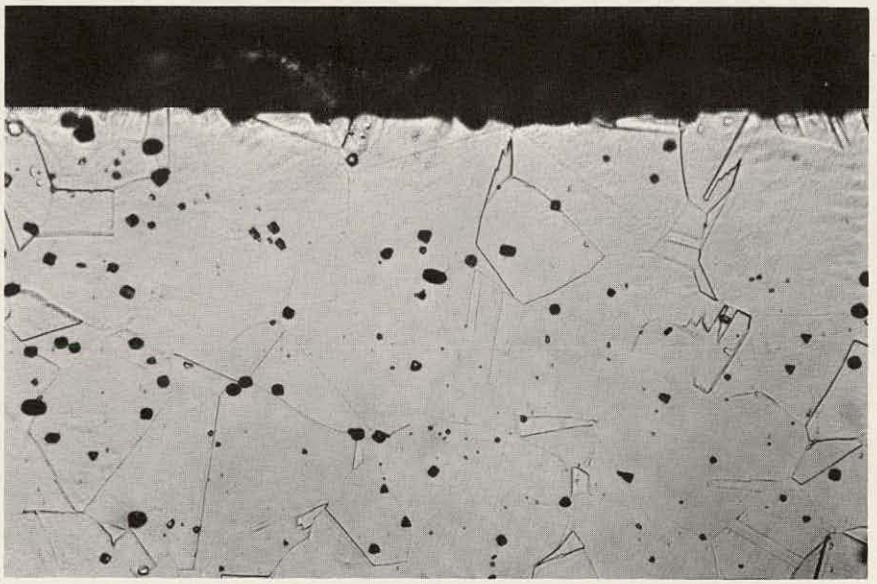


500 X Oxalic Acid Etch
Sample Untreated



500 X Oxalic Acid Etch
Sample Exposed to Decontamination Treatment

Fig. 47 - Photomicrograph of Type 304 Stainless Steel Tubing Simulated APPR-1 Decontamination-Loop Test No. 47

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8.4.2 Corrosion Evaluation - Metal Coupons

The second run was performed with 3-1/2 x 1/2 x 1/16-inch metal coupons of the following materials: Type 304 stainless steel (annealed and sensitized), Babcock and Wilcox Croloy 16-1, Inconel, and AISI C1010 carbon steel. The coupons were exposed for a total contact time of approximately 28 hours. This included the proposed time for the final water rinse step. The history of the loop test is shown in Fig. 48 and the total weight loss results are tabulated in Table 12.

TABLE 12 Comparison of Weight Loss Results for Loop Test No. 48

Material	Previous History	Average Weight Loss Mgs/dm^2 (Total)	Penetration (mils)
Type 304 SS (Annealed)	Exposed in Reactor	16.2	0.008
Type 304 SS (Sensitized)	Exposed in Reactor	35.6	0.017
Type 304 SS (Annealed)	New	4.1	0.002
Type 304 SS (Sensitized)	New	50.8	0.025
AISI C1010 Carbon Steel	New	3643 (one coupon)	0.182
Croloy 16-1	New	58.6	0.029
Inconel	New	3.5 (one coupon)	0.002

The weight loss results for the contaminated Type 304 stainless steel (sensitized) were about twice as high as the annealed weight loss results. The ratio for new samples is substantially higher and may indicate that the sensitized weight loss result (50.8 mgs/dm^2) is in error. The ratio between the Babcock and Wilcox Croloy 16-1 and the Type 304 stainless steel (annealed) is approximately the same as that found in decontamination loop tests using citric acid and ammonium citrate as a secondary solution rinse. One Inconel coupon resulted in a weight loss of 3.5 mgs/dm^2, about the same as observed for Type 304 stainless steel (annealed).

Five water flushes were sufficient to restore the loop to constant pH. The resistivity was still increasing after five water flushes (Fig. 49).

Photomicrographs of the contaminated Type 304 stainless steel coupons (annealed and sensitized) revealed no evidence of cracking, localized attacks or intergranular corrosion (Fig. 50).

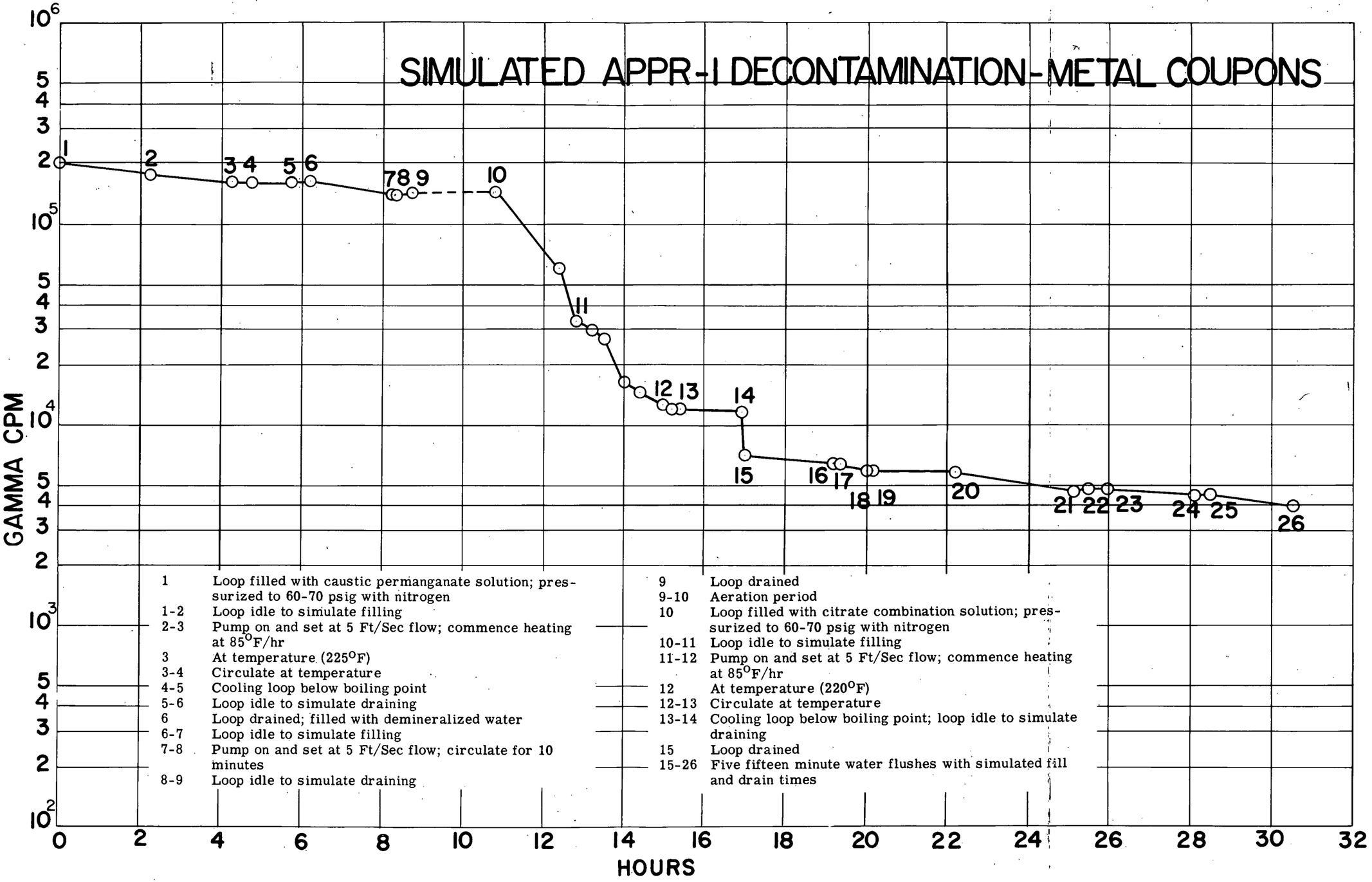

Fig. 48 Simulated APPR-1 Decontamination-Loop Test No. 48 (Metal Coupons)

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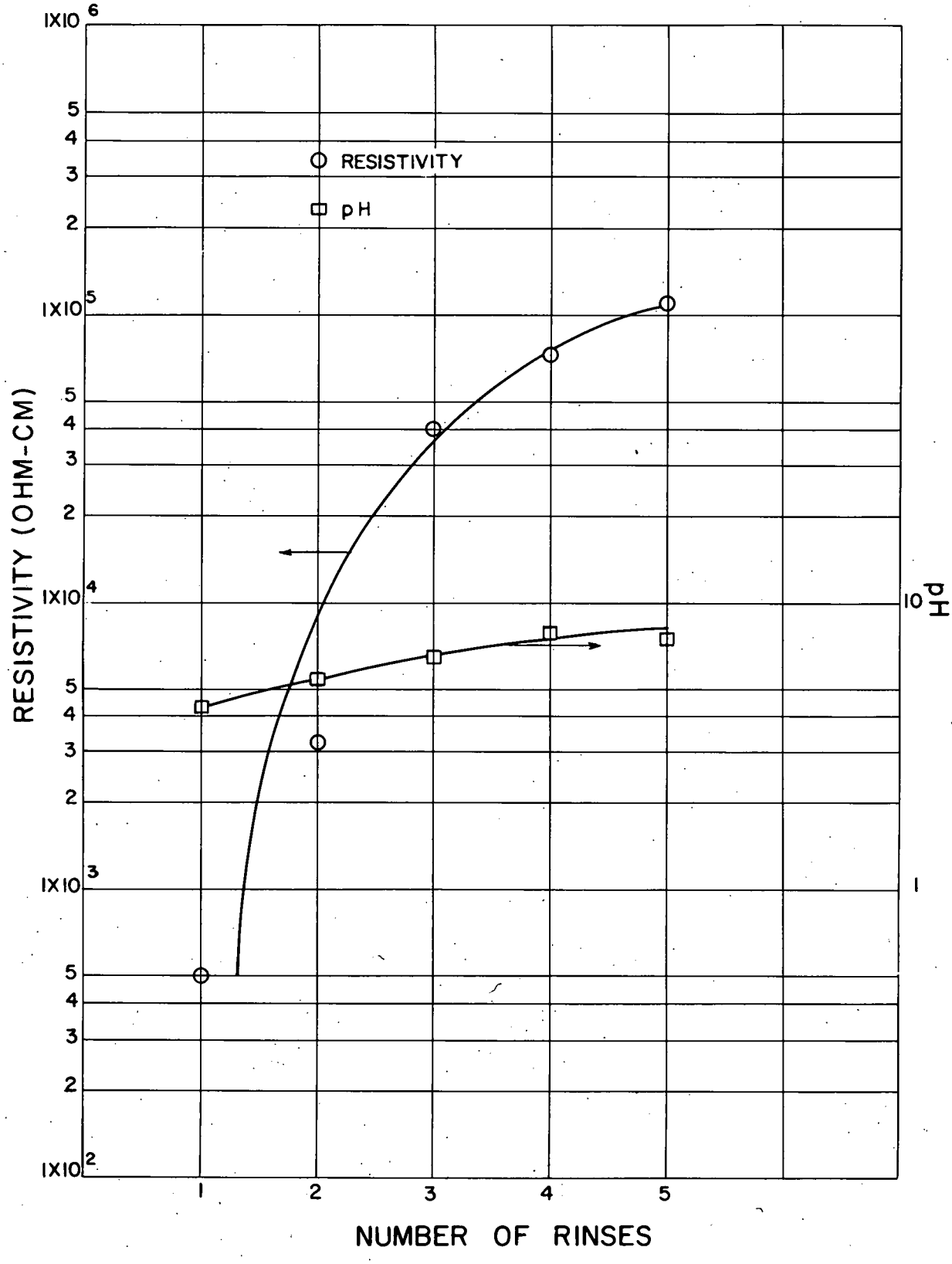

Fig. 49 Variation of Resistivity and pH with Number of Water Rinses-Loop Test No. 48

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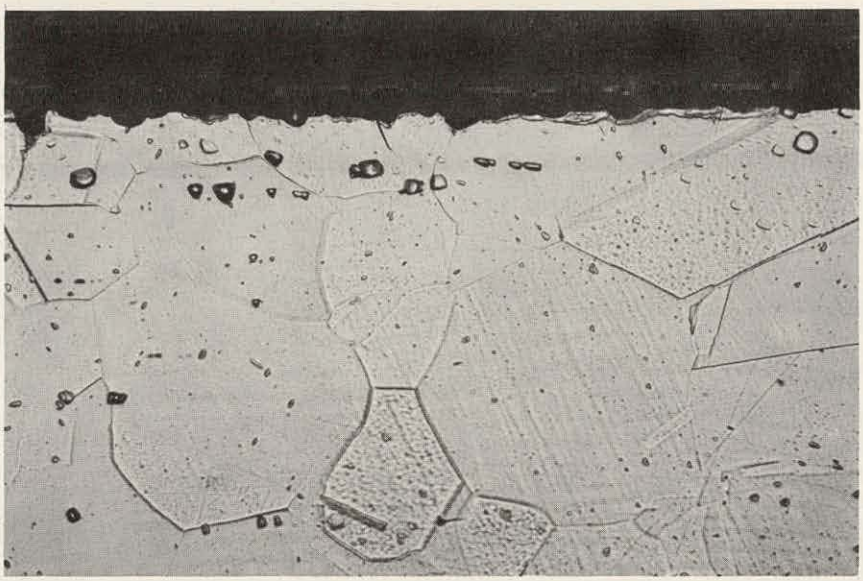
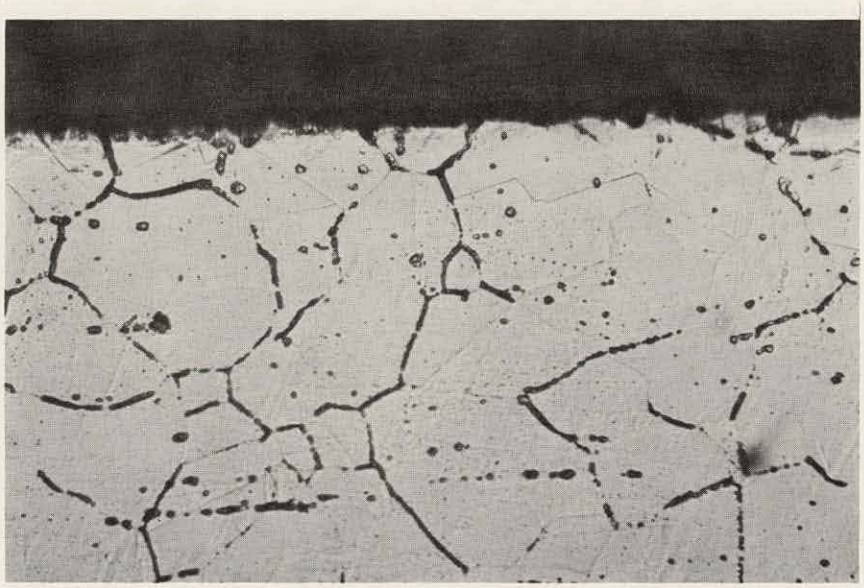


500 X Oxalic Acid Etch

Annealed Sample



500 X Oxalic Acid Etch

Sensitized Sample

Fig. 50 - Photomicrograph of Type 304 Stainless Steel-Simulated APPR-1 Decontamination Loop Test. No. 48

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8.5 Post Decontamination Effects

Chemical decontamination is of little value if corrosion rates and activity pickup are increased as a result of the decontamination treatment. Consequently, it was of particular interest to determine the relative corrosion rate and activity pickup on metal surfaces that had been exposed to the caustic permanganate-citrate solutions.

A number of metal specimens (3 1/2 x 1/2 x 1/16-inch) were placed in the APPR-1 purification blowdown line. These specimens included Type 304 stainless steel (annealed and sensitized), Babcock and Wilcox stainless steel Croloy 16-1, and AISI C1010 carbon steel. The specimens were placed in three categories, viz.

(a) New specimens

(b) New specimens used in loop corrosion studies with caustic permanganate-citrate solutions.

(c) New specimens exposed to the APPR-1 primary coolant and decontaminated in loop studies with caustic permanganate-citrate solutions (Type 304 stainless steel).

The new specimens were used to establish the weight loss and activity pickup of undecontaminated surfaces, and as a basis for comparison with decontaminated specimens.

The weight loss was based on the difference, expressed as mgs/dm^2, between the initial unexposed weight and the weight obtained after removal from the APPR-1 purification line. This is referred to as "exposed weight loss". Prior to weighing, exposed samples were vigorously scrubbed with soap and water to remove all loose particulate matter. The beta and gamma dose rates emanating from these specimens were determined by means of a calibrated Technical Associates Juno Model 3 Meter. The sensitive chamber of the instrument was placed in the same position for the measurements, i. e. approximately one inch from the specimen. The weight loss and activity pickup results are given in Tables 13, 14 and 15.

The curve in Fig. 51 was determined from "exposed weight loss" results on new Type 304 stainless steel coupons exposed for various periods of time in the APPR-1 purification system. A comparison of the weight loss results was made with five coupons which had previously been exposed in the APPR-1 purification blowdown line, decontaminated by the caustic permanganate-rinse treatment, and re-exposed in the same manner for an additional 461 hours. It was desired to determine whether a decontaminated surface exhibited the corrosion and activity buildup characteristics of a new or previously corroded surface. This comparison was performed using Student's T Distribution and two hypotheses were tested:[11]

A. The subsequent weight loss on a decontaminated sample (previously contaminated), re-exposed to reactor coolant is the same as a new unexposed surface.

B. The subsequent weight loss on a decontaminated sample (previously contaminated), re-exposed to reactor coolant is the same as if the coupon had not been decontaminated.

Test of Hypothesis A

	Decontaminated Sample (d) (461 hours)	New Sample (n) (461 hours)
$\overline{X}$ (mean value)	1.0 mgs/dm^2	2.6
S (variance)	0.22	0.71
N (No. of samples	5	2

$$\hat{S} \text{ (Estimate of universe variance)} = \sqrt{\frac{N_d S_d^2 + N_n S_n^2}{N_d + N_n - 2}}$$

$$= \sqrt{\frac{(5)\ (0.22)^2 + (2)\ (.71)^2}{5}}$$

$$= 0.50$$

$$t = \frac{\overline{X}_n \pm \overline{X}_d}{S\sqrt{1/N_d + 1/N_n}} = \frac{2.6 \pm 1.0}{(0.50)\ (.835)} = 3.85$$

At the 95 percent level of confidence, for both tails of the t distribution and 5 degrees of freedom, $t = 2.571$ as compared to $t = 3.85$ from hypothesis A. Since the value of t for hypothesis A is greater than that which could be expected from random fluctuations, the difference is significant and hypothesis A is rejected.

2. Test of Hypothesis B

	Decontaminated Sample (d) (1825 + 461 hours-1825 hours)	New Sample (c) (1825 + 461-1825 hours)
$\bar{X}$	1.0 mgs/dm^2	0.3 mgs/dm^2 (Fig. 51)
S	0.22	-
N	5	-

The incremental value of 0.3 mgs/dm^2 is assumed to be a universe value for this calculation.

$$t \quad \frac{\bar{X}_c \pm \bar{X}_d}{S/\sqrt{N-1}} = \frac{0.3 + 1.0}{0.22/2} = 6.4$$

At the 95 percent level of confidence, for both tails of the t distribution and 4 degrees of freedom, $t = 2.78$ as compared to $t = 6.4$ from hypothesis B. The difference is significant and hypothesis B is rejected. Therefore, the Type 304 stainless steel (annealed) decontaminated samples re-exposed to the reactor coolant did not behave as new samples, nor did they behave as samples which did not receive the decontamination treatment. The decontamination treatment resulted in subsequent corrosion less than that which could be expected from a virgin surface and more than that which could be expected from a precorroded surface. However, apart from statistical considerations, the average weight loss results for the decontaminated samples appear to be more representative of a sample shown by the dotted line in Fig. 51. In summation, the decontamination treatment would be expected to result in a surface which exhibits more of the corrosion rate characteristics of a previously corroded surface than that of a new surface.

The statistical evaluation of the weight loss results was not repeated for the sensitized metal because of insufficient data. However, on the basis of available data, the weight loss results for the decontaminated samples indicate the same conclusion as noted in the case of the annealed metal.

Figure 52 is presented to show the relationship between beta activity pickup on new Type 304 stainless steel (annealed) and "exposed weight loss". The linearity of the relationship is apparent. The lower weight loss result at 1825 hours exposure is probably due to the reduction of those factors which tend to increase the corrosion rate in a nuclear reactor system, e.g. oxygen level. The relationship between beta activity pickup and weight loss results for Type 304 stainless steel and Babcock and Wilcox Croloy 16-1 after 1825 hours exposure to the reactor coolant is shown in Fig. 53.

While not linear, the curve does indicate an increased activity pickup with increasing weight loss. It would be expected that the subsequent activity pickup on decontaminated samples would be less than a new uncontaminated surface. This is true since exposed weight loss on decontaminated samples was found to be less than that on new samples. It might prove feasible to precorrode the reactor surfaces prior to reactor startup as a means of reducing the initial corrosion rate with its associated activity buildup.

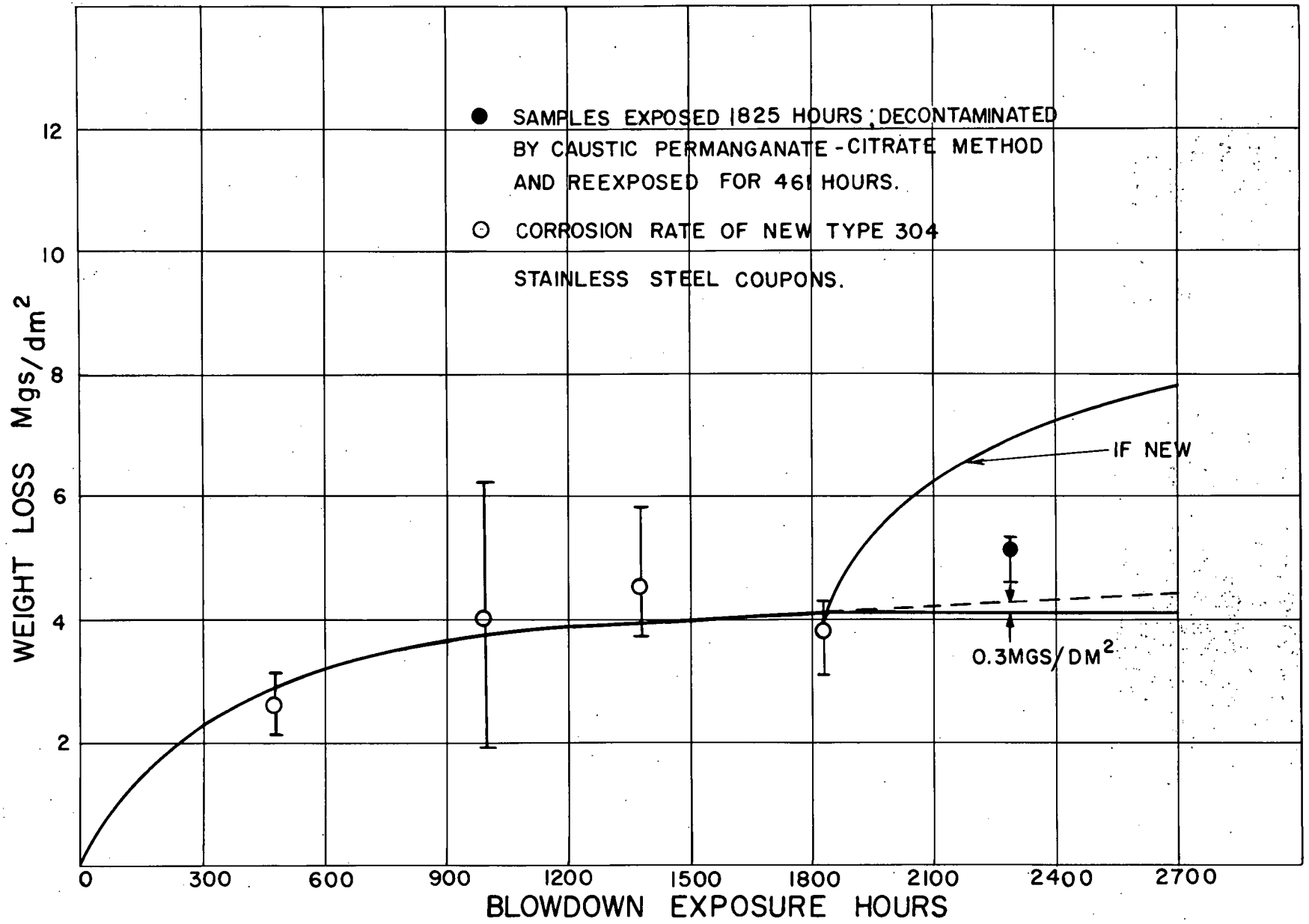

Fig. 51 Comparison of Weight Loss Results on New and Decontaminated Type 304 Stainless Steel Exposed to APPR-1 Coolant

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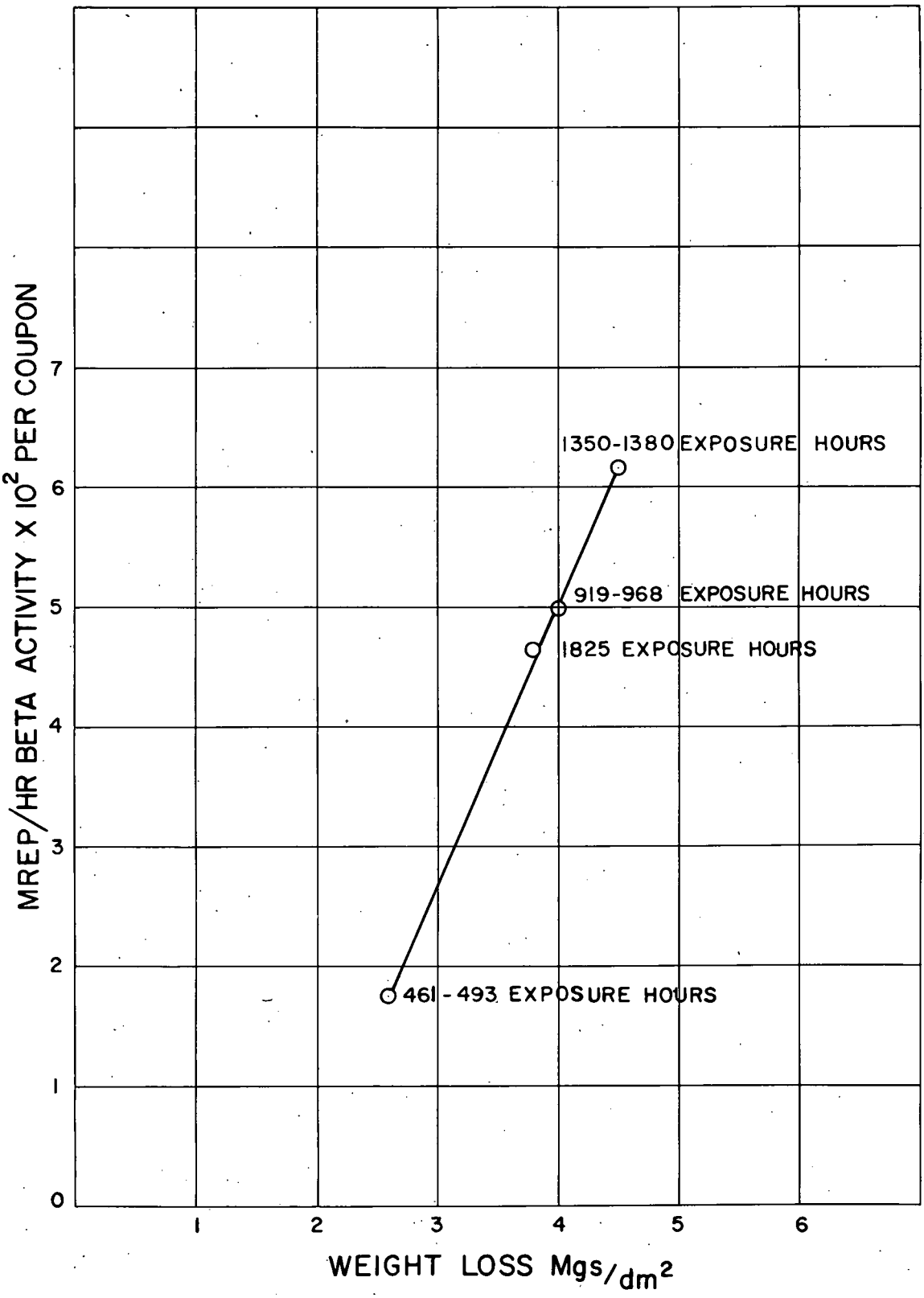

Fig. 52 Relationship Between Beta Activity Pickup and Weight Loss for Annealed Type 304 Stainless Steel Exposed in the APPR-1 Purification System for Different Periods of Time

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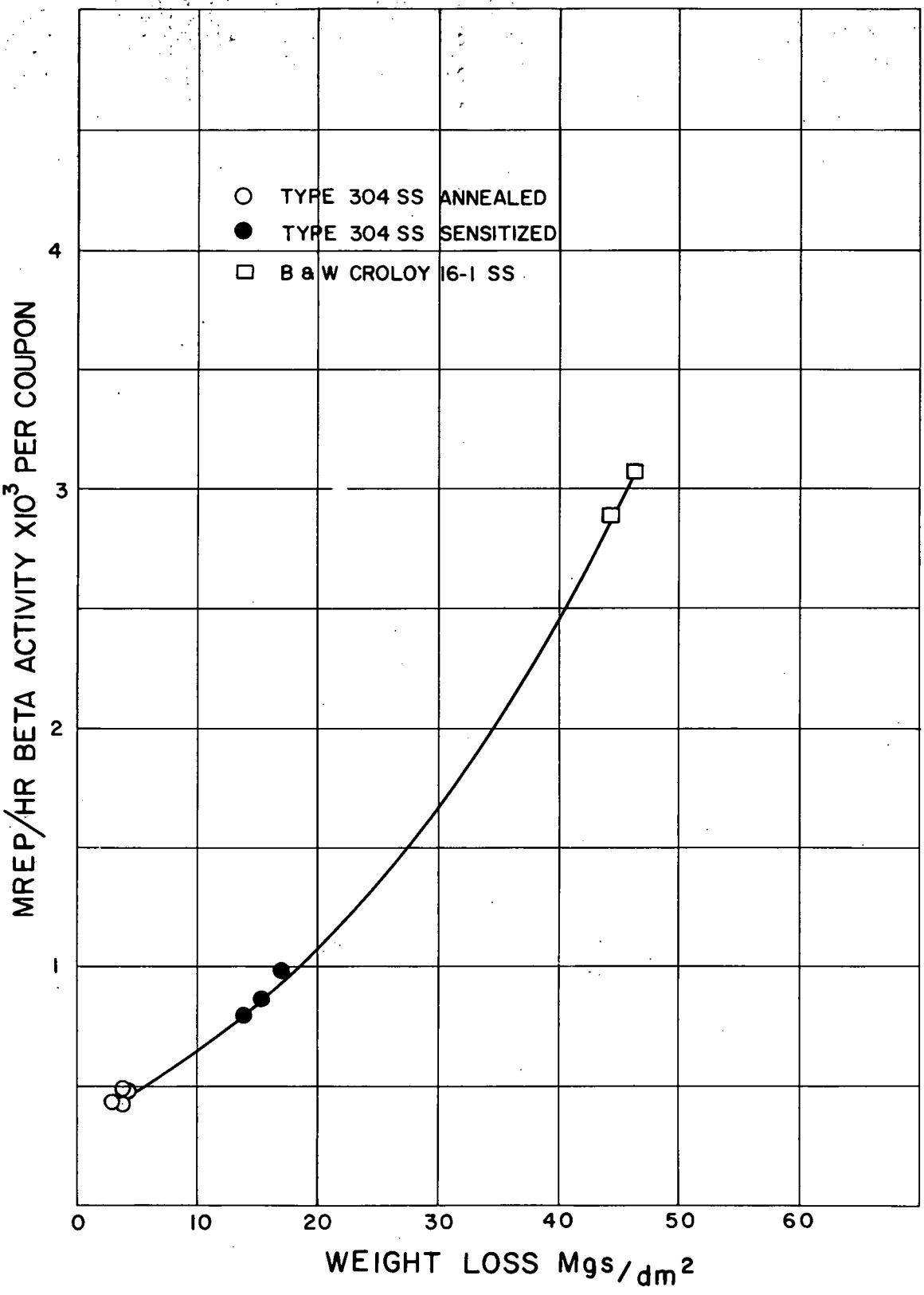

Fig. 53 Relationship Between Beta Activity Pickup and Weight Loss for Stainless Steel Coupons Exposed in the APPR-1 Purification System for 1825 Hours

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TABLE 13 Weight Loss and Activity Pickup Results for New Type 304 Stainless Steel Specimens Exposed to APPR-1 Primary Coolant

Total Exposure Hours	Total E. F. P. H*	Annealed Weight Loss mgs/dm^2	Annealed Activity mrep/hr on surface	Sensitized Weight Loss mgs/dm^2	Sensitized Activity mrep/hr on surface
461	325	3.1	193	11.6	704
493	390	2.1	357	7.8	775
		$\bar{X}$ 2.6	275	9.7	739
		S 0.71			
919	420	N. C. **	626	17.8	1472**
968	833	4.1	442	14.0	
		1.9		15.1	716
		3.7	422	17.6	819
		6.2	492	17.4	730
		$\bar{X}$ 4.0	496	16.4	755
1350	815	3.9	592	7.2**	890
		3.7	554	12.4	1075
1380	745	5.8	694	8.5	970
				26.6**	3100**
		$\bar{X}$ 4.5	613	10.4	978
1825	1258	3.9	432	16.9	960
		3.9	498	15.7	857
		21.9**	368**	14.1	798
		4.3	492		
		3.1	436		
		N. C. **	445		
		$\bar{X}$ 3.8	461	15.6	872

* EFPH – equivalent full power hours
** not used in calculating averages
N. C. – no change

TABLE 14 Weight loss and Activity Pickup Results for New Babcock And Wilcox Croloy 16-1 and AISI C1010 Carbon Steel Specimens Exposed to APPR-1 Primary Coolant

Total Exposure Hours	Total E. F. P. H. *	B & W Croloy 16-1 Weight Loss mgs/dm^2	B & W Croloy 16-1 Activity mrep/hr on surface	AISI C1010 Carbon Steel Weight Loss mgs/dm^2	AISI C1010 Carbon Steel Activity mrep/hr on surface
493	390	27.9	1965	34.7	191
919	420	84.7	4730	193.4	1110
				99.2	278
968	833	42.6	3340	81.8	407
		38.2	2740	163.9	304
		40.7	2560	82.8	328
1350	815	39.3(P)	2790	169.4	247
		38.2	3350	167.4	245
1380	745	89.5	6290	194.4	179
1825	1258	46.3	3070	179.8	246
		44.8	2900	263.9	244

* EFPH – equivalent full power hours

P indicates specimen passivated in 25 percent nitric acid for 60 minutes at 160°F

TABLE 15 Weight Loss and Activity Pickup Results for New Type 304 Stainless Steel Exposed for 1825 Hours, Decontaminated and Re-Exposed in the APPR-1 Purification Blowdown Line

Total Exposure Hours	Total E. F. P. H*.	Annealed		Sensitized	
		Weight Loss mgs/dm^2	Activity Pickup mrep/hr on surface	Weight Loss mgs/dm^2	Activity Pickup mrep/hr on surface
461	325	1.0	131	2.9	302
		0.6	38.5**	N. C. **	325
		1.0	117	N. C. **	122
		N. C. **	119		
		1.2	148		
		1.0	162		
		$\bar{X}$ 1.0	135	2.9	249
		S 0.22			

* EFPH – equivalent full power hours
** not used in calculating average
N. C. no change

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APPENDIX A

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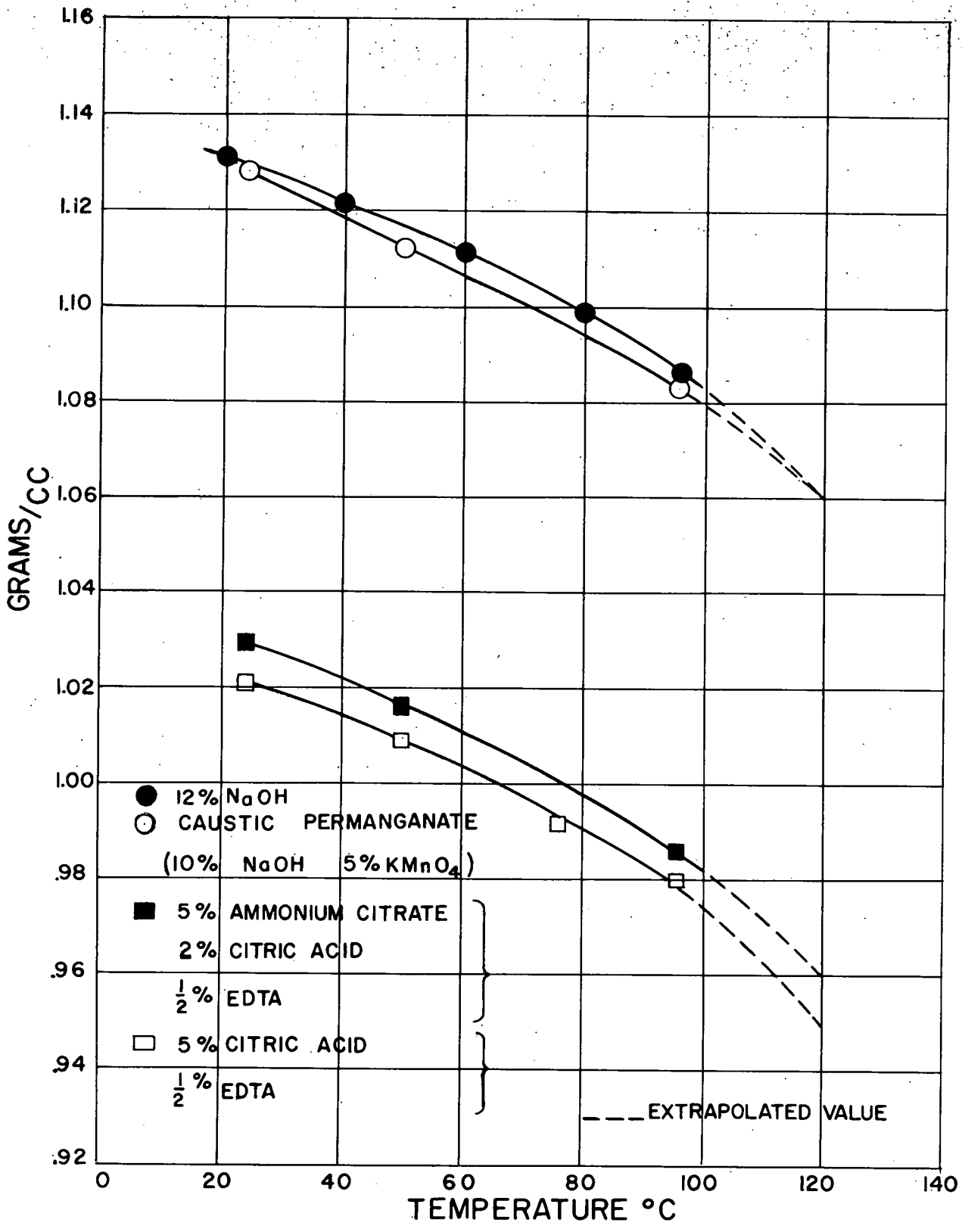

Fig. A-1 Density of Various Decontamination Solutions

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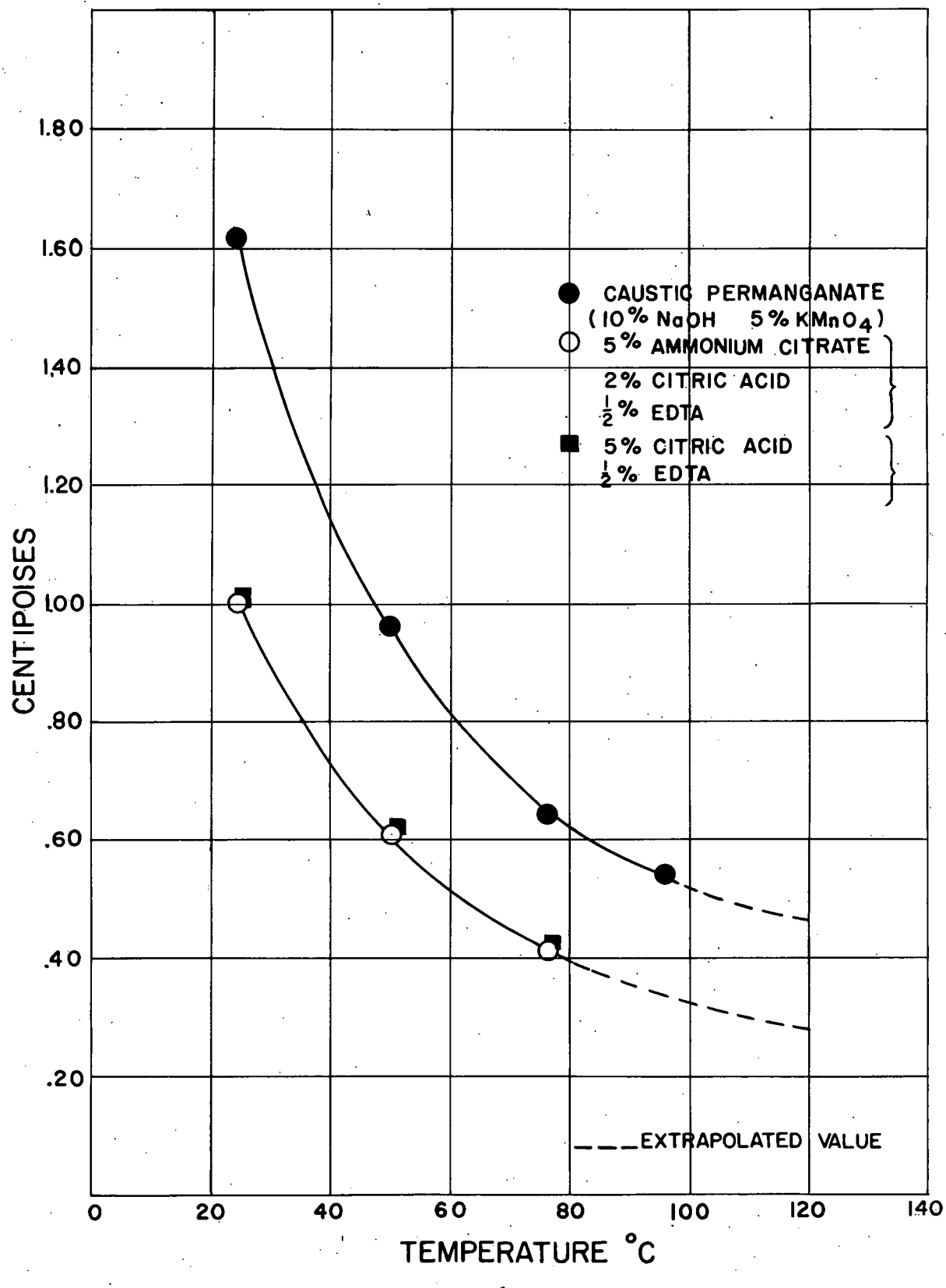

Fig. A-2 Viscosity of Various Decontamination Solutions

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APPENDIX TABLE B-1

Weight Loss Results (Mgs/dm^2-hr) Obtained for New Type 304 Stainless Steel Exposed to Caustic Permanganate (225-250°F) - Rinse Treatment in Loop Decontamination Tests

	RINSE SOLUTION										
	5% Ammonium Citrate			5% Citric Acid-1/2% Versene			Citric Acid-Ammonium Citrate-Versene Comb.				
Material	Mgs/dm^2-hr		Temp. °F	Flow Rate (fps)	Mgs/dm^2-hr		Temp. °F	Flow Rate (fps)	Mgs/dm^2-hr		Temp. °F	Flow Rate (fps)
Type 304 SS Annealed		1.4	200	3.5		2.1	200	5	3.8			2
		1.4	200	5		2.0	200	5		0.7		2
		1.4	200	5		2.4	200	5		0.8		2
	4.3a		200	5		2.7	200	5		0.9	b175	2
	3.8a		200	5		1.1	200	5		0.9		2
		1.4	200	5		1.2	200	5		0.9		2
		1.7	200	5		1.1	200	5		1.2		2
	1.3a'		200	5		1.1	175	1		1.0	c200	2
		1.1	200	1		1.1	175	1		1.3		2
		1.3	200	1						1.2		2
		1.2	200	1								
$\bar{X}$		1.4				1.6				1.0		
Type 304 SS Sensitized	7.9a		200	5		5.7	200	5	17.2			2
		3.3	200	5		5.8	200	5		9.0		2
		3.2	200	5	14.8		200	5		6.5	b175	2
	3.7a'		200	5		3.5	200	5		9.4		2
		4.2	200	1		4.9	200	5		5.8		2
		7.0	200	1		9.2	175	1		6.3		2
		3.9	200	1						5.2	c220	2
										5.0		2
$\bar{X}$		4.3				5.8				6.7		

a 10% Ammonium Citrate
a' 10% Ammonium Citrate
"CP105" Temp. at 170°F

b 5% Citric Acid
2% Ammonium Citrate
1/2% Versene

c 2% Citric Acid
5% Ammonium Citrate
1/2% Versene

APPENDIX TABLE B-2

Weight Loss Results (Mgs/dm^2-hr) Obtained for New Babcock and Wilcox Croloy 16-1 and AISI C1010 Carbon Steel Exposed to Caustic Permanganate (225-250°F) - Rinse Treatment in Loop Decontamination Tests

	RINSE SOLUTION					
	5% Ammonium Citrate			5% Citric Acid + 1/2% Versene		
Material	Mgs dm^2-hr	Temp. °F	Flow Rate (fps)	Mgs dm^2-hr	Temp. °F	Flow Rate (fps)
Babcock and Wilcox Croloy 16-1	17.0	200	5	2.4	200	5
	15.9	200	5	2.6	200	5
	19.4a'	200	5	81.0	200	5
	20.6a'	200	5	13.4	200	5
	10.3	220	1	38.3	175	1
$\bar{X}$	14.4			27.5		
AISI C1010 Carbon Steel	480	200	3.5	135	200	5
	453	200	3.5	145	200	5
	181	200	5	462	200	5
	334a	200	5	394	200	5
	382	200	5	346	200	5
	357	200	5	326	175	1
	390a'	200	5			
	362	220	1			
$\bar{X}$	407			382		

a 10% Ammonium Citrate
a' 10% Ammonium Citrate "CP105" Temp. at 175°F

APPENDIX TABLE B-3

Weight Loss Results (Mgs/dm^2-hr) Obtained from Various Metals Exposed to More Than One Caustic Permanganate (225-250°F) - Rinse Treatment in Loop Decontamination Tests

RINSE SOLUTION

	5% Ammonium Citrate				5% Citric Acid + 1/2% Versene				Citric Acid-Ammonium Citrate -Versene Combination			
Material	Mgs/dm^2-hr	Temp. °F	No. Cycles	Flow Rate (fps)	Mgs/dm^2-hr	Temp. °F	No. Cycles	Flow Rate (fps)	Mgs/dm^2-hr	Temp. °F	No. Cycles	Flow Rate (fps)
Type 304 SS Annealed	1.3	200	2	5	1.0	200	3	5	0.6		3	2
	2.9a	200	2	5	1.6	200	4	5	0.6		3	2
	2.5a	200	2	5	0.6	200	2	5	1.8	b175	3	2
	0.9	200	2	5	1.3	200	4	5	0.3		2	2
	1.5	200	2	5	1.0	200	5	5	0.6		2	2
	0.5a'	200	2	5	0.7	175	2	1	0.8		2	2
	0.7a'	200	2	5	0.9	175	2	1	0.5		2	2
	0.7a'	200	2	5	0.9	175	2	1	0.6	c220	2	2
	3.3	220	5	1					0.8		2	2
	0.8	220	6	1					0.9		2	2
Type 304 SS Sensitized	1.8	200	3	5	2.5	200	5	5	0.9		3	2
	1.5	200	2	5	1.7	200	3	5	0.6	b175	3	2
	1.1a'	200	4	5	8.4	200	2	5	2.0		2	2
	1.7a'	200	2	5	1.8	200	6	5	1.9		2	2
	0.5a'	200	2	5	3.4	200	4	5	1.2	c220	2	2
	1.5	220	6	1	1.8	175	2	1	1.6		2	2
	8.0	220	4	1	1.5	175	2	1				
					1.8	175	2	1				

a 10% Ammonium Citrate
a' 10% Ammonium Citrate "CP105" Temp. at 170°F
b 5% Citric Acid 2% Ammonium Citrate 1/2% Versene
c 2% Citric Acid 5% Ammonium Citrate 1/2% Versene

APPENDIX TABLE B-4

Weight Loss Results (Mgs/dm^2-hr) Obtained from Various Metals Exposed to More Than One Caustic Permanganate (225-250°F) - Rinse Treatment in Loop Decontamination Tests

	RINSE SOLUTION											
	5% Ammonium Citrate				5% Citric Acid + 1/2% Versene				Citric Acid-Ammonium Citrate -Versene Combination			
Material	Mgs/dm^2-hr	Temp. °F	No. Cycles	Flow Rate (fps)	Mgs/dm^2-hr	Temp. °F	No. Cycles	Flow Rate (fps)	Mgs/dm^2-hr	Temp. °F	No. Cycles	Flow Rate (fps)
Babcock & Wilcox Croloy 16-1	17.3	220	2	5	16.3	200	4	5	29.4	b175	2	1
	16.4	220	2	5	17.5	200	4	5	7.5		2	1
	12.8a'	220	2	5	12.7	200	5	5	8.2		2	1
	15.0a'	220	2	5	10.5	175	3	1	12.2		3	2
	10.3	220	2	1	10.3	175	3	1				
	9.8	220	5	1								
AISI C1010 Carbon Steel	266a	200	2	5	198	200	4	5	447	b175	3	1
	141	200	2	5	175	200	3	5	207		2	2
	281	200	2	5	271	200	3	5				
	254	200	2	5	153	200	2	5				
	306a'	200	2	5	109	175	3	1				
	262a'	200	2	5	92	175	2	1				
	236a'	200	2	5	182	175	2	1				

a 10% Ammonium Citrate

a' 10% Ammonium Citrate "CP105" Temp. at 170°F

b 5% Citric Acid 2% Ammonium Citrate 1/2% Versene

APPENDIX C

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APPENDIX TABLE C-1

Weight Loss Results on Metal Coupons (1-3/4 x 1/2 x 1/16 - inch) in Dynamic Autoclave (1 gpm - .025 fps)
Caustic Permanganate at 195°F

Material Sample No.	Heat Treatment Conditions	Total Weight Loss-Mgs/dm^2 at Time Indicated (Hours) 1/2	1	2	4	8	16	Total Average Penetration (Mils)
Type 304 SS	Annealed							
C-30		3.8	4.6	6.5	8.8	11.1	18.0	
C-31		4.6	5.8	8.9	9.6	11.5	18.9	.010
C-32		6.9	8.1	10.0	11.9	13.9	20.0	
$\bar{X}$		5.1	6.2	8.1	10.1	12.2	19.0	
Type 304 SS	Sensitized							
S-14		6.7	7.7	9.2	12.3	16.1	23.0	
S-15		6.7	7.7	11.5	13.5	17.3	23.5	.012
$\bar{X}$		6.7	7.7	10.4	12.9	16.7	23.3	
Carbon Steel AISI - C1010	Hot Rolled							
I-19		4.2	7.3	13.8	15.8	36.5	61.2	.035
I-20		4.2	8.5	-	24.5	58.4	77.8	
$\bar{X}$		4.2	7.9	13.8	20.2	47.9	69.5	

Area of sample = 0.129 dm^2

APPENDIX TABLE C-2

Weight Loss Results on Metal Coupons (1-3/4 x 1/2 x 1/16 - inch) in Dynamic Autoclave (1 gpm-.025 fps)
5% Citric Acid, 1/2% Versene at 175°F

Material Sample No.	Heat Treatment Conditions	Total Weight Loss - Mgs/dm² at Time Indicated (Hours) 1/2	1	2	4	7-1/2	15-1/2	Total Average Penetration (Mils)
Type 304 SS	Annealed							
C-163-A		1.1	1.5	1.5	1.5	1.5	2.2	
C-163-B		0.0	0.4	0.8	0.8	1.2	1.7	.001
C-164-B		0.0	1.5	1.5	1.5	2.1	3.6	
$\overline{X}$		0.3	1.1	1.3	1.3	1.6	2.5	
Type 304 SS	Sensitized							
S-103-A		24.6	25.0	25.0	25.0	25.0	25.8	
S-103-B		10.9	11.6	11.6	12.3	12.3	13.0	
S-104-A		23.9	25.0	26.1	26.1	26.1	26.8	.010
S-104-B		12.3	13.6	13.6	13.6	13.6	15.3	
$\overline{X}$		17.9	18.8	19.1	19.3	19.3	20.2	
Carbon Steel AISI - C1010	Hot Rolled							
I-9		885	1125	1546	2167	3537*		
I-10		915	1135	1478	2096	3742*		1.75**
I-64-A		890	1120	1480	2008	3306*		
I-64-B		920	1130	1540	2069	3478*		
$\overline{X}$		902	1127	1511	2069	3515		

* Specimen Removed after 8 hours
** For 8 hours exposure

Area of Sample = 0.129 dm²

APPENDIX TABLE C-3

Weight Loss Results on Metal Coupons (1-3/4 x 1/2 x 1/16 - inch) in Dynamic Autoclave (1 gpm-.025 fps)
5% Ammonium Citrate - 175°F

Material Sample No.	Heat Treatment Conditions	Total Weight Loss-Mgs/dm^2 at Time Indicated (Hours) 1/2	1	2	4	8	16	Total Average Penetration (Mils)
Type 304 SS	Annealed							
C-153-A		0.0	--	--	1.2	1.9	2.7	.001
C-153-B		0.0	1.2	1.2	1.9	1.9	2.3	
C-154-A		0.0	1.6	1.6	1.9	2.3	3.5	
C-154-B		0.0	1.2	1.6	1.6	2.3	3.9	
$\overline{X}$		0.0	1.3	1.5	1.7	2.1	3.1	
Type 304 SS	Sensitized							
S-93-A		--	--	5.4	7.8	13.2	16.3	
S-93-B		5.0	7.8	7.8	13.6	15.5	17.8	.008
S-94-A		5.0	7.8	7.8	10.5	12.4	16.3	
S-94-B		5.8	7.0	8.5	10.0	12.4	16.3	
$\overline{X}$		5.3	7.5	7.4	10.5	13.4	16.7	
Carbon Steel AISI - C1010	Hot Rolled							
I-61-A		695	1049	1778	3145	6186*		2.97**
I-61-B		685	1096	1617	2982	5736*		
$\overline{X}$		690	1072	1697	3063	5961		

* Specimen removed after 8 hours
** For 8 hour exposure
Area of Sample = 0.129 dm^2

APPENDIX TABLE C-4

Weight Loss Results on Metal Coupons (1-3/4 x 1/2 x 1/16 - inch) in Dynamic Autoclave (1 gpm-.025 fps)
5% Ammonium Citrate, 2% Citric Acid, 1/2% Versene at 175°F

Material Sample No.	Heat Treatment Conditions	Total Weight Loss - Mgs/dm² at Time Indicated (Hours) 1/2	1	2	4	8	16	Total Average Penetration (Mils)
Type 304 SS	Annealed							
C-155-A		0.0	0.0	0.0	0.0	1.2	1.6	
C-155-B		0.4	0.4	0.4	0.4	0.4	0.8	.001
C-156-A		4.3	4.3	4.3	4.3	4.7	5.4	
C-156-B		1.6	1.6	2.3	2.3	4.3	4.2	
$\bar{X}$		1.6	1.6	1.8	1.8	2.7	3.0	
Type 304 SS	Sensitized							
S-95-A		5.8	6.6	10.1	13.2	15.5	16.3	
S-95-B		6.9	10.5	10.5	13.9	16.3	17.1	.009
S-96-A		9.7	11.2	12.0	15.9	17.1	18.6	
S-96-B		6.9	8.9	8.9	13.2	16.3	17.1	
$\bar{X}$		7.3	9.3	10.4	14.1	16.3	17.3	
Carbon Steel AISI - C1010	Hot Rolled							
I-62-A		782.6	1226.7	2091.5	3819.4	8570*		4.27**
I-62-B		720.9	1062.8	1805.4	3865.3	8565*		
$\bar{X}$		751.8	1144.8	1948.5	3842.4	8568		

* Specimen removed after 8 hours
** For 8 hours exposure
Area of Sample = 0.129 dm^2

APPENDIX D

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APPENDIX TABLE D-1

Weight Loss Results Obtained on Type 304 Stainless Steel (1-3/4 x 1/2 x 1/16 - Inch Coupons) Exposed in Caustic Permanganate at 77°F (25°C)

Material Sample No.	Heat Treatment	Total Weight Loss - Mgs/dm^2 at Time Indicated (Days)							
		7	14	21	28	35	42	49	56
Type 304 SS	Annealed								
C-27		2.3	4.6	6.2	7.8	-	-	-	-
C-28		4.3	4.3	5.8	6.6	6.6	8.1	7.8	9.7
C-29		1.9	3.5	5.8	7.8	7.8	9.7	10.5	10.8
$\bar{X}$		2.8	4.1	5.9	7.4	7.2	8.9	9.1	10.3
Type 304 SS	Sensitized								
S-41		3.9	5.0	8.5	14.0	-	-	-	-
S-42		6.2	8.5	11.6	15.1	17.	20.2	21.7	22.5
S-43		3.5	5.8	9.7	14.3	16.7	19.	20.2	20.6
$\bar{X}$		4.5	6.4	9.9	14.5	16.9	19.6	20.9	21.5

Area of Sample = 0.129 dm^2

APPENDIX TABLE D-2

Weight Loss Results Obtained on Type 304 Stainless Steel (1-3/4 x 1/2 x 1/16 - Inch Coupons) Exposed in Caustic Permanganate at 122°F (50°C)

Material Sample No.	Heat Treatment	Total Weight Loss - Mgs/dm^2 at Time Indicated (Days)							
		7	14	21	28	35	42	49	56
Type 304 SS	Annealed								
C-24		3.9	7.8	6.2	10.1	11.6	13.2	13.2	16.3
C-25		3.5	6.6	9.3	10.1	10.8	12.0	13.2	14.0
C-26		3.1	6.2	8.5	8.9	-	-	-	-
$\bar{X}$		3.5	6.9	8.0	9.7	11.2	12.6	13.2	15.2
Type 304 SS	Sensitized								
S-22		-	13.2	16.7	19.0	25.2	26.4	29.8	31.4
S-24		-	12.8	15.9	-	-	-	-	-
S-25		-	14.7	18.6	20.2	25.6	27.1	29.4	31.0
$\bar{X}$		-	13.6	17.1	19.6	25.4	26.8	29.6	31.2

Area of Sample = 0.129 dm^2

APPENDIX TABLE D-3

Weight Loss Results Obtained on Type 304 Stainless Steel and AISI C1010 Carbon Steel (1-3/4 x 1/2 x 1/16 - Inch Coupons) Exposed in Caustic Permanganate at 167°F (75°C)

Material Sample No.	Heat Treatment	Total Weight Loss - Mgs/dm^2 at Time Indicated (Days)					
		4	9	11	16	22	27
Type 304 SS	Annealed						
110-A		3.4	5.4	5.4	7.0	7.0	9.3
110-B		1.9	4.7	6.2	6.6	8.1	9.3
111-A		2.3	4.6	5.0	7.8	8.5	9.6
111-B		3.1	5.1	4.7	6.6	9.4	10.2
$\overline{X}$		2.7	4.9	5.3	7.0	8.3	9.6
Type 304 SS	Sensitized						
S-56-A		6.2	10.1	12.4	15.1	17.1	18.6
S-56-B		6.2	9.4	11.3	14.8	16.0	18.0
S-57-A		5.9	10.5	12.9	15.1	16.8	18.4
S-57-B		4.9	8.8	13.7	17.2	17.6	19.1
$\overline{X}$		5.8	9.7	12.6	15.6	16.9	18.5
Carbon Steel	Hot Rolled						
I-38-A		3.5	—	33.7	62.8	—	—
I-38-B		-	—	33.1	80.9	125	169
I-39-A		-	—	30.6	63.9	115	148
I-39-B		-	—	34.6	76.5	131	164
$\overline{X}$		3.5	—	33.0	71.0	124	160

Area of Sample = 0.129 dm^2

APPENDIX TABLE D-4

Weight Loss Results Obtained on Type 304 Stainless Steel and AISI C1010 Carbon Steel (1-3/4 x 1/2 x 1/16 - Inch Coupons) Exposed in Caustic Permanganate at 203°F (95°C)

Material Sample No.	Heat Treatment	Total Weight Loss - Mgs/dm^2 at Time Indicated (Days) 2	4	9	14	18	22	28
Type 304 SS	Annealed							
C-126-A		4.7	7.8	9.0	12.9	13.3	18.4	22.3
C-126-B		—	7.5	9.0	11.7	14.3	18.1	21.4
C-127-A		2.3	7.1	8.7	12.8	14.3	18.4	21.4
C-127-B		2.7	7.8	9.4	12.5	14.1	18.4	22.7
$\overline{X}$		3.2	7.6	9.0	12.5	14.0	18.3	22.0
Type 304 SS	Sensitized							
S-70-A		7.8	14.1	19.1	25.8	29.7	36.7	41.4
S-70-B		8.3	13.6	18.2	25.0	28.8	36.7	40.5
S-71-A		6.4	12.4	16.5	22.9	27.8	33.8	39.1
S-71-B		5.5	14.8	18.4	24.2	29.3	35.2	42.2
$\overline{X}$		7.0	13.7	18.6	24.5	28.9	35.6	40.8
Carbon Steel	Hot Rolled							
I-52-A		7.8	43.8	63.7	75.8	—	129	211
I-52-B		6.3	51.9	78.0	88.1	139	—	—
I-53-A		—	45.3	69.9	83.6	115	143	222
I-53-B		—	59.4	91.7	—	127	149	238
$\overline{X}$		7.1	50.1	75.8	82.5	127	140	224

Area of Sample = 0.129 dm^2

APPENDIX TABLE D-5

Weight Loss Results Obtained on Type 304 Stainless Steel and AISI C1010 Carbon Steel (1-3/4 x 1/2 x 1/16-Inch Coupons) Exposed in 5% Ammonium Citrate, 2% Citric Acid, 1/2% Versene at 77°F (25°C)

Material Sample No.	Heat Treatment	Total Weight Loss - Mgs/dm^2 at Time Indicated (Days)				
		5	8	13	20	28
Type 304 SS	Annealed					
C-149-B		-	-	-	-	1.6
C-150-A		1.2	1.2	1.2	2.7	3.1
C-150-B		0.8	1.6	1.6	2.7	3.9
$\bar{X}$		1.0	1.4	1.4	2.7	3.5
Type 304 SS	Sensitized					
S-89-A		6.2	7.8	8.1	12.8	17.1
S-89-B		7.0	7.0	8.1	12.0	15.5
S-90-A		5.4	6.2	7.0	12.0	15.9
S-90-B		5.0	7.4	8.1	12.8	15.5
$\bar{X}$		5.9	7.1	7.8	12.4	16.0
Carbon Steel	Hot Rolled					
I-28		3048	4735	7068	10,567	14,042
I-31		3360	4567	6687	10,032	13,402
$\bar{X}$		3204	4651	6877	10,300	13,722

Area of Sample = 0.129 dm^2

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ACKNOWLEDGEMENT

The authors wish to acknowledge the valuable assistance of Miss Jean M. Krause who performed most of the corrosion tests and who assisted in the final tabulation of the data; Mr. C. Richard Bergen in interpreting certain aspects of the data and assisting in the operation of the loop; Mr. David Reali for his assistance in interpreting the metallurgical and corrosion results.