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CORROSION STUDIES FOR THE HRT CHEMICAL PROCESSING PLANT

J. L. English
J. C. Griess
D. J. Krause

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REACTOR EXPERIMENTAL ENGINEERING DIVISION

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J. L. English, J. C. Griess, and D. J. Krause

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ABSTRACT

The corrosion resistance of a number of materials considered for use in the HRT Chemical Processing Plant was determined in sulfuric acid solutions. Tantalum was found to be fully resistant to boiling 4 *M* and 10.8 *M* H_2SO_4 solutions used for the dissolution of corrosion and fission products removed from the homogeneous-reactor fuel solution. Tantalum was immune to hydrogen embrittlement in these solutions. Crystal-bar zirconium and Zircaloy-2 were fully resistant to attack by boiling 4 *M* H_2SO_4 solution but were attacked at rates between 5 and 10 mpy in boiling 10.8 *M* H_2SO_4 solution. Carpenter 20-Cb stainless steel was completely resistant to 4 *M* H_2SO_4 solutions at 38°C, the temperature in the decay storage vessels of the chemical processing plant, and generally was resistant to similar sulfuric acid solutions at atmospheric boiling temperature, ~110°C. In a few isolated cases, however, the alloy was prone to stress-corrosion cracking and to knife-line attack in several of the boiling 4 *M* H_2SO_4 environments. Corrosion rates of types 347 and 316 stainless steel in boiling 4 *M* H_2SO_4 solution were in excess of 75,000 mpy; however, in the presence of synthetic corrosion and fission products, corrosion attack was reduced to 10 mpy or less. A similar, but less drastic, reduction in the rate of attack on Carpenter 20-Cb stainless steel was experienced with additives present in the boiling 4 *M* H_2SO_4 solution. The corrosion rate of the latter alloy in boiling and helium-aerated 4 *M* H_2SO_4 solution was accelerated by ruthenium, a fission-product element.

INTRODUCTION

One of the objectives of the Homogeneous Reactor Test is to demonstrate that insoluble corrosion and fission products can be removed continuously from the circulating fuel solution of an operating reactor. Removal of these materials is of importance to homogeneous reactors from the standpoint of neutron economy and reduction of biological hazard in case of accidental discharge of some of the fuel to the atmosphere.

The removal of the undesired solids from the fuel stream at full reactor temperature is accomplished by the use of a hydraulic cyclone separator (hydroclone). The solids leaving the bottom part of the hydroclone are collected in an underflow pot. The contents in the pot (solids and fuel solution) are periodically discharged to a dissolving system in which the D_2O is removed by evaporation and a preliminary treatment is made with 10.8 *M* H_2SO_4 solution at 160°C for 4 to 6 hr. The mixed oxides (containing small quantities of fission-product and fuel sulfates) are slowly converted to sulfate salts, which are of limited solubility in the 10.8 *M* H_2SO_4 solution. The concentrated acid is diluted with water to 4 *M*, at which concentration the sulfate salts are soluble. After refluxing for 4 to 6 hr, the acid is reconcentrated to 10.8 *M* by evaporation and the cycle is repeated. Solution samples are taken at various intervals and the dissolving cycle is repeated until dissolution is complete. The solution is then transferred to decay storage vessels for recovery

of uranium by suitable solvent extraction methods. The decay storage vessels are equipped with water-cooled coils to maintain a maximum solution temperature of 38°C. Details of the processing development work with homogeneous reactor fuel solution and the operation of the HRT Chemical Processing Plant have been reported.[1,2]

The use of sulfuric acid solutions for dissolving the corrosion and fission products required corrosion studies to determine suitable materials for the processing plant under the projected conditions of operation. In particular, it was desired to obtain general corrosion information and the effect of the type of atmosphere on the behavior of the test materials. The immediate objectives of the program were to determine a satisfactory material for: (1) the dissolver tank using 4 and 10.8 *M* H_2SO_4 solutions at a maximum temperature of 160°C; (2) the decay storage vessels containing 4 *M* H_2SO_4 solution at 38°C maximum; and (3) accessory equipment such as piping, valve bodies, pumps, etc., which would be contacted some of the time by 4 *M* H_2SO_4 solution containing corrosion and fission products at around 38°C. In addition, several nonmetals were tested for possible service as pump bearings.

The corrosion program was conducted by the Materials Research Section of the Reactor Experimental Engineering Division at the request of the Chemical Technology Division.[3,4]

TEST MATERIALS AND METHODS

Based upon the results of a literature survey, 15 metals and nonmetals with varying degrees of resistivity to attack by sulfuric acid solutions were selected for corrosion testing. The materials were used in a number of fabricated forms, including sheet, plate, bar, pipe, and other assorted shapes. The nominal chemical compositions of the test materials are listed in Table 1. When geometry permitted, specimens were abraded on 80- and 120-grit papers. All specimens were degreased in benzene vapor, dried at 100°C, and weighed to the nearest 0.1 ± 0.2 mg. Graphitar and aluminum oxide specimens were repeatedly dried and weighed until the weight was constant.

Specimens were removed from the test solutions at frequent intervals for weighing and microscopic examination. Corrosion rates were determined from as-scrubbed weight losses since generally the films on exposed specimens were negligible.

Boiling tests were run in either 3- or 5-liter, three-neck Pyrex flasks equipped with a water-cooled Graham or Allihn condenser, aeration tube, and thermometer well. The flasks were heated with 375-w infrared lamps housed in insulated containers. The tests at 38°C were run in 500-ml Erlenmeyer flasks immersed in an agitated, thermostatically controlled water bath. The flasks were equipped with inlet and outlet tubes to permit aeration of the solution with different types of atmospheres. The test solutions were not changed during the course of the corrosion tests.

Table 1. Nominal Chemical Compositions of Corrosion-Test Materials

Material	Composition (wt %)
Aluminum oxide	Sintered high-purity alumina (>98% Al_2O_3)
Carpenter 20-Cb SS	0.07 C max., 20 Cr, 29 Ni, 2 Mo min., 2 Cu min., 0.75 Mn, 1 Si, balance iron
Graphitar 14	High-purity carbon
Hastelloy B	0.12 C max., 4-7 Fe, 26-30 Mo, 0.6 Mn, 0.3 V, balance nickel
Hastelloy C	0.15 C max., 15.5-17.5 Cr, 4.5-7 Fe, 16-18 Mo, 3.75-5.25 W, balance nickel
Illium R	3 Cu, 21 Cr, 8 Fe, 5 Mo, 1 Mn, 2 W, 1 Si, balance nickel
Lead	Chemical grade (99.9% Pb min.)
Stellite 6	55 Co min., 33 Cr max., 6 W max., 7.5 Fe max.
Stellite 98M2	38 Co, 30 Cr, 18 W, 2 C, 4 Ni, 0.8 Mo max., 2.2 Fe max., others 5
Tantalum	Commercial purity
Type 309SCb SS	0.08 C max., 2 Mn max., 1 Si max., 22-24 Cr, 12-15 Ni, 10 x C Cb min., balance iron
Type 316 SS	0.10 C max., 2 Mn max., 1 Si max., 17-19 Cr, 10-14 Ni, 2-3 Mo, balance iron
Type 347 SS	0.08 C max., 2 Mn max., 1 Si max., 17-19 Cr, 9-12 Ni, (10 x C) Cb min., balance iron
Zircaloy-2	1.5 Sn, 0.1 Fe, 0.1 Ti, 0.05 Ni, balance zirconium
Zirconium, crystal bar	0.1 Ti, 0.1 Fe, balance zirconium

Two sulfuric acid concentrations were examined, 4 *M* and 10.8 *M*. Tests in the 10.8 *M* solution were run at atmospheric boiling temperature (160°C); tests in the 4 *M* H_2SO_4 solution were run at 38°C and at atmospheric boiling temperature (110°C). The variables investigated included the type of atmosphere (air, oxygen, and helium) and the presence of synthetic corrosion and fission products.

TESTS IN 10.8 *M* H_2SO_4 SOLUTION

The preliminary tests evaluated the corrosion resistance of seven metals and alloys in the 10.8 *M* H_2SO_4 solution. The materials included Carpenter 20-Cb stainless steel, Hastelloy B, Illium R, lead, tantalum, Zircaloy-2, and crystal-bar zirconium. Tests were conducted at boiling temperature (~160°C) with (1) no aeration, (2) oxygen aeration, and (3) oxygen aeration with synthetic corrosion and fission products present.

Effect of Atmosphere

Corrosion rates of the materials in boiling 10.8 *M* H_2SO_4 solution, both without and with oxygen aeration, are shown in Tables 2 and 3, respectively. The reported values are average rates for duplicate specimens. In none of the tests was the deviation from the average value greater than 11%.

Tantalum was virtually unaffected in each of the environments, as indicated by corrosion rates of 0.2 mpy or less. Both crystal-bar zirconium and Zircaloy-2 exhibited moderately good corrosion resistance to the two environments; corrosion rates were between 6 and 11 mpy. Since under certain conditions, both tantalum and zirconium and its alloys are subject to hydrogen adsorption and subsequent embrittlement, a specimen of the former and one of the Zircaloy-2 that had been exposed in the oxygen-aerated solution were analyzed for hydrogen content by a vacuum fusion technique. In neither case had a significant increase in hydrogen occurred.

All the other materials showed excessive corrosion rates, although the presence of oxygen (even though its solubility must be very low) affected beneficially the corrosion resistance of several of the alloys. For example, the resistance of Carpenter 20-Cb stainless steel was increased by a factor of 2, Illium R by a factor of 8, and Hastelloy B by a factor of 2 when oxygen was present. Hastelloy B experienced localized attack in both environments. Oxygen had an opposite effect on the corrosion of lead; its corrosion rate was threefold greater with oxygen than it was in its absence.

Effect of Additives

The same alloys were tested in a boiling 10.8 *M* H_2SO_4 solution to which had been added simulated corrosion and fission products as sulfate salts. The salt concentrations are included in Table 4. Also shown in Table 4 are

Table 2. Corrosion of Various Materials By Boiling, Nonaerated 10.8 *M* H_2SO_4 Solution at 160°C

Material	Total Time (hr)	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Carpenter 20-Cb SS	5	39,000	Uniform	Heavy, black film
Hastelloy B	465	43	Localized	Thin, tan film
Illium R	65	10,000	Uniform	Heavy, black film
Lead	440	34	Uniform	Mottled, gray-white film
Tantalum	465	<0.1	Uniform	Metallic luster
Zircaloy-2	465	11	Uniform	Dull, gray-white film
Zirconium, crystal bar	465	6	Uniform	Dull, gray-white film

Table 3. Corrosion of Various Materials by Boiling, Oxygen-Aerated 10.8 *M* H_2SO_4 Solution at 160°C

Material	Total Time (hr)	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Carpenter 20-Cb SS	25	22,000	Uniform	Light-gray film
Hastelloy B	255	24	Localized	Metallic film
Illium R	25	1,200	Uniform	Dull, gray film
Lead	255	105	Uniform	Mottled, gray film
Tantalum	255	0.2	Uniform	Metallic luster
Zircaloy-2	255	6	Uniform	Gray-black film
Zirconium, crystal bar	255	8	Uniform	Gray-black film

the salt concentrations when the acid was diluted to 4 *M* H_2SO_4 in which tests to be discussed later were run. The concentrations in the two solutions are typical of those that might be expected after dissolution and dilution of the solids from the hydroclone underflow pot.[5]

Table 4. Concentration of Synthetic Corrosion and Fission Products in 10.8 *M* and 4 *M* H_2SO_4 Solutions

Additive	Concentration (*M*)	
	10.8 *M* H_2SO_4	4 *M* H_2SO_4
$Cr_2(SO_4)_3$	0.166	0.062
$CuSO_4$*	0.025	0.009
$Fe_2(SO_4)_3$	0.520	0.193
$Ru(SO_4)_2$	0.004	0.001
UO_2SO_4*	0.137	0.051
$Zr(SO_4)_2$	0.537	0.199

* Constituents in homogeneous-reactor fuel solution.

The average corrosion rates for duplicate specimens in boiling, oxygen-aerated 10.8 *M* H_2SO_4 solution containing the simulated corrosion and fission products are shown in Table 5. The agreement in rates for duplicate specimens was very good; the maximum deviation from the average value for a particular material was 15%. In all instances, uniform metal removal was produced by the corrosion attack.

Although all the materials except tantalum corroded at high rates, several interesting changes in corrosion behavior were observed. For example, the corrosion rate for Carpenter 20-Cb stainless steel was 267 mpy; without the additives, the rate was 22,000 mpy. The presence of cupric and ferric salts among the additives was possibly responsible for the improved corrosion resistance, since both salts have been used successfully to reduce attack on austenitic stainless steels by sulfuric acid solutions.[6]

Table 5. Corrosion of Various Materials at 160°C by Boiling, Oxygen-Aerated 10.8 *M* H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products

Material	Total Time (hr)	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Carpenter 20-Cb SS	25	267	Uniform	Dull, light-gray film
Hastelloy B	100	320	Uniform	Dull, black film
Lead	510	31	Uniform	Mottled, gray-white film
Tantalum	520	0.4	Uniform	Metallic luster
Zircaloy-2	100	202	Uniform	Lustrous, black film
Zirconium, crystal bar	100	683	Uniform	Mottled, gray-white film

Contrary behavior was exhibited by Hastelloy B, crystal-bar zirconium, and Zircaloy-2. These materials underwent an acceleration in the rate of attack in the additives-plus-oxygen environment; the observed rates were 320, 683, and 202 mpy, respectively. In the absence of additives with or without oxygen aeration, the corrosion rates were 45 mpy or less (Tables 2 and 3). The corrosion resistance of lead in the additives-plus-oxygen environment was the same as in the additives-and-oxygen-free environment; the rate in both cases was approximately 32 mpy. Because of the relatively poor resistance exhibited by Hastelloy B, crystal-bar zirconium, Zircaloy-2, and lead, these materials were excluded from consideration as a dissolver-vessel material.

TESTS IN 4 *M* H_2SO_4 SOLUTION

Corrosion tests were run in 4 *M* H_2SO_4 solution with and without simulated corrosion and fission products present at 38°C and at the atmospheric boiling temperature (~110°C). The effect of atmosphere on corrosion behavior was also examined.

Tests at 38°C

Effect of Helium Atmosphere and Synthetic Corrosion and Fission Products.-- The first series of tests at 38°C (100°F) was made to determine the effect of oxygen exclusion on the corrosion resistance of a number of the test materials.

Helium gas was bubbled into 4 *M* H_2SO_4 solution to remove oxygen. The average corrosion rates are shown in Table 6. With the exception of Stellite 6, deviation between rates for duplicate specimens was not greater than 0.1 mpy. The duplicate Stellite 6 specimens corroded at rates of 7 and 16 mpy. The materials underwent uniform attack with the exception of Stellite 6.

Table 6. Corrosion of Various Materials by Helium-Aerated 4 *M* H_2SO_4 Solution at 38°C

Material	Total Time (hr)	Corrosion Rate (mpy)	Specimen Appearance
Aluminum oxide	415	Gain	Pale yellow color
Carpenter 20-Cb SS	440	0.4	Original metallic luster
Hastelloy B	440	0.2	Original metallic luster
Illium R	440	0.2	Golden-tan thin film
Lead	440	0.1	Dull, gray-white film
Stellite 6	435	12	Mottled gray; pitting attack
Tantalum	440	<0.1	Original metallic luster
Type 316 SS	440	8	Dull, silver-gray film
Zircaloy-2	440	<0.1	Original metallic luster
Zirconium, crystal bar	440	<0.1	Original metallic luster

Type 316 stainless steel and Stellite 6 were the only materials attacked at rates exceeding 0.4 mpy. Type 316 stainless steel was attacked uniformly at a rate of 8 mpy, and, as shown in Fig. 1, the greater portion of the attack occurred during the first 250 hr of a 440-hr test. Stellite 6 experienced localized corrosion, which was responsible for the poor agreement between corrosion rates for duplicate specimens. Tantalum, crystal-bar zirconium, and Zircaloy-2 underwent near-negligible attack during 440-hr tests.

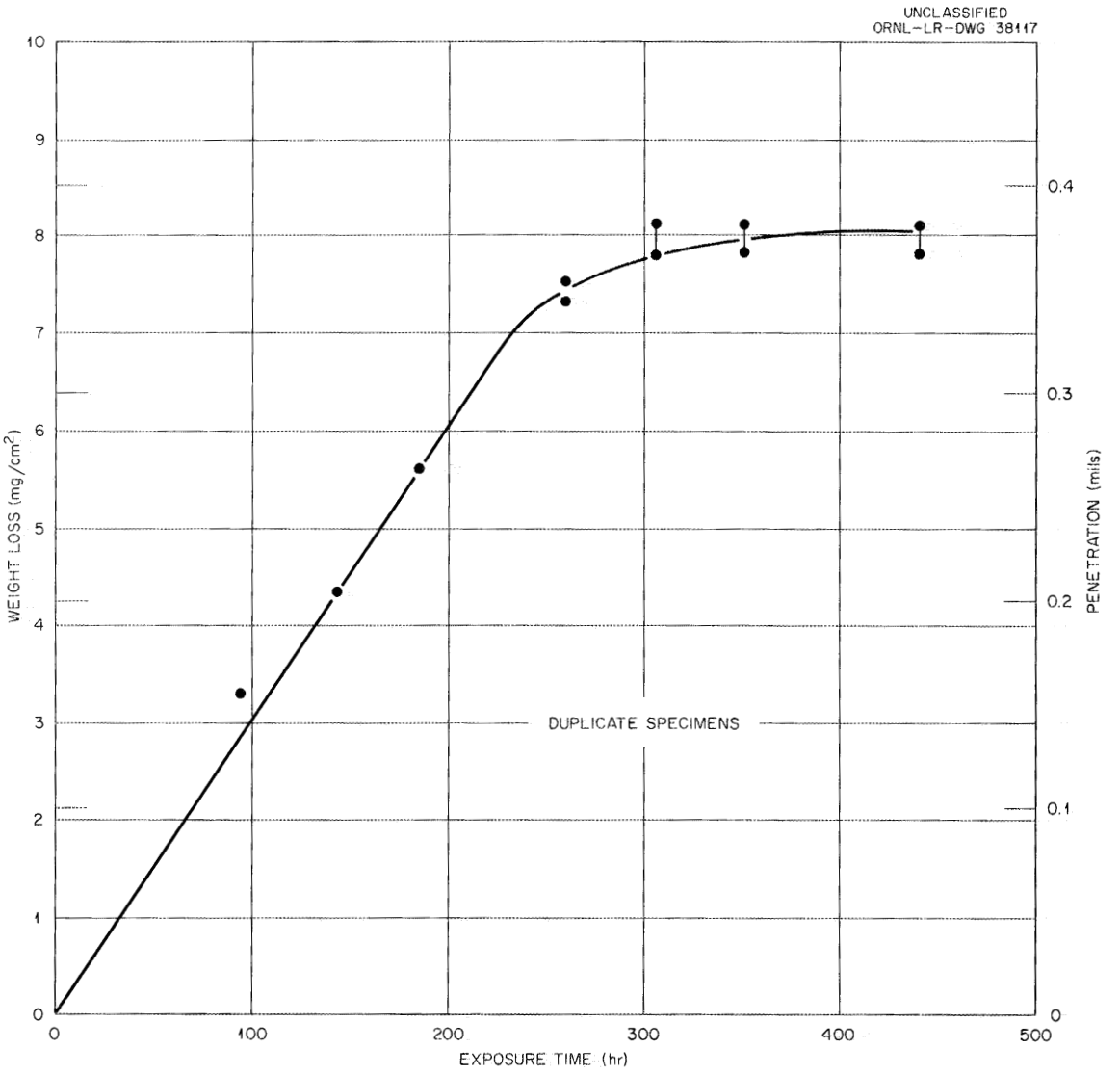

Fig. 1. Corrosion of Type 316 Stainless Steel by Helium-Aerated 4*M* H_2SO_4 Solution at 38°C.

In a second series of tests at 38°C with the same materials listed in Table 6, synthetic corrosion and fission products were present in the 4 *M* H_2SO_4 solution in the concentrations listed in Table 4. The test solutions were oxygen-aerated. The observed corrosion rates for all test materials were 0.2 mpy or less during 1000- and 1500-hr tests.

Tests with Carpenter 20-Cb Stainless Steel.--Tests to be described later indicated that Carpenter 20-Cb had sufficient corrosion resistance in 4 *M* H_2SO_4 solutions to be useful in the chemical processing plant. For that reason, additional tests were run with four different heats of the alloy in 4 *M* H_2SO_4 solution containing synthetic corrosion and fission products at 38°C. The four heats included 1/16-in.-thick sheet, 2 1/4-in.-dia. bar, 3 1/4-in.-square bar, and 3/4-in. sched-40 pipe. The specimens were exposed for periods of 1000 and 1500 hr. Oxygen aeration of the solutions was employed. The concentrations of corrosion and fission products were the same as shown in Table 4.

The corrosion resistance of all specimens was excellent; no rate in excess of 0.2 mpy was observed. Attack was uniform and resulted in little change in appearance from the original condition of the specimens.

Tests at Boiling Temperature (~110°C)

Effect of Helium Atmosphere.--Although boiling 4 *M* H_2SO_4 solution with corrosion and fission products absent would presumably not be encountered during operation of the chemical processing plant, it was of interest to determine the corrosion behavior of a number of materials in the additive-free environment. Thirteen materials were tested in the boiling, helium-aerated 4 *M* H_2SO_4 solution. The exposure time was determined by the behavior of a particular material. When the attack was severe, exposure times were limited to 40 hr or less. In a few cases, tests were continued for 545 hr. The average corrosion rates for duplicate specimens are included in Table 7. In every case except that of lead, the maximum deviation from the average value was 5%. The duplicate lead specimens corroded at rates of 0.1 and 1.0 mpy.

Observed corrosion rates for tantalum, Zircaloy-2, and crystal-bar zirconium were less than 0.1 mpy; attack was uniform. Hastelloy B also corroded uniformly, at a rate of 3 mpy. The remaining nine materials corroded at rates ranging from 10 mpy for aluminum oxide (considered as a pump bearing material) to nearly 100,000 mpy for type 347 stainless steel.

Graphitar 14, also considered for a pump bearing material, was relatively inert in the boiling, helium-aerated 4 *M* H_2SO_4 environment. Both specimens exhibited slight weight gains. Dimensional measurements made before and after the test showed an increase of 0.001 in. in approximately 1 in. of length.

Table 7. Corrosion of Various Materials by Boiling, Helium-Aerated 4 *M* H_2SO_4 Solution at 110°C

Material	Total Time (hr)	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Aluminum oxide	545	10	Uniform	Pale yellow color
Carpenter 20-Cb SS	525	32	Cracking	Dull, gray film
Graphitar 14	530	Gain	Uniform	Original condition
Hastelloy B	435	3	Uniform	Thin, tan film
Illium R	435	15	Preferential grain	Varicolored, thin film
Lead	435	0.6	Uniform	Mottled, gray-white film
Stellite 6	2	42,800	Uniform	Dull, gray-black film
Stellite 98M2	40	5,900	Uniform	Dull, gray-black film
Tantalum	440	<0.1	Uniform	Metallic luster
Type 316 SS	4	76,300	End-grain	Dark brown film
Type 347 SS	4	99,500	End-grain	Dark brown film
Zircaloy-2	435	<0.1	Uniform	Silver-gray film
Zirconium, crystal bar	435	<0.1	Uniform	Silver-gray film

Illium R, which corroded at a rate of 15 mpy, underwent selective grain attack, as shown in Fig. 2. Several of the large grains also contained pits.

An unexpected type of attack occurred on the duplicate Carpenter 20-Cb stainless steel specimens, which corroded at an average rate of 32 mpy. For the most part, the attack produced uniform metal removal; however, near the edges of the specimens in the test solution, an intense localized cracking type of attack occurred, as shown in Fig. 3. The cracks on the lower portion of the specimen are near a sheared edge surface, whereas the other edges had

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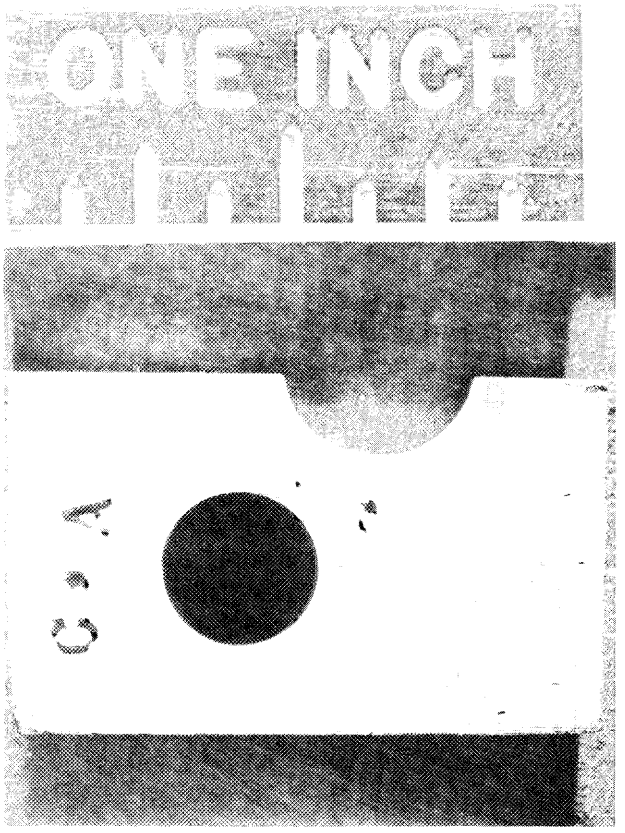

Fig. 2. Appearance of Illium R Specimen After 435 hr in Boiling, Helium-Aerated 4 M H_2SO_4 Solution. Test C-A.

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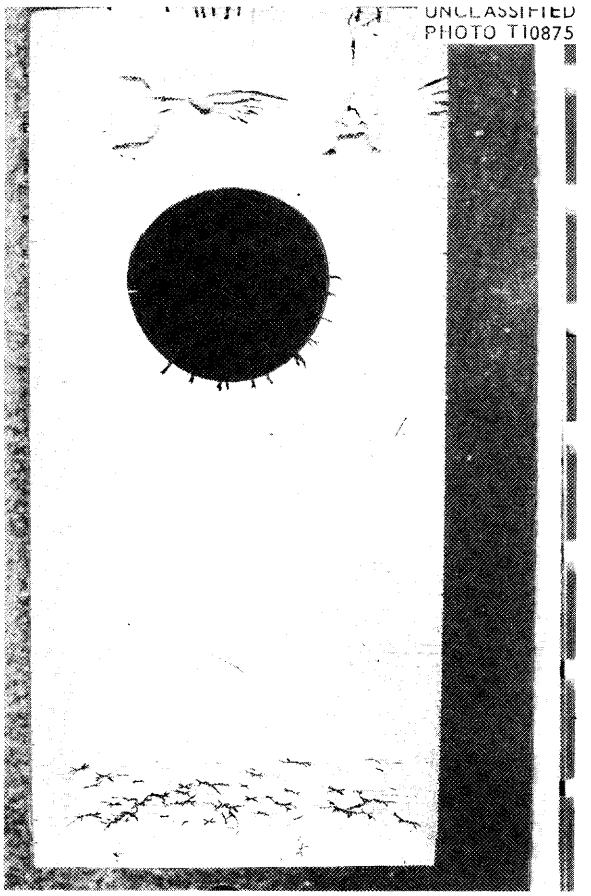


Fig. 3. Cracks in Carpenter 20-Cb Stainless Steel Exposed for 525 hr in Boiling, Helium-Aerated 4 M H_2SO_4 Solution. Test D-A. 5X.

been sawed from a large plate. Figure 4 shows an enlarged view of the cracks in this area. Cracking also occurred along machined edges as shown in Fig. 3. A typical cross-sectional view of several of the cracks located near the sheared edge surface appears in Fig. 5. Although not readily apparent in the photomicrograph, the cracks were of a transcrystalline type. The location of the cracks strongly suggested that residual stresses in the affected areas were responsible for crack initiation and propagation. Other investigators have reported a similar cracking sensitivity of Carpenter 20-Cb stainless steel in sulfuric acid solutions.[7]

Stress-Corrosion Cracking Test with Carpenter 20-Cb Stainless Steel.--The observed susceptibility of residually stressed areas in Carpenter 20-Cb stainless steel to cracking in boiling, helium-aerated 4 *M* H_2SO_4 solution prompted additional testing. A U-bend stress specimen was prepared from the same 1/4-in.-thick annealed plate that had been used for the original specimens (Table 7). In cold forming, the bending was accidentally carried too far so that the two ends of the U touched one another. To introduce elastic stresses, a 1/4-in.-thick insert was placed between the ends to spring them apart. Tensile stresses were thus exerted on the inner surface of the U-bend rather than on the outer surfaces as is the case in conventional, elastically stressed U-bend specimens.

The stressed specimen was exposed for 317 hr in boiling 4 *M* H_2SO_4 solution. During the first 255 hr the solution was aerated with helium; for the final 62 hr oxygen aeration was used instead of the helium. At the end of the first 64 hr with helium aeration, cracks were observed on areas under tensile stress. The intensity and frequency of the cracks increased with increased exposure time. Two low-magnification views of the cracks at the end of the test are shown in Fig. 6. The corrosion rate for the specimen was approximately 40 mpy, indicating no significant stress-induced acceleration in the over-all rate of attack.

Effect of Oxygen Atmosphere.--The same 13 materials that were exposed to boiling, helium-aerated 4 *M* H_2SO_4 solution (Table 7) were exposed to a similar solution at boiling with oxygen aeration. Average corrosion rates for duplicate specimens are reported in Table 8. With the exception of lead, the deviation from average corrosion-rate values was 9% or less; the deviation for lead specimens was 19%.

Aluminum oxide, Carpenter 20-Cb stainless steel, lead, tantalum, Zircaloy-2, and crystal-bar zirconium corroded at rates of 6 mpy or less during exposure periods of 1550 to 1575 hr. The latter three materials corroded at rates less than 0.1 mpy. The attack was uniform in all cases.

The effect of oxygen aeration was quite pronounced on a number of the materials. For example, in the presence of oxygen, Carpenter 20-Cb stainless steel corroded at a rate of 3 mpy, an eleven-fold improvement over the rate obtained with helium aeration. The effect of atmosphere is shown in Fig. 7.

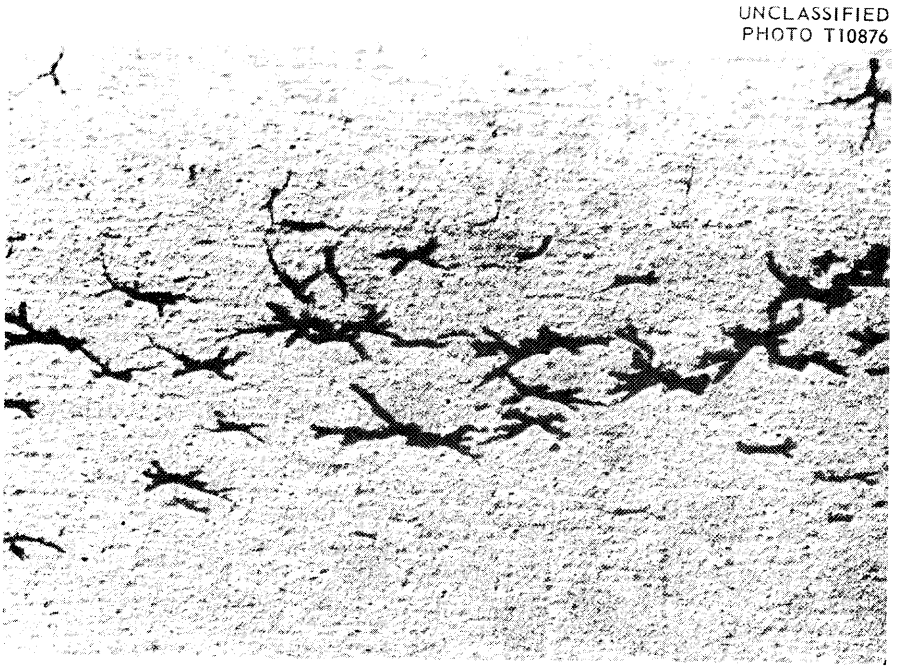
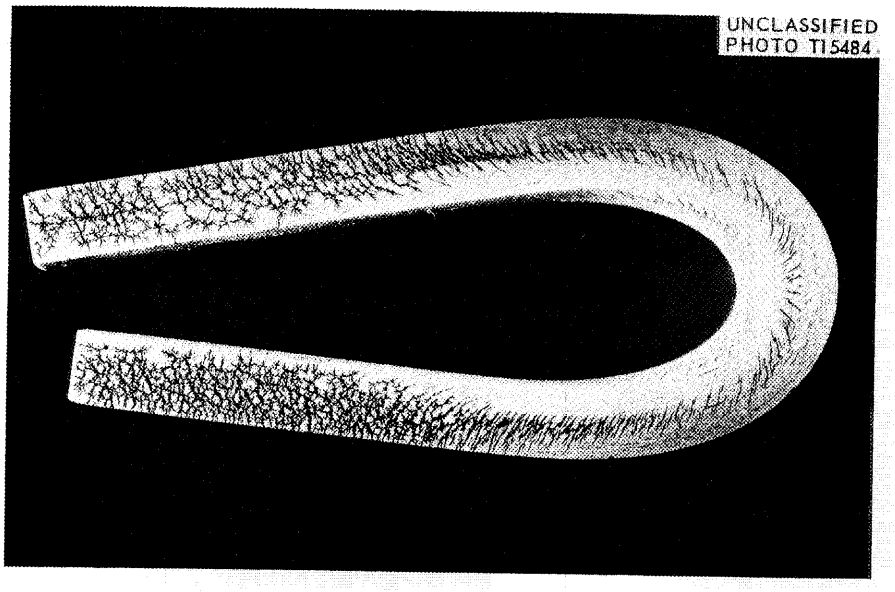
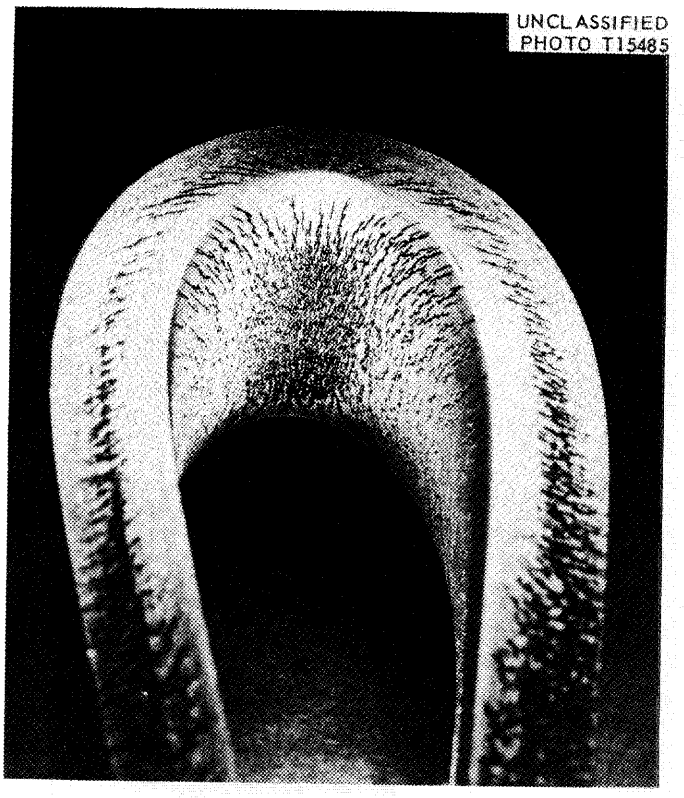


Fig. 4. Cracks Near Sheared Edge of Carpenter 20-Cb Stainless Steel Exposed in Boiling, Helium-Aerated 4 M H_2SO_4 Solution. Test D-A. 25X.

Fig. 5. Cross-Sectional View of Cracks Formed in Carpenter 20-Cb Stainless Steel Exposed for 525 hr in Boiling, Helium-Aerated 4 M H_2SO_4 Solution. Test D-A. Etched in glyceria-regia. 100X.



(a) Edge View. 2X.



(b) Inside View. $2\frac{1}{4}$X.

Fig. 6. Cracks on Carpenter 20-Cb Stainless Steel Stress. Specimen (Insert Removed) After 317 hr in Boiling 4 M H_2SO_4 Solution.

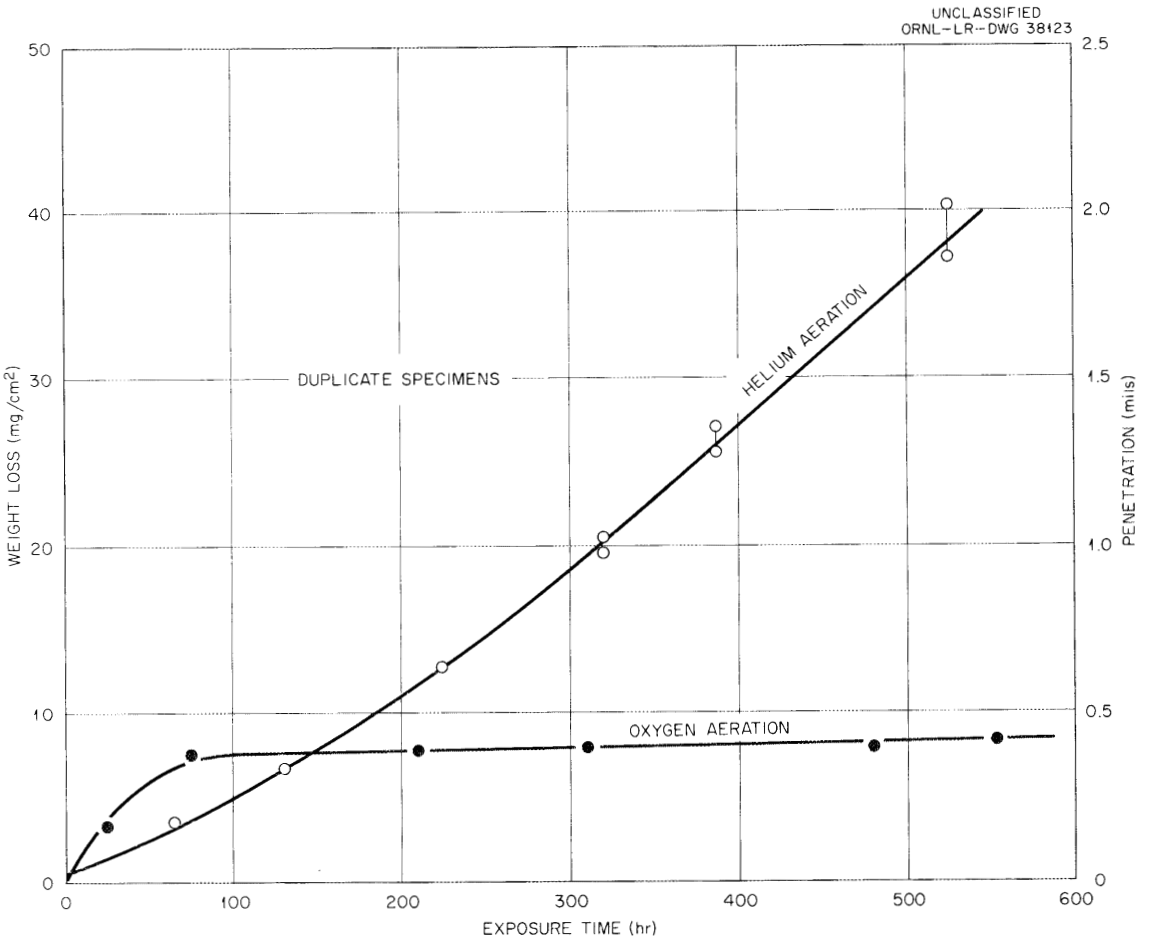


Fig. 7. Effect of Atmosphere on the Corrosion of Carpenter 20-Cb Stainless Steel by Boiling 4*M* H_2SO_4 Solution.

With helium a near-linear relation between weight loss and time was obtained during a 525-hr test; with oxygen practically no attack occurred after the first 100 hr.

Table 8. Corrosion of Various Materials by Boiling, Oxygen-Aerated 4 *M* H_2SO_4 Solution at 110°C

Material	Total Time (hr)	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Aluminum oxide	1575	6	Uniform	Pale pink color
Carpenter 20-Cb SS*	1550	3	Uniform	Silver-gray, thin film
Graphitar 14	1575	Gain	Uniform	Original condition
Hastelloy B	785	375	Selective grain	Light, gray film
Illium R	1080	78	Pitting	Light, gray film
Lead	1575	4	Uniform	Dark, gray film
Stellite 6	4	28,300	Selective grain	Dark, green-black film
Stellite 98M2	100	2,400	Selective grain	Dark, green-black film
Tantalum	1575	<0.1	Uniform	Metallic luster
Type 316 SS	4	79,000	Uniform	Dull, black film
Type 347 SS	4	113,000	Uniform	Dull, black film
Zircaloy-2	1575	<0.1	Uniform	Metallic luster
Zirconium, crystal bar	1575	<0.1	Uniform	Metallic luster

* Welded pipe specimen.

Oxygen accelerated the rate of attack on Hastelloy B and Illium R. With helium the rates were 3 and 15 mpy, respectively; with oxygen they were 375 and 78 mpy. The effect of atmosphere on weight losses as a function of exposure time for the two alloys is shown in Figs. 8 and 9.

No drastic effect resulting from the type of atmosphere employed was experienced in tests with Stellites 6 and 98M2 and types 316 and 347 stainless steel. Rates in all cases were excessive.

Graphitar 14 specimens exhibited weight gains during a 1575-hr exposure. There was no detectable change in the appearance of the specimens during the test.

Effect of Additives with Helium Atmosphere.--The effect of synthetic corrosion and fission products on the behavior of 15 materials in boiling, helium-aerated 4 *M* H_2SO_4 solution was determined. The concentrations of the additives are reported in Table 4. Average corrosion rates for duplicate specimens in 2000-hr tests are shown in Table 9. With two exceptions, Illium R and Stellite 6, the deviation from average corrosion-rate values was 5% or less. The duplicate Illium R specimens corroded at rates of 21 and 41 mpy; Stellite 6 specimens corroded at rates of 11 and 18 mpy.

Tantalum, Zircaloy-2, and crystal-bar zirconium were the most corrosion-resistant materials tested. Observed corrosion rates were 0.2 mpy or less; the attack was uniform on all three materials.

Other materials which exhibited satisfactory corrosion resistance were lead and types 309SCb, 316, 347, and Carpenter 20-Cb stainless steel, all of which corroded at rates of 4 mpy or less. The substantial improvement in corrosion resistance of these alloys, particularly of the 300-series stainless steels, was attributed to the presence of cupric and ferric ions among the additives. In the absence of the additives and with either helium or oxygen aeration, corrosion rates for the 300-series stainless steels were greater than 75,000 mpy.

The two heats of Carpenter 20-Cb stainless steel showed excellent resistance, as evidenced by rates of 1 and 2 mpy. The 3/16-in.-thick specimens were prepared from the laboratory test materials supply; the 1/16-in.-thick specimens were prepared from sheet that was used to fabricate remotely operated bellows-type valves in areas of the chemical processing plant where solution temperatures were not in excess of 38°C. All specimens underwent uniform attack. There was no evidence of susceptibility to cracking in the environment, in contrast to the behavior of the alloy in a similar environment free of synthetic corrosion and fission products.

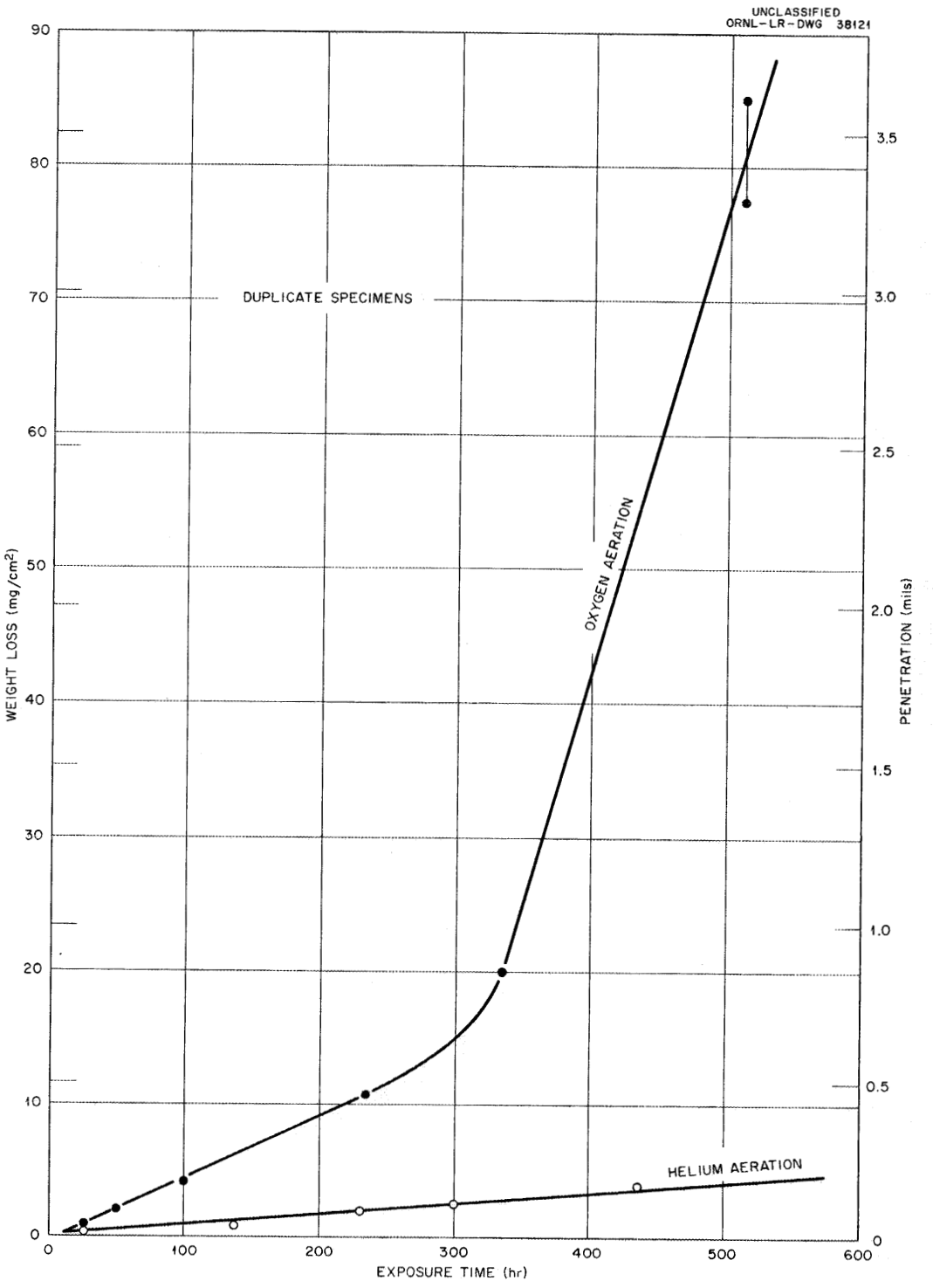


Fig. 8. Effect of Atmosphere on the Corrosion of Hastelloy B by Boiling 4 *M* H_2SO_4 Solution.

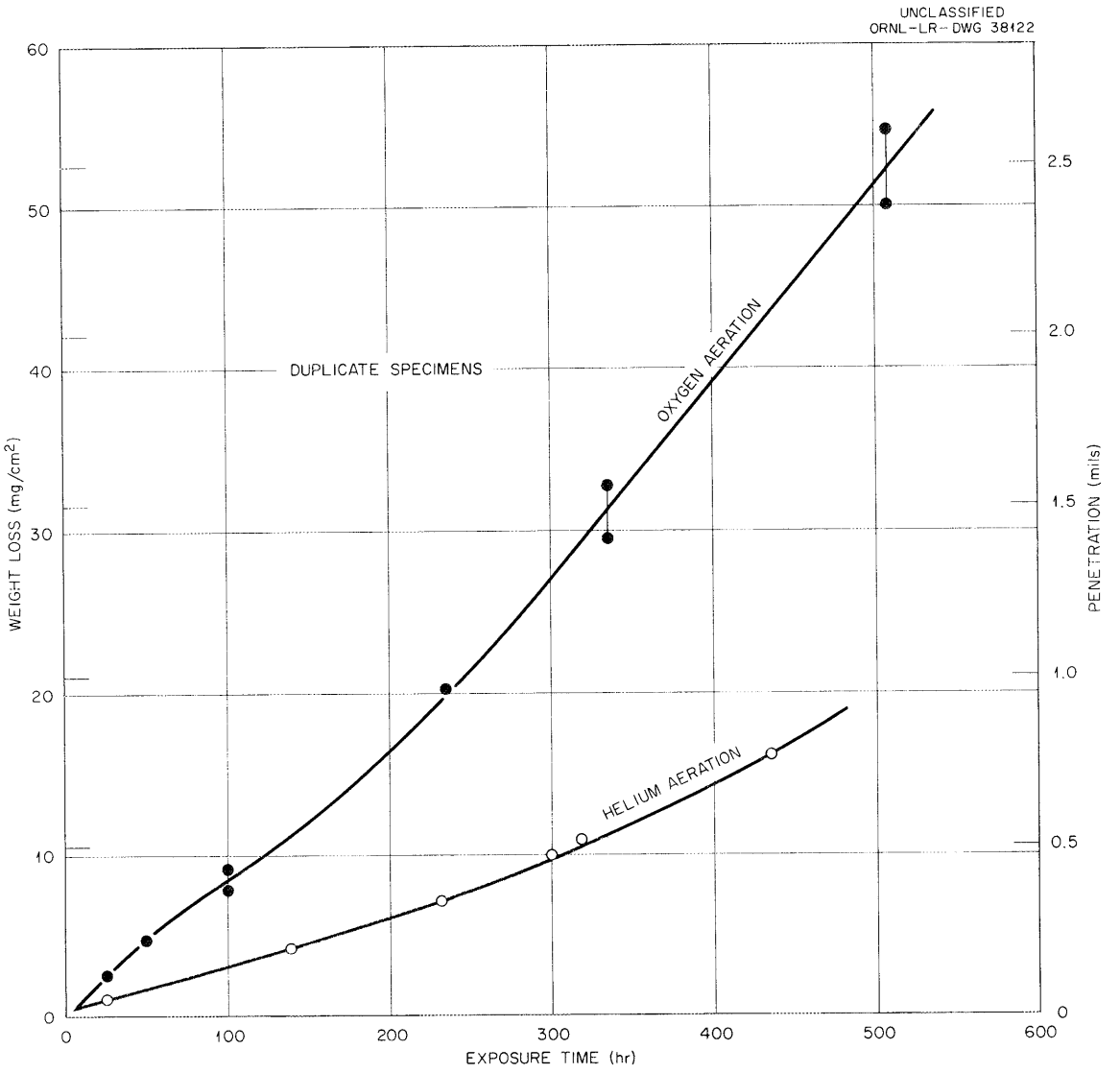


Fig. 9. Effect of Atmosphere on the Corrosion of Illium R by Boiling 4*M* H_2SO_4 Solution.

Table 9. Corrosion of Various Materials at 110°C by Boiling, Helium-Aerated 4 *M* H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products

(Test Time - 2000 hr)

Material	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Aluminum oxide	7	Uniform	Original white color
Carpenter 20-Cb SS (3/16-in.-thick plate)	1	Uniform	Lustrous silver-gray film
Carpenter 20-Cb SS (1/16-in.-thick sheet)	2	Uniform	Lustrous silver-gray film
Graphitar 14	Gain	Uniform	Original condition
Hastelloy B[a]	>15,000	-	Specimens disintegrated
Hastelloy C[b]	215	Uniform	Gray-black film
Illium R	31	Intergranular	Silver-gray film
Lead	1	Uniform	Mottled, gray-white film
Stellite 6	15	Pitting and intergranular	Gray-brown film
Stellite 98M2	135	Pitting and intergranular	Brown-green film
Tantalum	<0.1	Uniform	Metallic luster
Type 309SCb SS	2	Uniform	Silver-gray film
Type 316 SS	4	Uniform	Gray-tan film
Type 347 SS	4	Uniform	Gray-brown film
Zircaloy-2	<0.1	Uniform	Golden-tan film
Zirconium, crystal bar	0.2	Uniform	Mottled, tan film

(a) 25-hr test
(b) 50-hr test

Moderately good corrosion resistance was exhibited by aluminum oxide, with a rate of 7 mpy for a 2000-hr test. Illium R specimens corroded at an average rate of 31 mpy, and both specimens suffered pitting and intergranular attack as shown in Fig. 10. Hastelloy B specimens completely disintegrated during a 25-hr test period; the corrosion rates were in excess of 15,000 mpy. The test with Hastelloy C was stopped after 50 hr because of excessive attack amounting to an average rate of 215 mpy. The rate increased substantially with time as shown by the fact that the average corrosion rate was only 15 mpy after the first 25 hr of exposure.

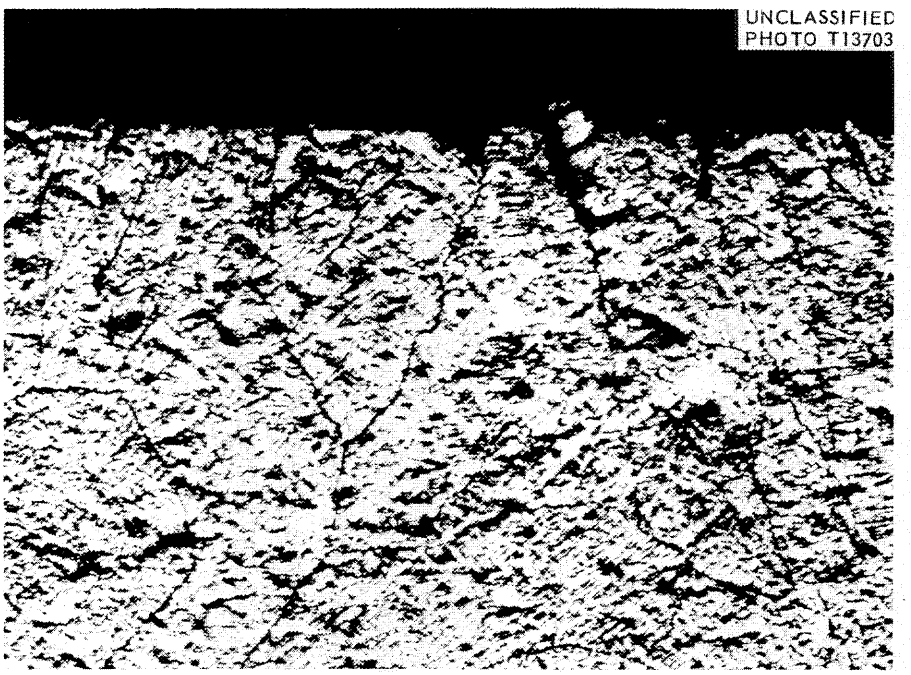
As in the case of the stainless steels, the effect of additives in improving the corrosion resistance of Stellites 6 and 98M2 was pronounced. In the absence of the additives, corrosion rates for the two alloys, respectively, in boiling, helium-aerated 4 *M* H_2SO_4 solution were 43,000 and 6,000 mpy (Table 7). With the additives present, the rates were suppressed to 15 mpy for Stellite 6 and 135 mpy for Stellite 98M2. However, both alloys underwent a random selective attack which may have been associated with an intermetallic phase.

Graphitar 14 specimens, as had been the previous experience, gained weight during a 2000-hr test. There was no physical evidence of any change in the condition of the specimens during test.

Effect of Additives with Oxygen Atmosphere.--Tests similar to the above were conducted with synthetic corrosion and fission products added to boiling 4 *M* H_2SO_4 solution but in the presence of an oxygen atmosphere. Average corrosion rates for duplicate specimens of 14 test materials are shown in Table 10. The deviation of individual rates from the average rate for any of the test materials did not exceed 15%. Since the exposure times were different for the helium-aerated tests, it was not possible to establish firm conclusions on the effect of atmosphere on corrosion behavior. However, the results generally indicated no apparent difference attributable to the gas (see Tables 9 and 10).

An extended test with type 347 stainless steel for 8000 hr in the oxygen environment disclosed that the corrosion rate of 8 mpy was relatively constant with time. However, the extended exposure time resulted in severe end-grain attack on the specimens. Stressed specimens of the same alloy (not included in Table 10) were also exposed in the boiling, oxygen-aerated 4 *M* H_2SO_4 solution containing the additives for a period of 8000 hr. No cracking was observed, and the average corrosion rate for the duplicate stress specimens was also 8 mpy.

Tests with Carpenter 20-Cb Stainless Steel.--Since the data indicated that Carpenter 20-Cb stainless steel had relatively good corrosion resistance to 4 *M* H_2SO_4 solutions, its use in a number of components in the low-temperature areas in the chemical processing plant was decided upon. As a result of this decision, a number of additional tests were carried out with specimens



Surface View

Fig. 10. Intergranular Attack on Illium R Exposed for 2000 hr in Boiling, Helium-Aerated 4 M H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products. Test C-M. 25X.

Table 10. Corrosion of Various Materials at 110°C by Boiling, Oxygen-Aerated 4 *M* H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products

Material	Total Time (hr)	Corrosion Rate (mpy)	Type of Attack	Specimen Appearance
Aluminum oxide	455	10	Uniform	Black discoloration
Carpenter 20-Cb SS	515	1	Uniform	Silver-gray film
Graphitar 14	455	Gain	Uniform	Original condition
Hastelloy B	25	>15,000	-	Specimens disintegrated
Hastelloy C	150	475	Pitting	Dark, green-black film
Illium R	515	30	Uniform	Silver-gray film
Lead	515	4	Uniform	Dark, gray film
Stellite 6	505	21	Pitting	Dark, gray film
Stellite 98M2	110	238	Uniform	Dull, black film
Tantalum	515	<0.1	Uniform	Metallic luster
Type 316 SS	510	5	Uniform	Lustrous, tan film
Type 347 SS	8000	8	End-grain	Dull, brown film
Zircaloy-2	510	0.3	Uniform	Golden-tan film
Zirconium, crystal bar	510	0.3	Uniform	Golden-tan film

representative of heats of the alloy to be used in making the components. Although it was considered unlikely that the alloy in service would be contacted by process solution above 38°C, the environment selected for the present tests was boiling, oxygen-aerated 4 *M* H_2SO_4 solution containing additions of the simulated corrosion and fission products. The concentrations of the additives are shown in Table 4. Average corrosion rates for the different heats of the alloy are included in Table 11. Excellent agreement was obtained between rates for duplicate specimens; maximum deviation from the average values was 10%.

Table 11. Corrosion of Carpenter 20-Cb Stainless Steel at 110°C by Boiling, Oxygen-Aerated 4 *M* H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products

Material Form	Identity	Total Time (hr)	Corrosion Rate (mpy)
2 1/4-in.-dia bar	B	985	27[a]
	M	1485	2
	P	1485	3
	D	1030	3
3 1/4-in. square bar	B	1485	3
	M	1030	4
Bar[b]	B59690	2500	6
	59490	2500	2
	C5954-1	2500	6
	C5993-1	2500	5
	C5952-0	2500	2

(a) Cracking observed on specimens.

(b) Material supplied by Chem-Pump Company.

With one exception, all specimens exhibited acceptable corrosion resistance; corrosion rates were 6 mpy or less after exposure periods up to 2500 hr. In all cases except one, the attack was uniform.

The exception was the specimens identified as "B" in Table 11 which were prepared from 2 1/4-in.-dia bar. The average corrosion rate after 985 hr was 27 mpy; the rate increased substantially with increased exposure time. Not only was the corrosion rate appreciably higher than that for other specimens, but a more disturbing feature of the attack was the presence of numerous cracks. The nature of the cracks was similar to that experienced by the alloy in boiling, helium-aerated 4 *M* H_2SO_4 solution containing no synthetic corrosion and fission products (Figs. 3, 4, and 5). The cracks were apparently associated with areas of residual stress in the specimens.

In view of the one incidence of cracking, numerous other stress-corrosion cracking tests were run in boiling 4 *M* H_2SO_4 solutions containing either oxygen or oxygen plus synthetic corrosion and fission products. Elastically

stressed U-bend specimens prepared from either 1/4- or 1/16-in.-thick plate were used. Not a single case of stress-corrosion cracking was encountered during tests that lasted as long as 4500 hr.

Thus, with the one exception referred to above, no stress-corrosion cracking of Carpenter 20-Cb stainless steel was observed in boiling 4 *M* H_2SO_4 when either oxygen or oxygen and the mixture of synthetic corrosion and fission products were present. Under similar conditions in the absence of oxygen and the corrosion and fission products, stress-corrosion cracking was always observed.

Weld Tests with Carpenter 20-Cb Stainless Steel.--Since the fabrication of Carpenter 20-Cb stainless steel components for the processing plant would involve a considerable amount of welding, tests were run to determine weld-corrosion behavior of the alloy. The environment was boiling, oxygenated 4 *M* H_2SO_4 solution containing the synthetic corrosion and fission products (Table 4). Multipass Heliarc welds were made in 1/2-in.-thick plate by using Carpenter 20-Cb stainless steel filler rod. The specimens were prepared in the field and were representative of welding procedures that were actually used during fabrication of the processing plant. Unwelded specimens from the same plate were also tested for control purposes.

A graph of weight losses on both welded and unwelded specimens during a 3000-hr test period is shown in Fig. 11. The points on the curves are average values for duplicate specimens; the agreement of individual weight-loss values with the average value was within 5%. Based upon weight-loss data, the welded specimens corroded at a rate of 2.2 mpy, as compared with 1.5 mpy for the unwelded specimens. The slightly higher rate for weld specimens was attributed to several forms of preferential corrosion to be discussed later. A disturbing feature of the curves in Fig. 11 was that both types of specimens showed weight losses during the last 1000 hr of the 3000-hr tests that were about the same as for the first 2000 hr for the respective specimens.

Although the attack on the flat pickled surfaces of the specimens appeared uniform, there were definite indications of localized attack in other areas. Both welded and unwelded specimens exhibited a moderately severe stringer-type pitting attack on edge surfaces. In addition, the weld specimens showed knife-line attack, the most intense of which was found on the cross-sectional areas. These areas, in most cases, would not normally be contacted by process solution. The severity of the knife-line attack is shown in Figs. 12 and 13. The maximum depth of penetration was approximately 50 mils, and the attack was typically intergranular in the heat-affected zone adjacent to the weld metal. Knife-line attack of considerably less intensity was also found in the heat-affected zones adjacent to both face and root welds on the flat surfaces of the specimens. Figure 14 shows the attack along one of the root welds. The penetration was approximately 5 to 6 mils.

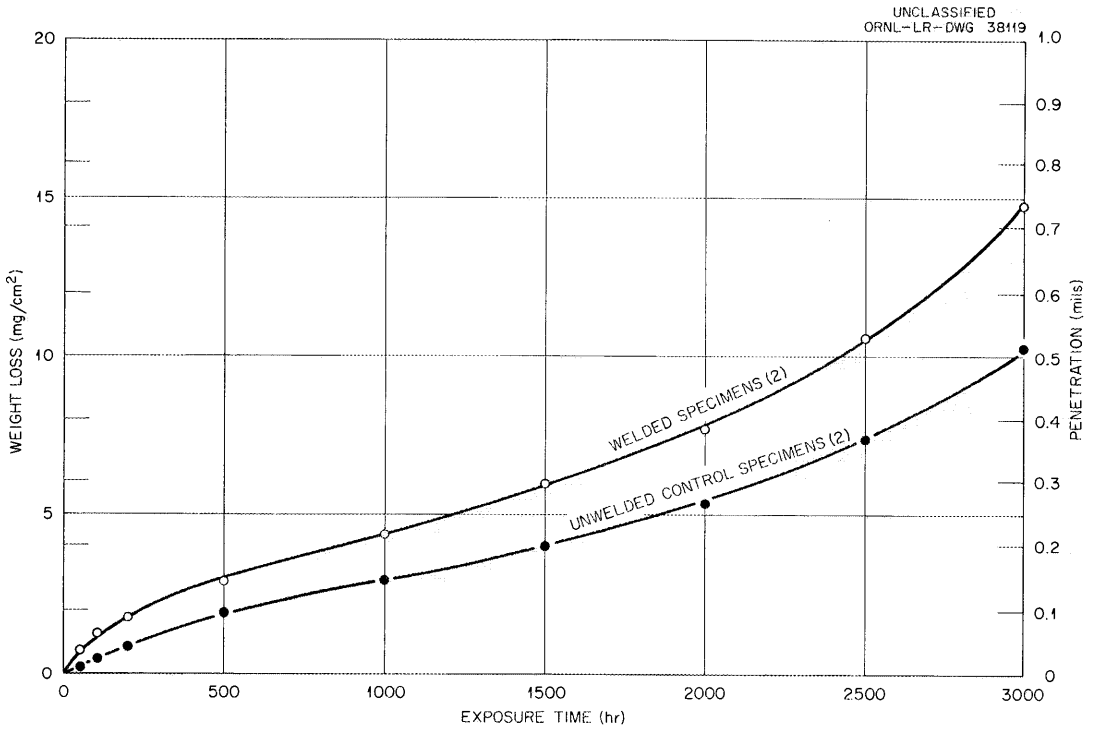


Fig. 11. Corrosion of Welded and Unwelded Carpenter 20-Cb Stainless Steel by Boiling, Oxygenated 4 *M* H_2SO_4 Solution Containing Additives.

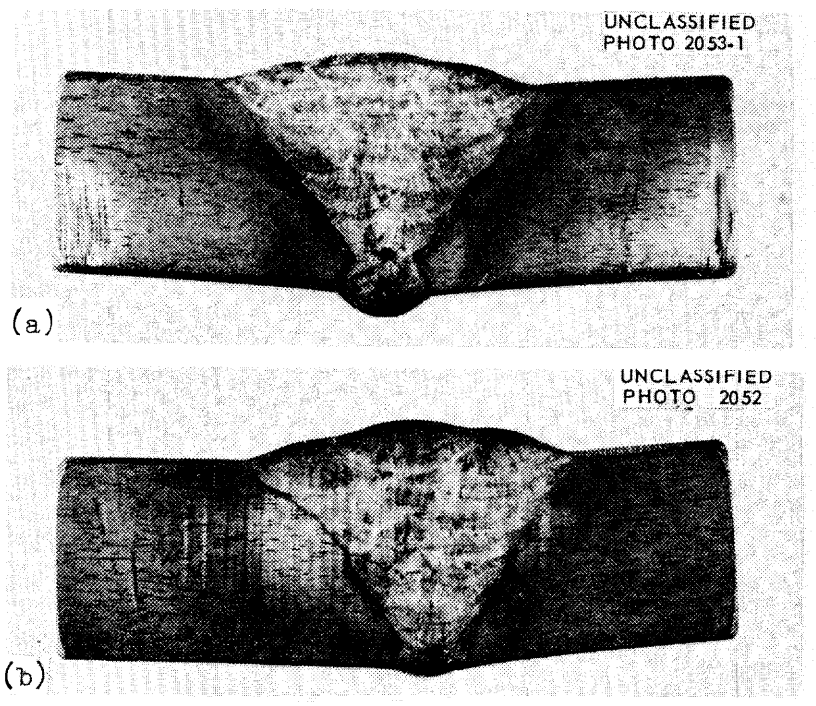


Fig. 12. Knife-line Attack on Exposed Cross Section of Carpenter 20-Cb Stainless Steel Specimens After 3000 hr in Boiling, Oxygen-Aerated 4 M H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products. (a) Test D-V. (b) Test D-U. 2X.

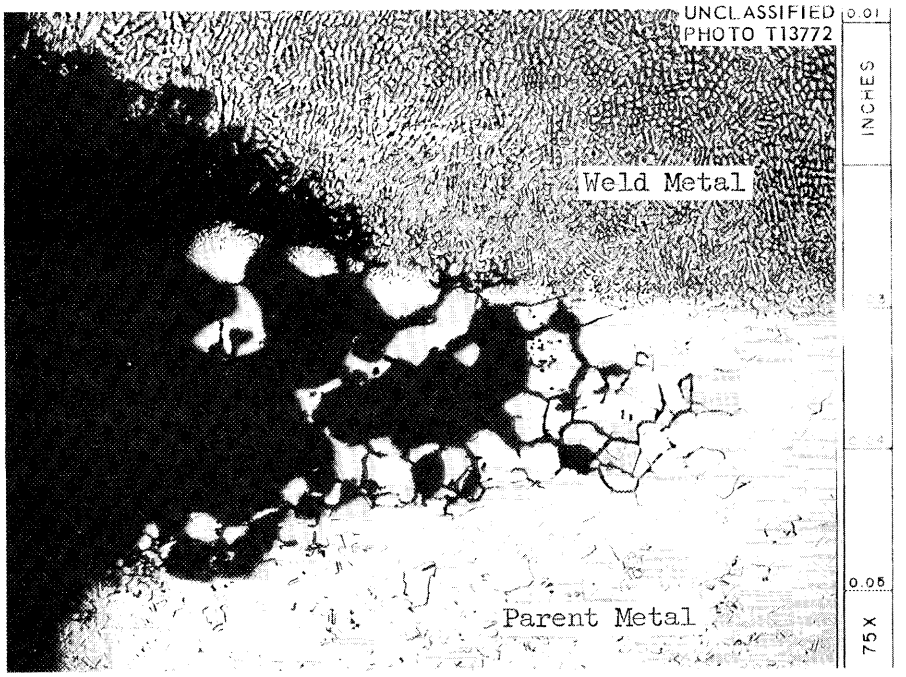


Fig. 13. Knife-line Corrosion Attack on Carpenter 20-Cb Stainless Steel Weld Specimen Exposed for 3000 hr in Boiling, Oxygen-Aerated 4 M H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products. Test D-V. Etched in glyceria-regia. 75X.

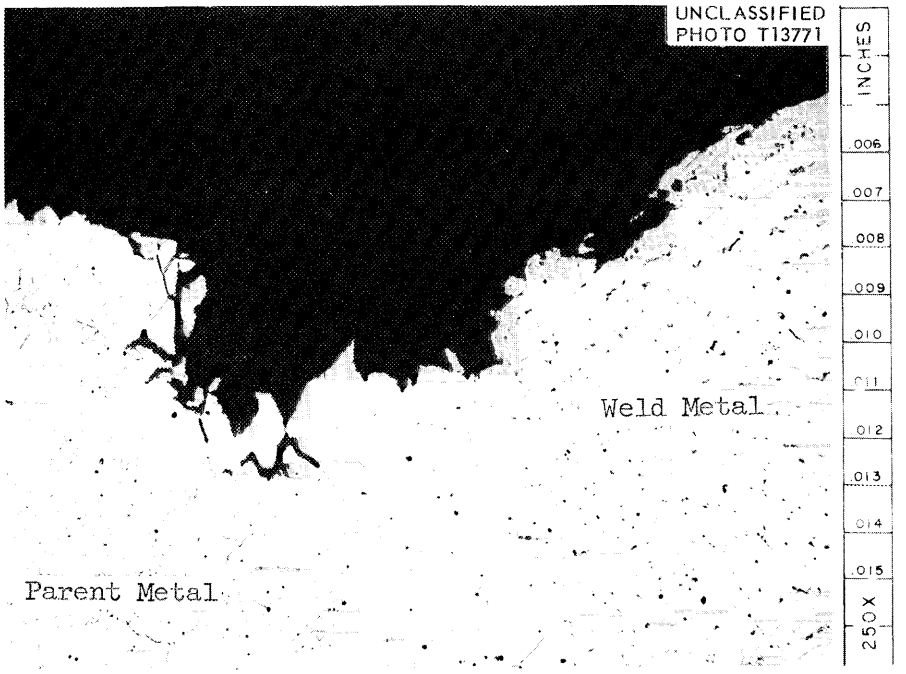


Fig. 14. Cross Section Showing Knife-line Attack Along Root Weld in Carpenter 20-Cb Stainless Steel Specimen Exposed for 3000 hr in Boiling, Oxygen-Aerated 4 M H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products. Test D-V. Etched in glyceria-regia. 250X.

The Carpenter 20-Cb stainless steel weld metal underwent a selective form of corrosion attack as shown in Fig. 15. The attack, which extended to a depth of nearly 4 mils, was selective along the grain boundaries of the large dendrites.

The type of attack experienced by the flat, pickled surfaces of the Carpenter 20-Cb stainless steel is shown in Fig. 16. The attack was preferential along grain boundaries for a maximum depth of 2 mils. Few of the metal grains were found to be completely encircled by the attack.

Tests with Type 347 Stainless Steel.--In addition to Carpenter 20-Cb stainless steel, the corrosion resistance of type 347 stainless steel in certain environments appeared adequate for use in parts of the chemical processing plant. In particular, its corrosion resistance was good enough for certain process piping in which the design operating temperature of process solutions would be appreciably below atmospheric boiling temperature. In previously discussed laboratory tests, it was found that at 38°C, the alloy corroded at a rate less than 1 mpy in oxygenated 4 *M* H_2SO_4 solution containing synthetic corrosion and fission products. In the present tests, the same environment was used except that the solution temperature was increased to atmospheric boiling, approximately 110°C. Tests were run to determine the general corrosion behavior of the alloy and also to determine the effects of welding and stressing.

The control specimens were machined from annealed 1/16-in.-thick sheet; elastically stressed U-bend specimens were also prepared from the same material. The Heliarc weld specimens were made from 3/16-in.-thick plate by using type 347 stainless steel filler rod.

Weight losses are plotted as a function of exposure time in Fig. 17; the curves were almost linear in each case. The corrosion rates for the control, stress, and weld specimens were 8, 11, and 9 mpy, respectively. The attack was uniform. No knife-line corrosion was found on the weld specimens. The stressed specimens were not subject to cracking.

Figure 18 presents a comparison between the corrosion behavior of Carpenter 20-Cb and type 347 stainless steel control specimens in boiling, oxygenated 4 *M* H_2SO_4 solution containing synthetic corrosion and fission products. The Carpenter 20-Cb stainless steel specimens were from one of the heats of the alloy that showed no susceptibility to any localized forms of corrosion attack (Table 11). As is indicated, the corrosion resistance of the latter alloy was eight times better than that of type 347 stainless steel. Observed rates were 1 and 8 mpy, respectively.

Type 347 - Carpenter 20-Cb Stainless Steel Weldment Test.--Using both types 347 and Carpenter 20-Cb stainless steel in the same system would entail one or more welds joining the two materials. Accordingly, a corrosion

Fig. 15. Localized Attack on Carpenter 20-Cb Stainless Steel Weld Metal Exposed for 3000 hr in Boiling, Oxygen-Aerated 4 M H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products. Test D-V. Etched in glyceria-regia. 250X.

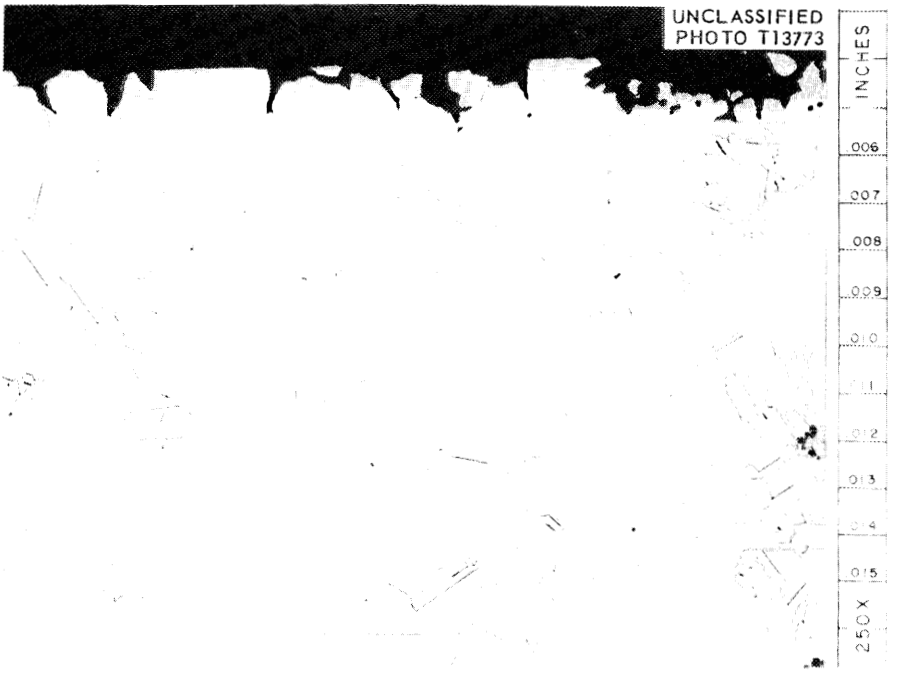


Fig. 16. Surface Attack on Carpenter 20-Cb Stainless Steel Exposed for 3000 hr in Boiling, Oxygen-Aerated 4 M H_2SO_4 Solution Containing Synthetic Corrosion and Fission Products. Test D-V. Etched in glyceria-regia. 250X.

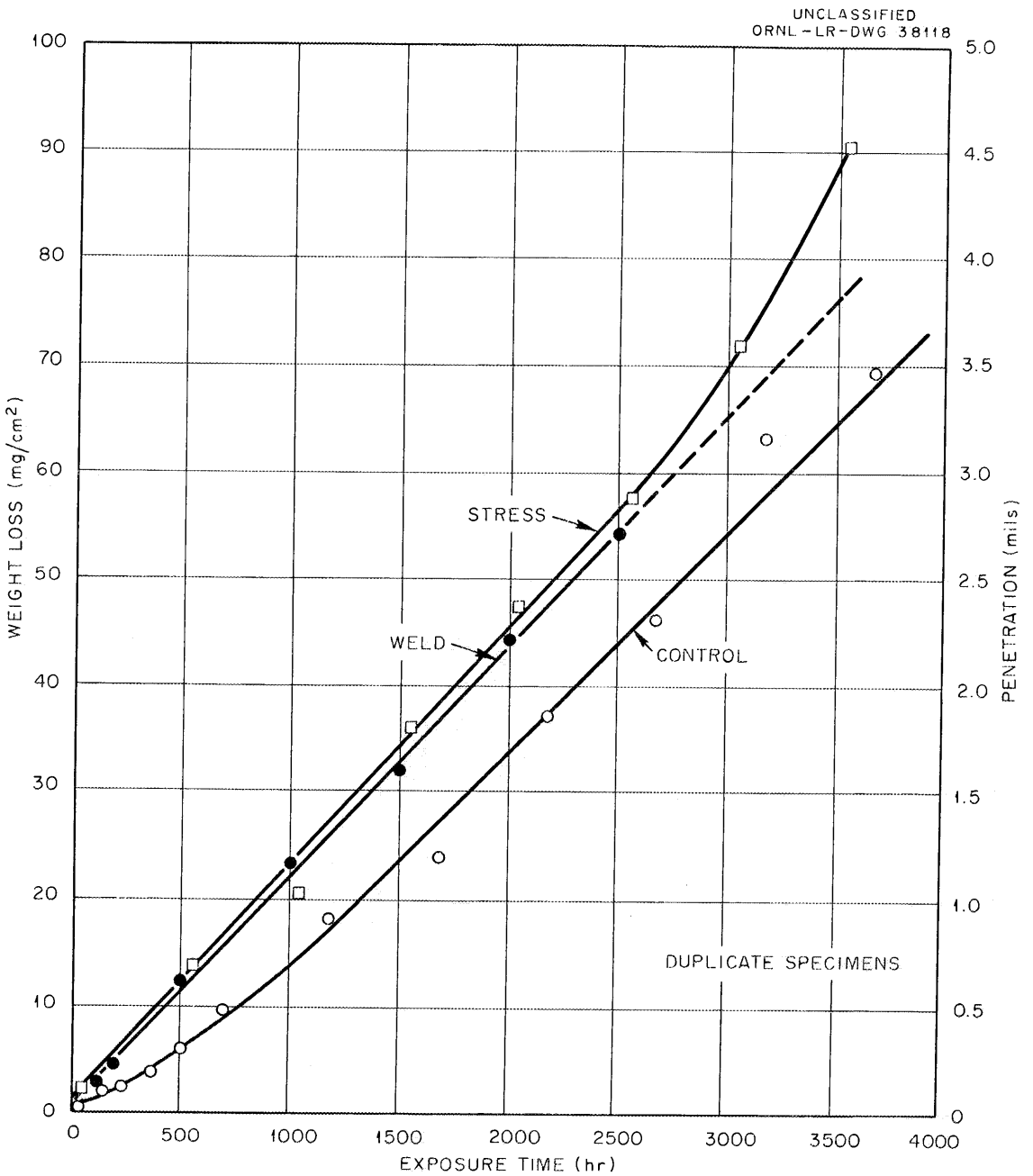


Fig. 17. Corrosion of Control Weld and Stress Specimens of Type 347 Stainless Steel by Boiling Oxygen-Aerated 4 *M* H_2SO_4 Solution Containing Additives.

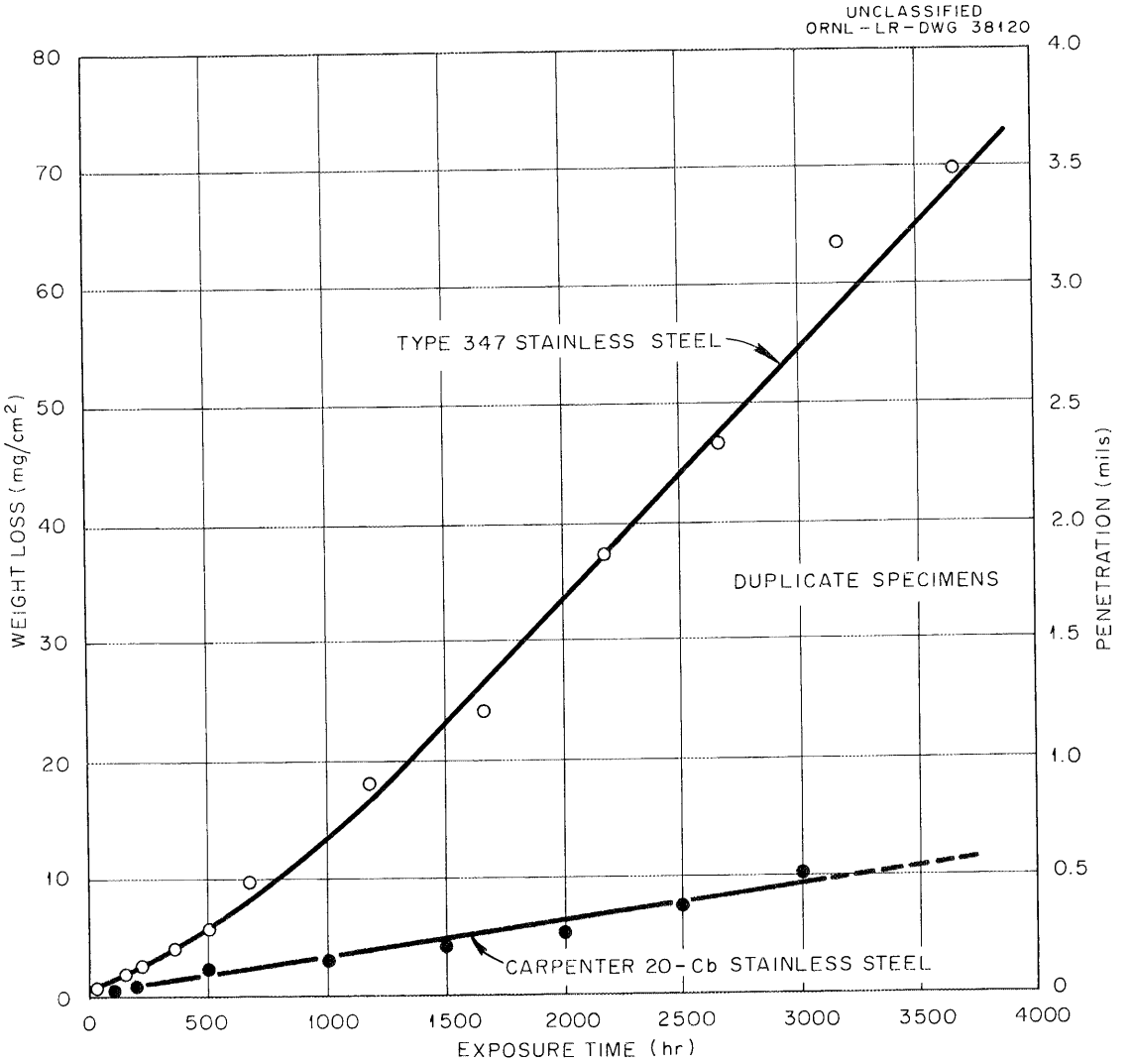


Fig. 18. Corrosion of Carpenter 20-Cb and Type 347 Stainless Steels by Boiling Oxygen-Aerated 4*M* H_2SO_4 Solution Containing Additives.

test was made with such a joint prepared from field materials of 1/2-in. sched-40 pipe of each alloy. The bimetallic specimen was exposed for 1000 hr in boiling, oxygenated 4 *M* H_2SO_4 solution containing synthetic corrosion and fission products. The Carpenter 20-Cb pipe was fusion-welded; the type 347 stainless steel pipe was seamless. Carpenter 20-Cb stainless steel rod was used to butt-weld the two pipe sections together.

The observed corrosion rate for the welded specimen was 27 mpy after 1000 hr. Attack on the type 347 stainless steel member was uniform. The Carpenter 20-Cb stainless steel member, in addition to uniform corrosion, underwent several forms of localized attack. One type of attack was severe knife-line corrosion along both sides of the longitudinal fusion weld in the pipe. The attack occurred in both the root and face of the weld. A second type of attack was a mildly severe center-line corrosion in the same weld. The attack consisted of almost continuously connected pits which were located in the center of the weld deposit and which extended for the full length of the weld. The third type of attack was random crater corrosion in the Carpenter 20-Cb circumferential weld. The attack was characterized by pitting. Knife-line corrosion was also found in the heat-affected zone of the Carpenter 20-Cb stainless steel adjacent to the circumferential weld.

Effect of Ruthenium on Corrosion Behavior.--Since the presence or the absence of synthetic corrosion and fission products exerted a profound effect on the corrosion behavior of a number of materials in boiling 4 *M* H_2SO_4 solution, tests were planned to examine singly the effect of some of the additives. In particular, it was desired to investigate the effect of ruthenium, ferric, and cupric ions. Unfortunately, the corrosion-test program was terminated before studies with the latter two species could be initiated.

Three materials, Carpenter 20-Cb stainless steel, Hastelloy B, and crystal-bar zirconium, were tested in boiling, helium-aerated 4 *M* H_2SO_4 solution containing 20 ppm of ruthenium. Carpenter 20-Cb stainless steel was selected because it had been shown that its corrosion rate in the boiling 4 *M* H_2SO_4 solution was reduced from 32 to 2 mpy by the addition of the synthetic corrosion and fission products. The 2-mpy rate was independent of whether oxygen or helium was used to aerate the solution. It was thereby indicated that one or more of the additives and not the type of aeration was responsible for the marked reduction in the rate of attack. Hastelloy B was chosen because its behavior in the boiling, 4 *M* H_2SO_4 solution was in direct contrast to that of Carpenter 20-Cb stainless steel; Hastelloy B corroded at a rate of 3 mpy in the acid without additives and at an extremely high rate in the presence of additives.

The tests in the ruthenium-containing environment were run for 45 hr. The results appear in Table 12. Data are also included on the corrosion behavior of the test materials during comparable exposure periods in a similar, ruthenium-free environment.

Table 12. Effect of Ruthenium on the Corrosion of Several Materials by Helium-Aerated, Boiling 4 *M* H_2SO_4 Solution at 110°C

Material	Ruthenium Concentration (ppm)	Total Time (hr)	Corrosion Rate (mpy)
Carpenter 20-Cb SS	0	65	25
Hastelloy B	0	25	3
Zirconium, crystal bar	0	25	1
Carpenter 20-Cb SS	20	45	172
Hastelloy B	20	45	41
Zirconium, crystal bar	20	45	1

The rate of attack of both Carpenter 20-Cb stainless steel and Hastelloy B was accelerated by ruthenium. The rate for the former was increased by a factor of 7; the rate for Hastelloy B, by a factor of 14. Crystal-bar zirconium was unaffected by the presence of ruthenium.

Although 20 ppm of ruthenium caused an acceleration in the rate of attack on Carpenter 20-Cb stainless steel, this effect was not evident in the combined presence of the additives including ruthenium and chromic, cupric, ferric, uranyl, and zirconium ions. As mentioned earlier, with all additives present, the observed rate for the alloy in boiling, helium-aerated 4 *M* H_2SO_4 solution was 2 mpy.

DISCUSSION OF RESULTS

A complete summary of corrosion data from the HRT Chemical Processing Plant test program is included in Table 13. The reported rates are average values for duplicate specimens.

10.8 *M* H_2SO_4 Solution

Of the seven metals and alloys examined in boiling 10.8 *M* H_2SO_4 solution with (1) no aeration, (2) oxygen aeration, and (3) oxygen aeration with synthetic corrosion and fission products present, tantalum was the only material which could be considered for a dissolver tank. The corrosion resistance of tantalum was near-negligible, and it was not subject to hydrogen uptake in any environments tested. Since only in the dissolver is 10.8 *M* H_2SO_4 present, the use of a tantalum liner for this part of the system is quite reasonable.

Table 13. Summary of Corrosion Data for HRT Chemical Processing Plant

Material	Corrosion Rate (mpy)								
	Boiling 10.8 *M* H_2SO_4			4 *M* H_2SO_4 at 38°C		Boiling 4 *M* H_2SO_4			
	No Aeration	Oxygen Aeration	Oxygen and Additives	Helium Aeration	Oxygen and Additives	Helium Aeration	Oxygen Aeration	Helium and Additives	Oxygen and Additives
Aluminum oxide	ND*	ND	ND	Gain	Gain	10	6	6	10
Carpenter 20-Cb SS	39,000	22,000	270	<1	<1	32	3	2	2
Graphitar 14	ND	ND	ND	ND	ND	Gain	Gain	Gain	Gain
Hastelloy B	43	24	320	<1	ND	3	725	>15,000	>15,000
Hastelloy C	ND	ND	ND	ND	ND	ND	ND	215	475
Illium R	10,000	1,150	ND	<1	<1	15	78	30	30
Chemical lead	34	108	31	<1	ND	<1	3	1	3
Stellite 6	ND	ND	ND	12	ND	43,000	25,000	15	20
Stellite 98M2	ND	ND	ND	ND	ND	5,900	2,400	135	240
Tantalum	<1	<1	<1	<1	<1	<1	<1	<1	<1
309SCb SS	ND	ND	ND	ND	<1	ND	ND	2	ND
316 SS	ND	ND	ND	8	<1	76,000	79,000	4	5
347 SS	ND	ND	ND	ND	<1	89,000	118,000	4	8
Zircaloy-2	11	5	680	<1	<1	<1	<1	<1	<1
Zirconium, crystal bar	6	8	200	<1	<1	<1	<1	<1	<1

* No data obtained.

It should be borne in mind, however, that should sulfur trioxide be formed by any means it could possibly have a detrimental effect on the corrosion resistance of tantalum. Severe attack of tantalum by concentrated sulfuric acid containing free sulfur trioxide has been reported.[8]

The other materials, including Carpenter 20-Cb stainless steel, Hastelloy B, Illium R, chemical-grade lead, Zircaloy-2, and crystal-bar zirconium corroded excessively in one or more of the environments, so that their use as a tank or tank liner could not be considered.

4 *M* H_2SO_4 Solution

If the Chemical Processing Plant of the Homogeneous Reactor Test is operated as designed, all parts of the plant except the dissolver are contacted only by 4 *M* H_2SO_4 solutions containing dissolved corrosion and fission products at temperatures not in excess of 38°C (100°F). If this condition could be guaranteed, types 309SCb, 316, 347, and Carpenter 20-Cb stainless steel would be suitable materials for construction. It is possible, however, that the design conditions may not always be fulfilled, and in such cases, insufficient soluble fission and corrosion products may be present to give corrosion inhibition or the temperature may be higher than expected.

The choice between the 300-series stainless steels and Carpenter 20-Cb stainless steel for the major material of construction is not easy. At 38°C, the design temperature, both materials have excellent general corrosion resistance to the 4 *M* H_2SO_4 solution, and neither appears susceptible to localized attack; at the boiling point both materials present problems. In the absence of synthetic corrosion and fission products, type 347 stainless steel (representative of the 300-series steels) is attacked at rates in excess of 100,000 mpy, a rate which could not be tolerated even for short periods of time. In the presence of a sufficient quantity of fission and corrosion products, type 347 stainless steel corrodes at the low rate of 4 mpy. Carpenter 20-Cb, on the other hand, has a relatively low general corrosion rate in the boiling acid even in the absence of dissolved corrosion and fission products, but it is susceptible to stress-corrosion cracking and does show localized attack in weld areas. However, the rate of localized attack is not as great as is the general penetration rate of type 347 stainless steel in the additive-free environment, and in the presence of the corrosion and fission products the frequency and severity of localized attack is greatly reduced.

In view of the above considerations it appears that Carpenter 20-Cb stainless steel would be a reasonable choice for the decay storage tanks, and type 347 stainless steel should be suitable for the piping system, which is only periodically contacted by the acid.

In the 4 *M* boiling acid, either zirconium or Zircaloy-2 would be expected to give excellent service and to be freer of corrosion problems than the austenitic stainless steels. The improvement in corrosion behavior, however, would be offset by the high cost of the material and by the difficulty of fabricating such a system from zirconium.

Both sintered aluminum oxide and Graphitar 14 showed reasonable corrosion resistance to the 4 *M* acid solutions. This combination could be used in pump bearings. Stellites 6 and 98M2 experienced high corrosion rates in most environments and showed localized attack in all cases. Their use in pumps and valves cannot be recommended.

General Observations

One of the purposes of this investigation was to determine the effect of the environment on the corrosion rate of several different alloys. As already discussed, the environment had little effect on tantalum; under all conditions of test, corrosion rates less than 1 mpy were observed. Aluminum oxide and Graphitar 14 were not exposed to the 10.8 *M* solutions, but in the 4 *M* solutions the presence of oxygen or additives in the sulfuric acid did not change significantly the attack rate on the materials.

As expected, zirconium and Zircaloy-2 behaved in a similar manner in all environments. In the 4 *M* H_2SO_4 solutions, corrosion rates were insignificantly low regardless of the presence of oxygen or synthetic corrosion or fission products. In 10.8 *M* H_2SO_4 solution, both alloys corroded at rates of 5 to 11 mpy regardless of the aerating gas. The addition of synthetic corrosion and fission products to the solution brought about a very large increase in the corrosion rate. Two of the constituents in the synthetic mixture, cupric and ferric sulfates, were probably responsible for the increased rate of attack. Golden et al[9] have shown that these two salts accelerate the rate of attack of zirconium by sulfuric acid solutions. For example, it was reported that the corrosion rate for arc-melted high-purity zirconium in boiling 75% H_2SO_4 (12.8 *M*) was 46 mpy. The addition of 0.05% copper as cupric sulfate caused the specimen to disintegrate within 24 hr. A similar but less drastic effect was observed with ferric sulfate.

The response of Carpenter 20-Cb and the 300-series stainless steels to environmental changes were about the same, although Carpenter 20-Cb corroded at a lower rate in all cases. In the absence of the corrosion and fission products, oxygen had a substantial effect in reducing the corrosion rate of Carpenter 20-Cb, but it was generally without effect on the 300-series stainless steel. However, the addition of the corrosion and fission products reduced the corrosion rate of both alloys substantially. In the case of type 347 stainless steel the rate was reduced by a factor of 15,000 to 20,000. As previously mentioned, the synthetic corrosion and fission products contained a large concentration of ferric ions and a lesser concentration of cupric ions, both of which inhibit the corrosion of the austenitic stainless steels in sulfuric acid solutions.[6] Generally, the austenitic stainless steels show lower corrosion rates in oxidizing environments than in nonoxidizing environments, and that trend is apparent in the data presented in this report.

Both types 347 and Carpenter 20-Cb stainless steel are stabilized and should be weldable without the necessity of subsequent heat treatment to improve corrosion resistance in the welded area. Type 347 stainless steel welds

behaved as expected and showed no evidence of localized attack in the weld area. On occasion, however, Carpenter 20-Cb stainless steel weld specimens were prone to knife-line corrosion attack in the heat-affected zones and to center-line and crater corrosion in weld deposits. The latter forms of attack are usually attributed to segregation effects during solidification after welding. Both types of attack were observed on the same specimen; namely, 1/2-in. sched-40 fusion-welded pipe. Center-line and crater corrosion were not found on any other weld specimens that were tested. Knife-line corrosion attack, however, was found on the above specimen, and it was also observed on a number of field-welded specimens. The cause for the random occurrence of knife-line attack in weld specimens of the alloy was not resolved. Although Carpenter 20-Cb stainless steel is a stabilized alloy, certain conditions may arise where the niobium does not act in the expected manner. For example, if the final annealing of a mill product were conducted at an unreasonably high temperature, 2200 to 2300°F, followed by fast cooling, conditions would be favorable for the retention of niobium in solution; the material would no longer be in a stabilized condition. Subsequent heating (or cooling) in the range between approximately 800 and 1600°F, such as occurs in the heat-affected zone in welds, would cause preferred precipitation of chromium carbides along the grain boundaries; corrosion resistance would be reduced materially in the affected areas. It is entirely possible, of course, for a similar mechanism to prevail during the welding operation itself, if welding temperatures or times at temperature are excessive.

The behavior of Hastelloy B was the opposite of that shown by Carpenter 20-Cb and the 18-8 austenitic stainless steels. Except in the 10.8 *M* acid the addition of either oxygen or the synthetic corrosion and fission products to the sulfuric acid caused a very large increase in the corrosion rate of the alloy. In the 10.8 *M* acid solution, oxygen appeared to decrease the corrosion rate; the corrosion and fission products increased the rate of attack.

Although the Stellites corroded excessively in all environments, an oxidizing environment was less corrosive than a nonoxidizing environment. The bubbling of oxygen through the solution caused about a two-fold reduction in the corrosion rate. Adding the mixture of synthetic corrosion and fission products brought about a 2000-fold reduction in the corrosion rate of Stellite 6 and about a 200-fold reduction for Stellite 98M2.

The effect of ruthenium on the corrosion resistance of Carpenter 20-Cb stainless steel and Hastelloy B in boiling, helium-aerated 4 *M* H_2SO_4 solution was to accelerate the corrosion rates. Crystal-bar zirconium was unaffected. Although the experimental data were too incomplete to explain the acceleration, it was postulated that the ruthenium ions underwent reduction to metallic ruthenium on cathodic sites, thereby reducing the cathodic polarization and allowing greater corrosion currents.

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CONCLUSIONS

The following conclusions are based upon an analysis of the data from the HRT Chemical Processing Plant corrosion-test program:

1. Tantalum was the only satisfactory corrosion-resistant material for use as a dissolver tank or tank liner for handling 10.8 *M* H_2SO_4 solution. Observed corrosion rates were less than 1 mpy in all cases. There was no susceptibility of the metal to hydrogen embrittlement. Materials such as Carpenter 20-Cb stainless steel, Hastelloy B, Illium R, chemical-grade lead, Zircaloy-2, and crystal-bar zirconium were considered unsatisfactory because of excessive attack by one or more of the boiling 10.8 *M* H_2SO_4 environments.

2. Aluminum oxide, Carpenter 20-Cb stainless steel, Hastelloy B, Illium R, lead, tantalum, types 309SCb and 347 stainless steel, Zircaloy-2, and crystal-bar zirconium were fully resistant to 4 *M* H_2SO_4 solution at the maximum design temperature of 38°C (other than dissolver). All materials underwent very light, uniform attack. No cracking of Carpenter 20-Cb stainless steel--the decay-storage-vessel construction material--was observed at this temperature.

3. Tantalum, Zircaloy-2, and crystal-bar zirconium were resistant to boiling 4 *M* H_2SO_4 solution under all conditions. Lead also exhibited satisfactory corrosion resistance; rates were not in excess of 3 mpy.

4. Generally, the corrosion behavior of Carpenter 20-Cb stainless steel in boiling 4 *M* H_2SO_4 environments was quite tolerable; with several exceptions, the observed corrosion rates did not exceed 6 mpy. The exceptions included rates of 32 mpy in helium-aerated 4 *M* H_2SO_4 solution and 27 mpy in oxygen-aerated 4 *M* H_2SO_4 solution containing synthetic corrosion and fission products. The alloy was subject to stress-corrosion cracking in the additive-free, helium-aerated sulfuric acid solution. In other tests in which the helium was replaced with oxygen, no cracking occurred. A single case of cracking was encountered with the alloy exposed in oxygen-aerated 4 *M* H_2SO_4 solution containing synthetic corrosion and fission products. The same environment produced severe knife-line attack, weld center-line attack, and weld crater corrosion in a set of field-welded specimens.

5. A spectacular improvement in the corrosion resistance of types 316 and 317 stainless steel was effected by the presence of synthetic corrosion and fission products in boiling 4 *M* H_2SO_4 solution. Corrosion rates were reduced from in excess of 75,000 mpy to less than 10 mpy when the additives were present. A similar but smaller improvement in corrosion resistance was observed on Carpenter 20-Cb stainless steel.

6. Ruthenium was found to be an accelerant of corrosion attack on Carpenter 20-Cb stainless steel and Hastelloy B in boiling and helium-aerated 4 *M* H_2SO_4 solution. The corrosion resistance of crystal-bar zirconium was unaffected by ruthenium.

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