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ORNL CF 56-1-167	Period Ending January 31, 1956
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ORNL CF 56-10-13	Period Ending October 31, 1956
ORNL CF 57-1-144	Period Ending January 31, 1957
ORNL CF 57-4-55	Period Ending April 30, 1957
ORNL CF 57-7-121	Period Ending July 31, 1957
ORNL CF 57-10-80	Period Ending October 31, 1957
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I. SUMMARY

A loop run has demonstrated the chemical stability of a solution containing 0.04 *m* UO_2SO_4, 0.025 *m* D_2SO_4, 0.03 *m* $CuSO_4$ and 750 ppm of nickel as nickel sulfate at 300°C in D_2O but both nickel and copper were lost from solution when the nickel concentration was increased to 1700 ppm. The chemical stability of a solution containing 0.036 *m* UO_2SO_4, 0.022 *m* D_2SO_4, 0.009 *m* $CuSO_4$, 0.013 *m* $NiSO_4$ and 0.0016 *m* $MnSO_4$ in D_2O was also demonstrated at 300°C. An attempt to precipitate nickel phosphate selectively from the latter solution either by addition of uranyl phosphate or phosphoric acid was unsuccessful.

The corrosion of stainless steel in 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 and 0.01 *m* $CuSO_4$ was found to be relatively severe above the critical velocity at 250 and 300°C. The critical velocities observed were 10 to 20 and 30 to 40 fps respectively at 250 and 300°C.

Loop runs in which oxygen was removed from solution have shown that as the uranium precipitated excess acid, ferrous and nickelous ions formed. On addition of oxygen to such a solution the uranium dissolved, and the ferrous ions were oxidized to ferric ions which precipitated from solution. The rate of uranium precipitation depended on the previous history of the loop and on the temperature.

A sixth test of the bellows and stainless steel-Zircaloy-2 transition joint mockup has been completed satisfactorily. The total exposure of the mockup has been 9153 hr, including 8600 hr on fuel solution, 312 thermal cycles between 300 and 100°C and 518 mechanical deflections. The satisfactory operation of the mockup has proven the adequacy of the joint insofar as an out-of-pile mockup can test it.

Tests to determine if type 304 stainless steel York mesh would corrode appreciably in uranyl sulfate solutions containing iodine and a hydrogen and oxygen atmosphere at 100°C produced negative results. No significant corrosion of the steel was observed.

over

A solution of 0.04 *m* UO_2SO_4 containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ proved to be unstable during a 200-hr run at 280°C. Both uranium and beryllium were lost from solution.

The addition of 100 ppm ruthenium as ruthenium nitroso sulfate to a 0.02 *m* UO_2SO_4 solution containing 0.025 *m* H_2SO_4 and 0.01 *m* $CuSO_4$ at 250°C provided substantial inhibition of corrosion of stainless steel. However, the inhibition appeared to be due to the substantial quantities of chromium (VI) that formed in the presence of ruthenium.

A solution of 0.17 *m* UO_2SO_4 containing 0.20 *m* Li_2SO_4, 0.10 *m* H_2SO_4, and 0.02 *m* $CuSO_4$ was stable at 280 to 295°C and was only slightly more corrosive to stainless steel at 250°C than 0.17 *m* UO_2SO_4 without additives.

Tests of inhibitors of corrosion of stainless steel in 0.05 *m* H_2SO_4 at 250°C showed 0.002 *m* potassium dichromate to be very effective. 0.04 *m* $MgSO_4$ and 0.05 *m* Li_2SO_4 also gave substantial inhibition though not so much as expected. 0.02 *m* UO_2SO_4 had little effect.

Stress-corrosion cracking characteristics of a number of alloys were investigated under conditions in which steam-heated pipe bends of the materials were cooled by a spray of chloride-containing potable water. MST Gr 3 titanium and Croloy 16-1 stainless steel did not crack during 5000-hr of exposure. Inconel and Nionel were resistant to cracking during test periods of 1000 and 2000 hr, respectively. Incoloy T cracked in 1000 hr. Cold-formed type 347 stainless steel pipe bends did not crack provided the surface was shot-blasted or cathodically protected with aluminum. Normally, cold-formed bends of the alloy crack during 1000 hr. Annealing of type 347 stainless steel pipes did not completely eliminate susceptibility to cracking but did reduce the frequency of cracks. No cracking of the alloy was experienced during a 1000-hr run in which the cooling water was added slowly enough to allow flash vaporization.

Stress specimens of several alloys have been tested in distilled water at 300°C containing oxygen and 100 ppm of chloride. Generally, at pH 10.5 the high nickel alloys such as Nionel and Incoloy were more resistant to cracking than the austenitic stainless steels, However, at pH 2.8 they were as susceptiable to cracking as the austenitic stainless steels. Croloy 16-1 stainless

steel cracked in a 200-hr test at pH 6.5; no cracking occurred, however, during 1500-hr at pH 10.5.

Niobium was susceptible to pitting attack by uranyl sulfate solutions at 100°C, acquired a smooth film at 200°C and underwent catastrophic attack at 300°C. Although the general corrosion behavior of type 17-4 PH stainless steel was acceptable in several reactor-related environments, the partially hardened material (37 Rockwell C) was subject to cracking during a 1000-hr test in chloride-free uranyl sulfate solution at 280°C. Croloy 16-1 stainless steel exhibited unsatisfactory corrosion resistance in uranyl sulfate solutions at 100, 200, and 300°C. Rexalloy 33 underwent severe localized corrosion attack in oxygenated distilled water at 300°C.

II. INTRODUCTION

The data presented in the following sections represent the detailed results obtained during the past quarter (January 31, 1958 to April 30, 1958) by the out-of-reactor solution corrosion group of the Homogeneous Reactor Project. A summary of the data has been reported in the Homogeneous Reactor Project Quarterly Progress Report for the period ending April 30, 1958.

It should be pointed out that the data presented below are, for the most part preliminary and the interpretation of the results may change as further experimentation is completed.

III. 100A LOOP PROGRAM (R. S. Greeley, S. R. Buxton, S. E. Bolt, W. C. Ulrich, H. C. Savage, J. C. Griess)

A. Stability of Dilute Fuel Solutions

1) 0.04 *m* UO_2SO_4 Containing 0.025 *m* D_2SO_4, 0.03 *m* $CuSO_4$, and Various Amounts of Nickel Sulfate in Heavy Water.

The study of the stability of dilute fuel solutions[1] was continued with the circulation in a stainless steel loop of a solution simulating

that used in HRT run No. 14, viz., 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 and 0.03 *m* $CuSO_4$ in heavy water at 300°C.

The solution was stable for 35 hr at 300°C. A solution of nickelous sulfate in heavy water was then pumped into the loop to bring the nickel concentration to about 400 ppm. The solution was stable for 133 hr. A second addition of nickelous sulfate was made to bring the nickel concentration to 750 ppm. The solution was stable 154 hr. Finally, a third addition was made to bring the nickel concentration to 1700 ppm. With this amount of nickel, the solution was not stable and within 15 hr, 35 percent of the total nickel and 7 percent of the copper precipitated. No detectable amount of uranium was lost from solution.

When the temperature of the loop was lowered to 150°C, the precipitated nickel dissolved but the precipitated copper remained insoluble. Upon raising the temperature again to 300°C, nickel precipitated as before. The limiting nickel solubility at 300°C was 1000 to 1200 ppm. The limiting copper solubility at 300°C was 1.7 to 1.8 gm/l (0.027 to 0.028 *m*). The nature of the precipitates of copper and nickel was not determined.

2) 0.036 *m* UO_2SO_4 Containing 0.022 *m* D_2SO_4, 0.009 *m* $CuSO_4$, 0.0126 *m* $NiSO_4$, and 0.0016 *m* $MnSO_4$ in D_2O.

At the conclusion of HRT run No. 13, the solution had the composition 0.036 *m* UO_2SO_4 containing 0.022 *m* D_2SO_4, 0.009 *m* $CuSO_4$, 0.0126 *m* $NiSO_4$ (740 ppm), and 0.0016 *m* $MnSO_4$ in heavy water. In order to determine the stability of the solution, a run was made in a stainless steel loop with a non-radioactive solution of similar composition. The oxygen concentration in solution was about 1000 ppm. No loss of any component of solution was observed during circulation of the solution for 72 hr at 250, 300 hr at 280, and 166 hr at 300°C.

A hydroclone was attached to the loop during the run and solution samples were withdrawn from the bottom of the hydroclone pot simulraneously with regular line samples. No significant amounts of

precipitates or oxide scale were found in the hydroclone samples and analyses of the solution from the hydroclone were not significantly different from analyses of the line samples.

3) Inability to Precipitate Nickel Phosphate Selectively from Fuel Solution.

An insoluble nickel salt is nickel phosphate. Therefore, it was hoped to be able to precipitate nickel phosphate selectively from the dilute fuel solution described in section (2) above by adding phosphate to the circulating solution and extracting the precipitate in the hydroclone.

The loop containing the circulating solution described in section (2) above was cooled from 300 to 225°C at the end of the solution stability test, and the hydroclone was isolated by freezing an ice plug in the inlet line. An addition of a slurry containing 110 gm $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ in 500 ml D_2O was made to the loop with the hope that metathesis of the uranyl phosphate with nickel (II) would occur and nickel phosphate would precipitate. After an hour of circulation at 225°C, the hydroclone inlet line was unfrozen and the underflow pot was sampled. The process was repeated at 250°C. At both temperatures less than 0.1 percent nickel was recovered in the precipitate separated by the hydroclone. The precipitate was uranyl phosphate.

The experiment was repeated at 250°C except phosphoric acid was added instead of uranyl phosphate. Again the precipitate was uranyl phosphate containing less than 0.1 percent nickel. Manganese and chromium were also absent in the precipitate.

Therefore, it was concluded that nickel cannot be selectively removed from dilute uranyl sulfate solution by precipitation as the phosphate.

B. Corrosiveness of Dilute Fuel Solutions.

The study of the stability of dilute fuel solutions has been accompanied by investigation of their corrosiveness to several metals and alloys.

In particular, 200-hr tests were made with 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 and 0.01 *m* $CuSO_4$ at 200, 250 and 300°C. The results for several stainless steel and titanium alloys are listed in Table 1.

At low flow rates where an oxide coating formed on the pins, weight loss rather than corrosion rate is tabulated. At high flow rates, where no coating formed, corrosion rate is tabulated.

The weight losses of type 347 stainless steel coupons are plotted as a function of velocity in Figure 1 from which it can be seen that the critical velocity at 250 and 300°C was 10 to 20 and 30 to 40 fps, respectively. When one compares the curves of Figure 1 with data previously given for 0.04 *m* UO_2SO_4 containing 0.020 *m* H_2SO_4 and 0.005 *m* $CuSO_4$[2] shown in Figure 2, it is observed that corrosion was not greatly affected at 200°C but was significantly greater at 250 and 300°C in the solution containing the greater amounts of acid and copper sulfate. It is apparent that the corrosiveness of this solution (0.04 *m* UO_2SO_4 + 0.025 *m* H_2SO_4 + 0.01 *m* $CuSO_4$) above the critical velocity at 250 and 300°C and its low critical velocity at 250°C make efforts to find an inhibitor necessary.

The solution was phase stable in each test.

C. Oxygen Exhaustion in Dilute Fuel Solutions.

1) 280°C.

The possibility that oxygen exhaustion occurred during the first few hours of power operation in HRT run No. 13[3] prompted a more complete investigation of the chemical behavior of dilute uranyl sulfate solutions in the absence of oxygen. The effect of oxygen exhaustion during circulation of dilute uranyl sulfate solutions at high temperature in a stainless steel system has been studied previously,[4] but no run has ever been made in which the precipitation of uranium, which occurs after oxygen exhaustion, was allowed to go to completion. Therefore, a run was made in a stainless steel loop at 280°C with 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 pressurized with a 4:1 helium-hydrogen mixture. Figure 3 is a plot of the concentration of various

TABLE I

Corrosion Data for Several Alloys in a Solution Containing 0.04 *m* UO_2SO_4, 0.01 *m* $CuSO_4$ and 0.025 *m* H_2SO_4

Alloy	Wt. Loss at 18 fps (mg/cm^2)	Corrosion Rate at 76 fps (mpy)	Critical Velocity of Type 347 SS Coupons (fps)
Run M-35 (200°C)			
304 L Stainless Steel	9.5	26	
309 SCb " "	4.6	17	
347 " "	11	30	ND[a]
Titanium 4Al, 4Mn	< 0.1	2.0	
Titanium 6Al, 4V	< 0.1	2.6	
Run M-36 (250°C)			
304 L Stainless Steel	9.4	140	
309 SCb " "	16	130	
347 " "	16	150	10-20
Titanium 4Al, 4Mn	0.2	1.1	
Titanium 6Al, 4V	0.2	1.5	
Run M-37 (300°C)			
304 L Stainless Steel	3.0	29	
309 SCb " "	4.1	20	
347 " "	3.9	47	30-40
Titanium 4Al, 4Mn	0.1	0.46	
Titanium 6Al, 4V	0.1	0.61	
Titanium RC-55	0.1	-	

(a) All specimens filmed over but lost weight proportional to flow rate.

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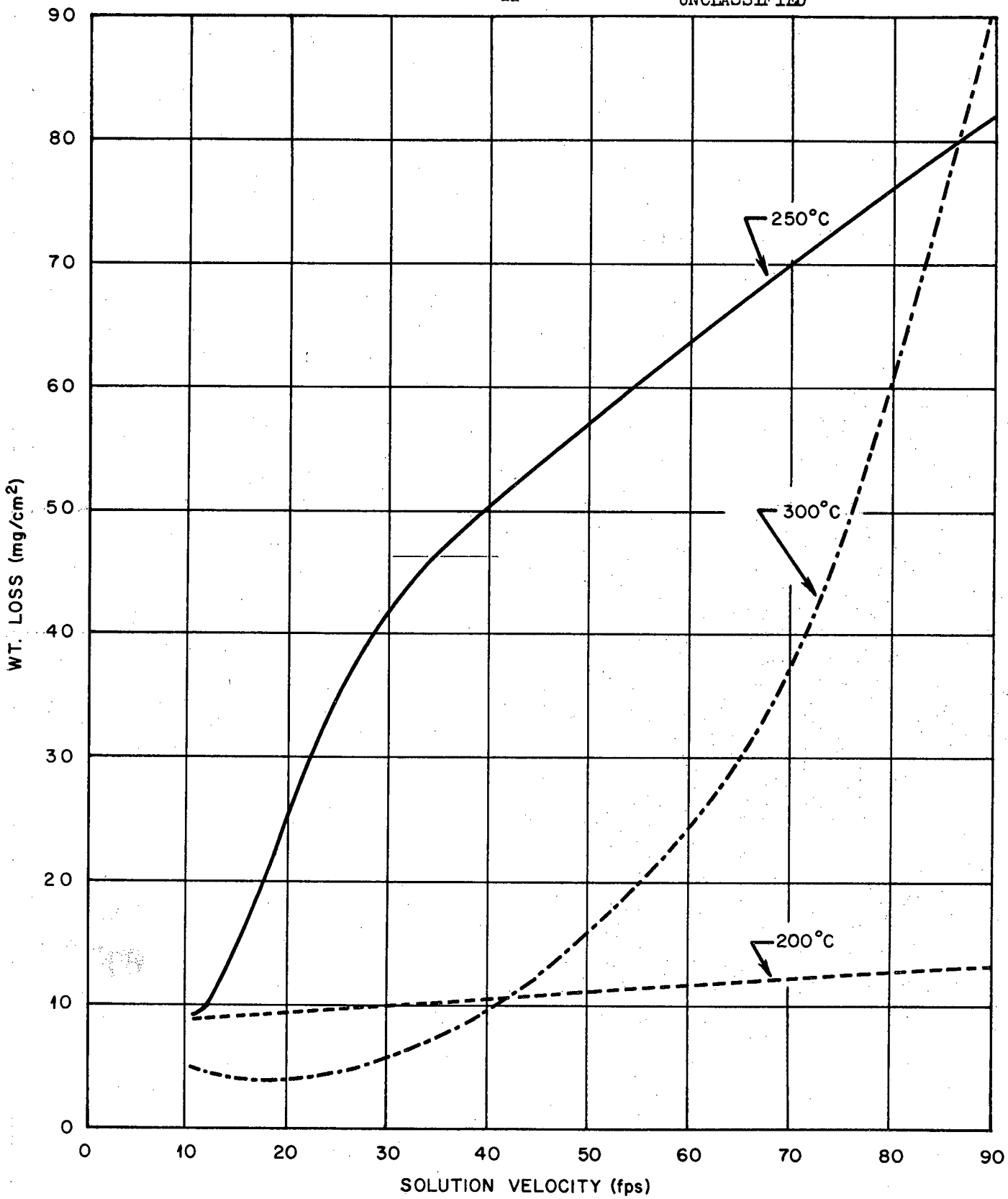

Fig. 1. Weight Losses of Type 347 Stainless Steel Coupons Exposed to 0.04 m UO_2SO_4 Containing 0.01 m $CuSO_4$ and 0.025 m H_2SO_4 for 200 hr

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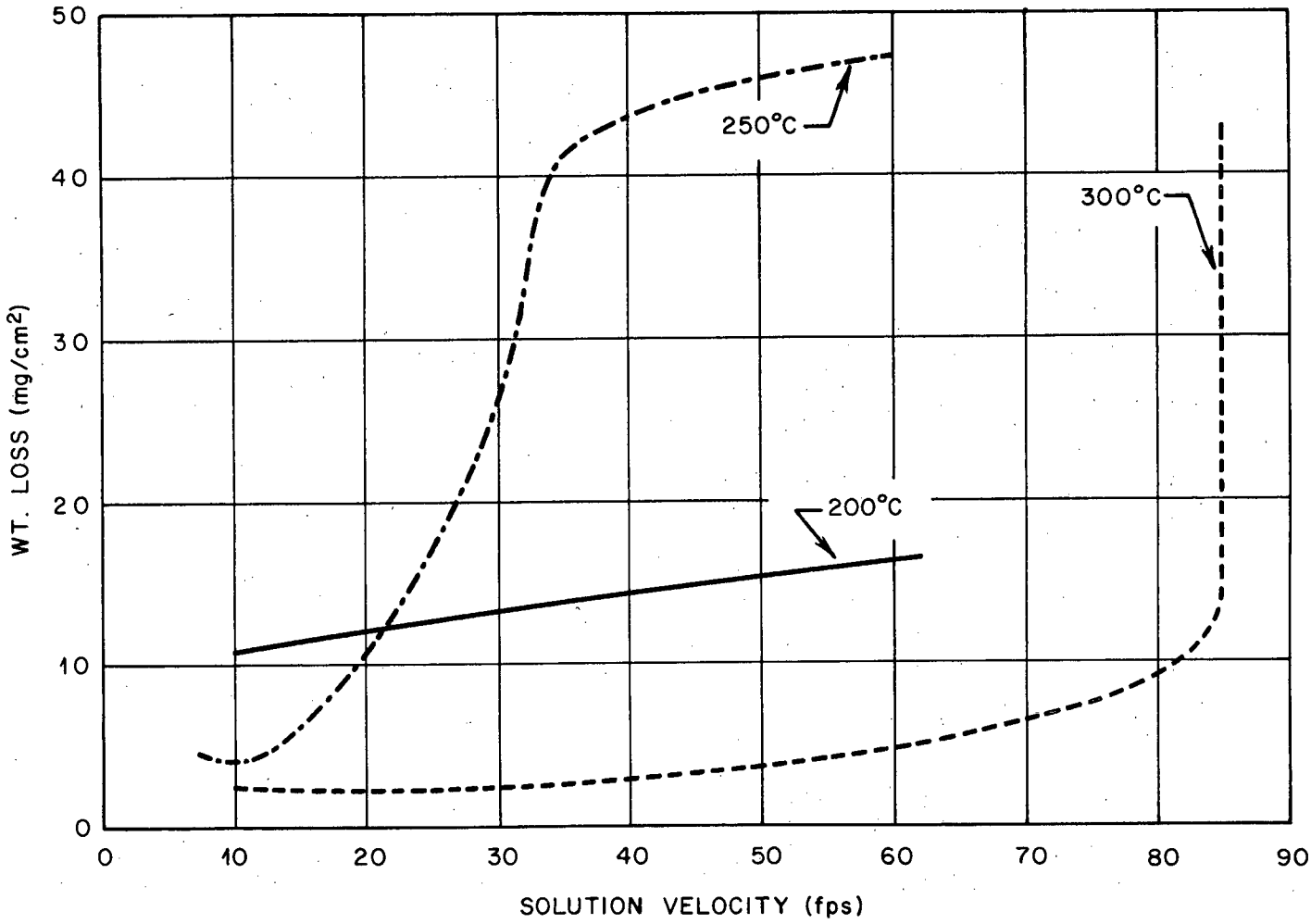

Fig. 2. Weight Losses of Type 347 Stainless Steel Coupons Exposed to 0.04m UO_2SO_4 Containing 0.005m $CuSO_4$ and 0.02m H_2SO_4 for 200 hr

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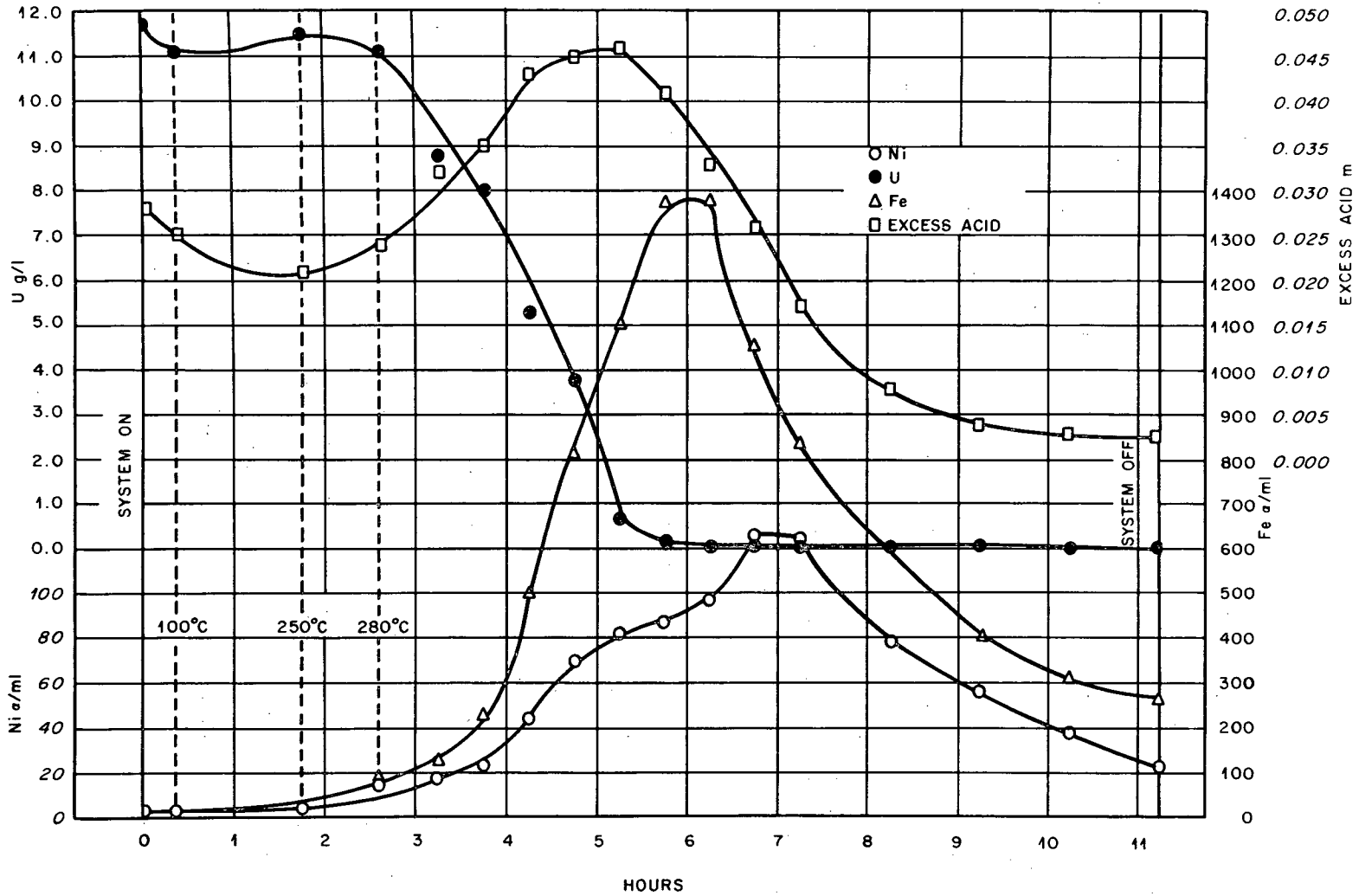

Fig. 3. Concentrations of Various Ions During Oxygen Exhaustion at 280°C from a Solution Initially 0.04m UO_2SO_4 + 0.025m H_2SO_4

ions versus time during the run. The temperatures indicated on the graph represent the loop temperature at that particular time while the loop was heating up.

In the absence of oxygen, uranyl ions are reduced by corroding steel and precipitate as U_3O_8, with the net production of hydrogen ions, or as UO_2 with no change in acidity. The effects of this reduction reaction are illustrated in Figure 3. The uranium concentration in solution began to decrease sharply within 40 minutes after the system reached 280°C, and became practically zero within three hours. Simultaneously, the free-acid concentration increased from 0.025 *m* to 0.046 *m*. The liberation of hydrogen ions intensified the attack on the steel and in this sense the corrosion was autocatalytic. When all of the uranium had precipitated, the free acid was steadily used up in the corrosion process and the pH increased. If the amount of free acid is calculated on the basis that uranium precipitated as U_3O_8, good agreement is obtained with the observed amount of free acid, iron, and nickel found in solution.

Also in the absence of oxygen, iron from the corrosion of steel remains soluble as ferrous ions. As can be seen in Figure 3, the iron and nickel concentrations reached high values roughly in the ratio Fe(II):Ni(II) = 10:1. The dip in the nickel curve between the fifth and seventh hours of the run has not been interpreted. The corrosion rate of the stainless steel loop calculated from the steepest portion of the nickel curve was about 150 mpy.

As the acid was used up in corrosion and the pH increased, the iron and nickel in solution became insoluble and precipitated, presumably as sulfates or basic sulfates since the sulfate concentration decreased simultaneously. Samples of scale centrifuged from solution samples taken at various times during the run were analyzed by X-ray diffraction. Only UO_2 and Fe_2O_3 were found. The absence of U_3O_8, Fe_3O_4, and basic iron and nickel sulfates has not been resolved although it is possible that U_3O_8 initially precipitated could have been further reduced by ferrous ion to give UO_2 and the very insoluble Fe_2O_3.

Following the oxygen exhaustion run, the loop was rinsed twice with 1% nitric acid at 250°C to dissolve the precipitated uranium, and then the loop was pretreated 50-hr with oxygenated 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 at 300°C to restore the filmed-over condition of the loop.

2) 250°C.

A very similar run without oxygen was then made in the same loop with 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 except the temperature was 250°C. However, after complete precipitation of uranium, oxygen was added in order to observe how the system would be restored. The changes in concentration of several ions are plotted in Figure 4.

After eight hours of running without oxygen, during which time the system behavior was qualitatively the same as during the run at 280°C, 350 psi of oxygen was added to the loop. Within 1/2 hr, 95% of the uranium had redissolved, and within an hour essentially all of the uranium was in solution. Within 2 hr the nickel concentration levelled off and the pH steadied at 1.65 to 1.70. The addition of oxygen oxidized the ferrous ions to ferric ions which hydrolyzed and precipitated from solution. No explanation can be offered for the peculiar shape of the nickel curve after the oxygen addition.

3) Conclusions.

It may be concluded that if for any reason oxygen exhaustion occurred with 0.04 *m* UO_2SO_4 in a stainless steel system at elevated temperatures, precipitation of uranium would occur within a few hours according to the equation

$$\begin{cases} 3UO_2^{++} + 2e^- + 2H_2O \longrightarrow U_3O_8 + 4H^+ \\ Fe,\ Cr,\ Ni(steel) \longrightarrow Fe^{++},\ Cr^{+++},\ Ni^{++} + 2e^- \end{cases} \quad (5).$$

The actual length of time for the precipitation to begin and to be completed would depend on the temperature and the previous history of the system. The acid produced by the precipitation would intensify

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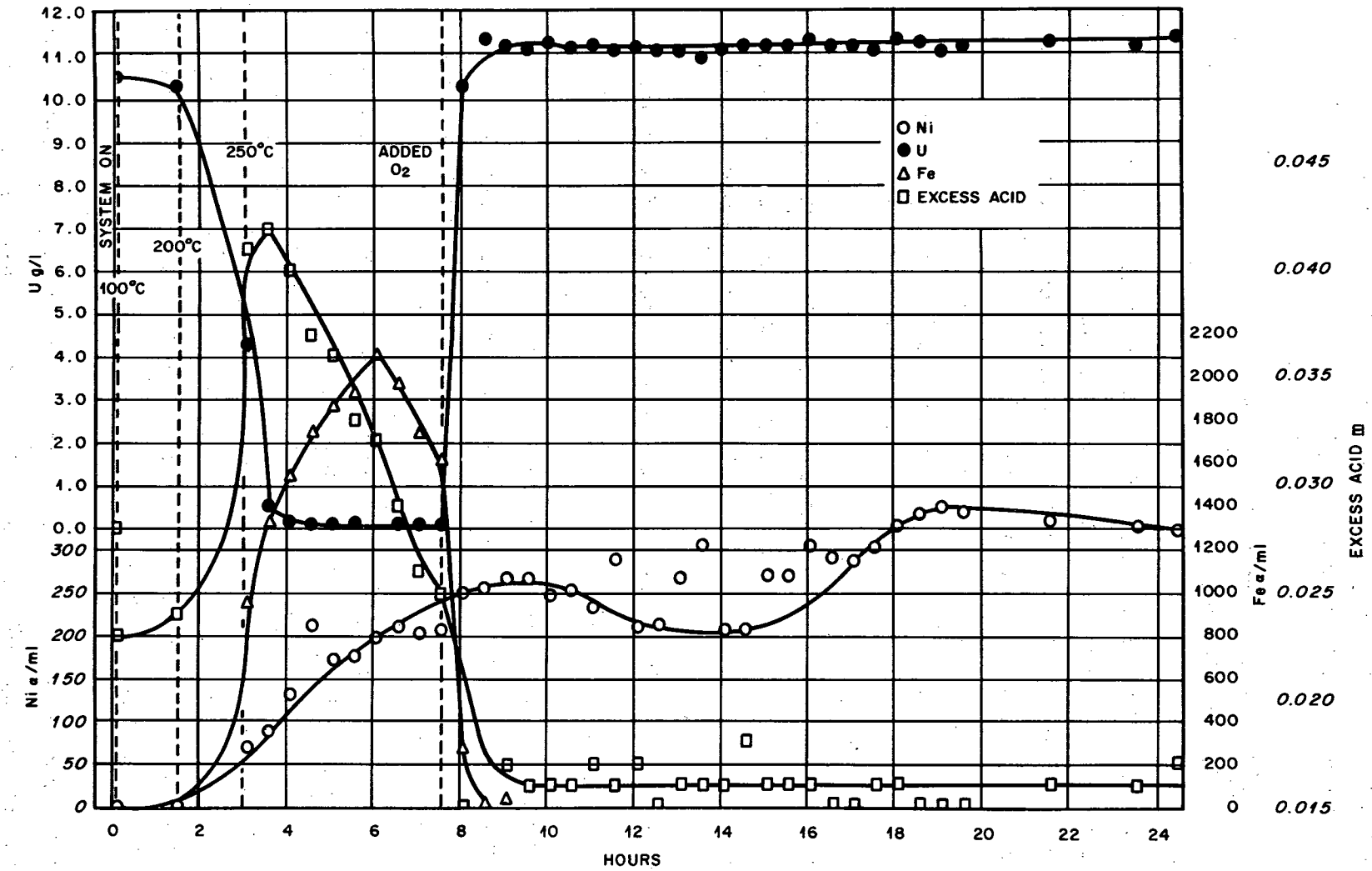


Fig. 4. Concentration of Ions During Oxygen Exhaustion at 250°C from a Solution Initially 0.04m UO_2SO_4 + 0.025m H_2SO_4

the attack on the steel, and ferrous and nickelous ion concentrations in solution would increase sharply:

$$\begin{cases} 2H^+ + 2e^- \longrightarrow H_2 \text{ (gas)} \\ Fe, Cr, Ni(steel) \longrightarrow Fe^{++}, Cr^{+++}, Ni^{++} + 2e^- \end{cases} \quad (5).$$

If oxygen exhaustion continued, the acid would be consumed in the corrosion process, and ferrous and nickelous sulfates would begin to precipitate. It is also possible that ferrous ions would reduce U_3O_8 to UO_2 and itself precipitate as Fe_2O_3:

$$\begin{cases} U_3O_8 + 4H^+ + 4e^- \longrightarrow 3UO_2 + 2H_2O \\ 4Fe^{++} + 3H_2O \longrightarrow 2Fe_2O_3 + 12H^+ + 4e^- \end{cases}.$$

If oxygen were added, the uranium would quickly reappear in solution, any remaining ferrous iron would precipitate as ferric oxide, and the corrosion rate of the steel would decrease to a nominal value.

D. Sixth Test of the HRT Core-Pressure Vessel Flange and Transition Joint Mockup.

A sixth test of the mockup of the Zircaloy-2 - stainless steel transition and expansion joint as used in the HRT reactor vessel has been made in 100A dynamic loop F. The first five tests were described previously.[6]

The test lasted 4084-hr, 29 hr on water and 4055-hr on solution (nominally 0.04 *m* UO_2SO_4 containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$). The system was thermally cycled 144 times (4-hr cooling to 100°C, 4-hr heating to 300°C, and 16-hr isothernal at 300°C). The thermal cycles were made once each day except for two roughly ten-day periods of continuous isothermal operation at 300°C. During each thermal cycle the expansion joint was mechanically deflected 5/8 in.

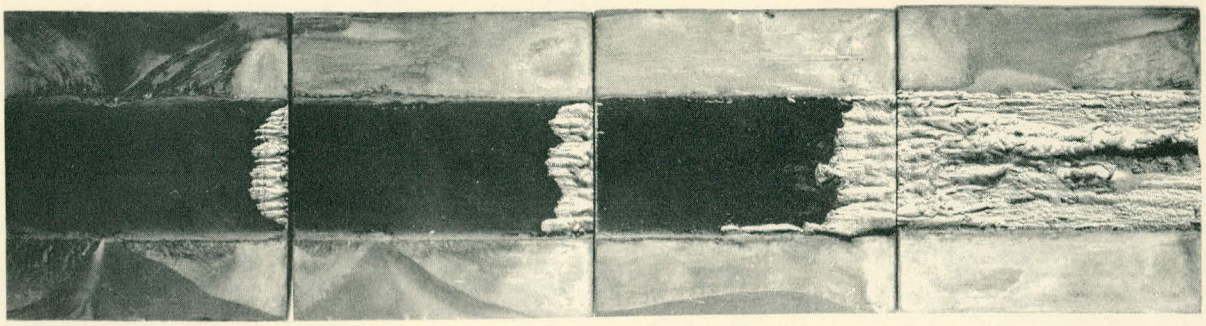
At the conclusion of the run and prior to disassembly, no leakage was detected through the 10 in. IPS, 1500-lb test vessel oval ring joint when tested with 200 psig of helium. Neither leakage of fuel solution into the oval ring joint gasket grooves nor leakage of fuel solution through

the bellows or across the transition joint occurred during the run. After disassembly the bellows and transition joint were leak-tight to 50 psi of helium.

The pitted areas on the bellows[7] were examined again by moving the reinforcing rings to reveal the crevice area between the rings and the bellows. No significant increase in the depth of the pits was found. This fact was surprising since the previous tests had indicated that the mechanical deflections of the bellows were causing the pitting.[8] It may have been that in repositioning the reinforcing rings after the fifth test the clearance between the rings and the bellows was increased. An increase in clearance would have allowed flow of solution between the rings and the bellows thereby preventing a concentration cell type of pitting.

All of the corrosion specimens were removed from the loop and test unit, except those welded inside the bellows, and were scrubbed and weighed. The most striking weight losses during the sixth test were for the type 347 stainless steel coupons exposed in the loop at 30 to 50 fps. Figure 5 is a photograph of these coupons after the sixth test. The shiny black oxide film, which had protected the coupons at flow rates up to 50 fps for 5069-hr during the first five tests (runs F-65 through F-69), broke down at bulk flow rates in excess of 30 fps at the edges of the coupons where turbulence took place. Localized attack occurred at a rate estimated to be approximately 15 mpy. The breakdown of the well-established film on the coupons exposed at 30 to 50 fps illustrates that the properties of the solution and the flow rate must be such that any break in the film is repaired if a protective film is to be completely reliable. The heavily grooved and pitted coupon shown in Figure 5 at the extreme right was exposed at 50 to 64 fps and was attacked in every run from the start of the test. The uneven attack is typical of conditions where film repair and breakdown occur at different times during a run (particularly under non-isothermal operation).

The pin-type corrosion specimens exposed at 12 fps in the loop proper gained small amounts of weight in the as-scrubbed condition during the sixth test, as did the commercially pure titanium, crystal bar zirconium, and Zircaloy-2 pins exposed at 68 fps.



30 34 40 50 64 fps

Figure 5. Type 347 Stainless Steel Coupons After Run F-70. Direction of Flow was Left to Right.

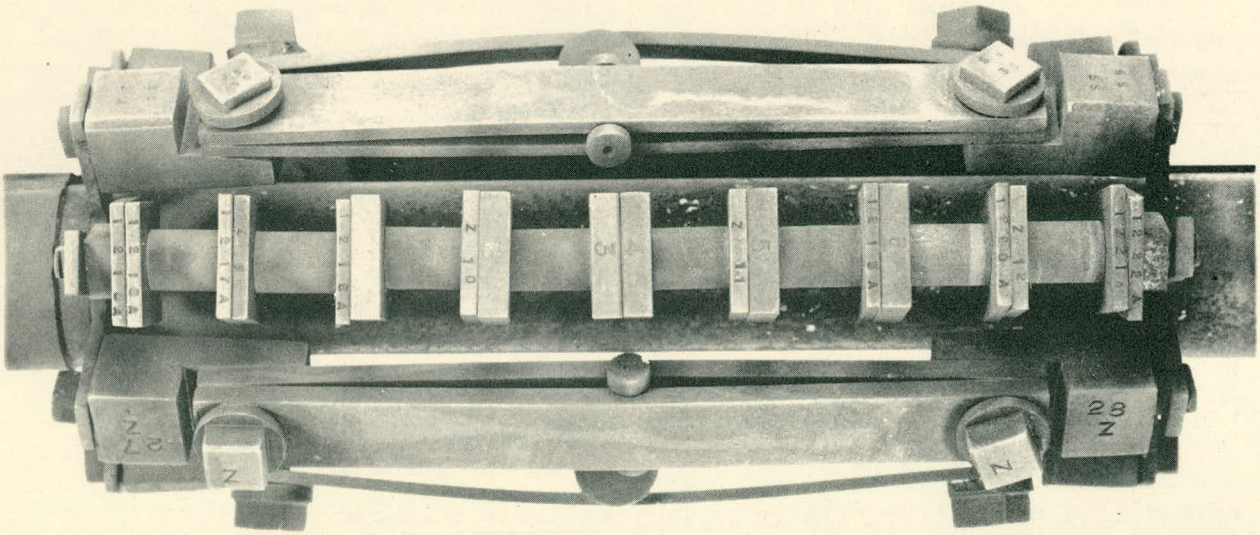


Figure 6. Stress, Crevice, and Galvanic Couple Specimen Assembly Exposed 8629-hr at 100 to 300°C to Fuel Solution at ~ 2 fps (runs F-65 through F-70).

The high strength titanium alloy pins (4% Al, 4% Mn; 3% Al, 5% Cr; 5% Al, 2-1/2% Sn; 6% Al, 4% V) continued, as in the previous runs, to lose small amounts of weight at 68 fps.

All of the specimens exposed in the test unit gained weight "as-scrubbed" during the sixth test except, again, the high-strength titanium alloys which lost small amounts of weight. No significant stress, crevice, or galvanic attack was noted on the specimens included for the purpose of studying such effects. The unit holding these stress, crevice, and galvanic coupled specimens is pictured in Figure 6 in a photograph taken "as-removed" after the sixth test. The flow rate of solution past the specimens was approximately 2 fps. Figure 7 is a photograph of the ring coupons also exposed inside the test unit.

The solution remained stable throughout the test. Figure 8 is a plot of the various concentrations of ions with time. As noted in the figure, one or two liters of make-up solution were added frequently to replenish solution used for analytical samples. The make-up solution was identical in concentration to that circulating except no corrosion products such as nickel or chromium were included. The increase in nickel-ion concentration, allowing for dilution by make-up, was 0.15 mpy, roughly the same rate as observed in the previous two tests. The uranium and copper concentration increased slightly during the run since condensate from solution was withdrawn periodically.

At the request of the Chemical Technology Division a hydroclone was installed on the loop for the sixth test. The underflow pot was sampled in three 50 ml portions daily at the start of the sixth test and thrice weekly after about 1000-hr. The solids collected were submitted to the Chemical Technology Division for further study. A total of 10.1 gm scale, identified by X-ray diffraction to be the expected α-Fe_2O_3 (with some Cr_2O_3 in solid solution), was collected. Collection of scale by the hydroclone averaged 67 mg per day during periods when the system was thermally cycled between 300 and 100°C each day, but the rate of collection dropped essentially to zero during isothermal operation of the system.

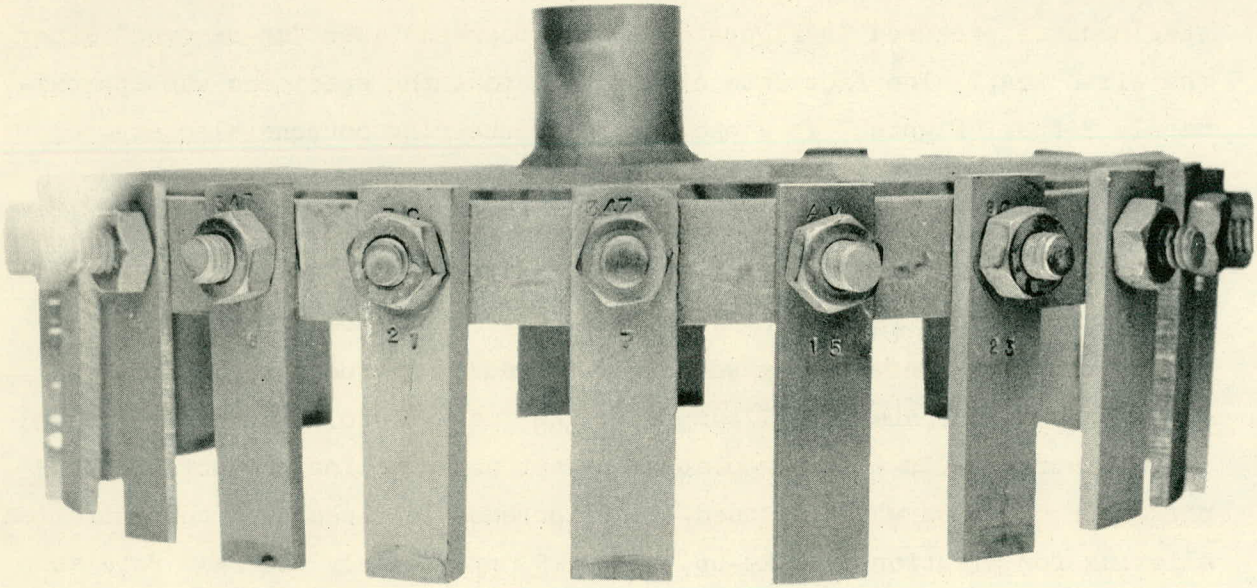


Figure 7. Ring Coupons Exposed 8629-hr at 100 to 300°C to Fuel Solution at ~ 2 fps (runs F-65 through F-70).

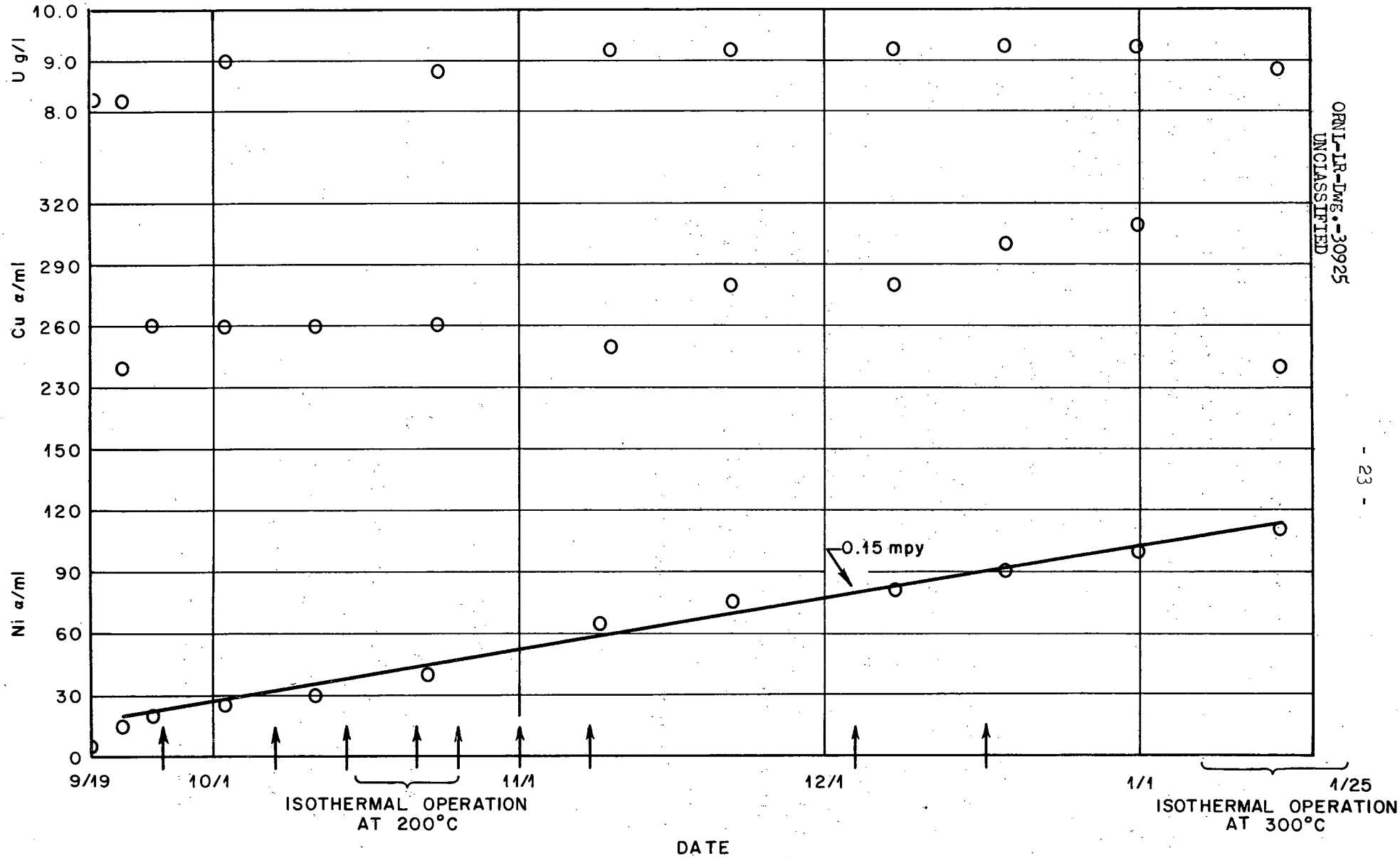


Fig. 8. Concentrations of Uranium, Copper, and Nickel Ions Vs. Time During Run F-70. (Arrows Indicate Times of Addition of One Liter of Make-up Solution)

A scale inventory balance was attempted. Table II lists the estimate of the amount of scale formed and the amount of scale deposited in various ways throughout the loop. The amount of scale collected in the hydroclone and that found lying loose on the bellows convolutions were weighed directly. The amount loosely adhering to the loop surface was estimated from the weight lost by the stainless steel pin specimens upon scrubbing with a soft brush (about 0.25 mg/cm^2 x 41.1 ft^2 x 929 cm^2/ft^2). The amount tightly adhering to the loop surface was estimated from the weight gained after scrubbing by the stainless steel pin specimens during run F-70 (about 0.89 mg/cm^2 x 41.1 ft^2 x 929 cm^2/ft^2). The amount that settled behind the corrosion sample holders was estimated from the amount that was collected and weighed (4 gm was collected which appeared to be about 80% of the amount originally there before some was inadvertently washed away). The total scale formed during the run was estimated from the nickel concentration in the solution at the end of the test (186 ppm Ni in 28.6 liters = 5.32 gm Ni) plus that withdrawn in solution samples throughout the test (1.79 gm Ni) times 7 (the steel averages 12-1/2% Ni) times the gravimetric factor to convert steel to the oxide. For the purpose of this inventory, iron and chromium were assumed to be equivalent and the scale weight is reported as Fe_2O_3. The agreement between scale formed and scale found is considered good.

TABLE II

Oxide Scale Inventory Balance for Run F-70

Scale Collected in Hydroclone (total)	10.1	gm
Scale Lying Loose on Bellows Convolutions	6.7	gm
Scale Loosely Adhering to Loop Surface	~ 10	gm
Scale Tightly Adhering to Loop Surface	~ 35	gm
Scale Settled Behind Corrosion Sample Holders	~ 5	gm
Total Scale Found	~ 67	gm
Total Scale Formed (as Fe_2O_3)	~ 71	gm

The preceding figures and Table II would indicate that the hydroclone operated satisfactorily in removing solids that reached it but that the bellows area, where the flow rate of solution drops sharply, was two-thirds as effective as the hydroclone in removing solids. Also an amount of scale probably equal to the amount collected was left on the loop as a loose deposit. The nature of the loose material and the reason for the failure of the hydroclone to collect it are not known at present. It may be that the loose particles are fines too small to be removed by the 'clone. The tightly adhering scale represents the majority of the oxide formed (in this case roughly 52%) even under thermal cycling stresses which may be expected to crack off some of the scale.

The total exposure of the mockup has been 9153-hr, including 8600-hr on fuel solution, 312 thermal cycles, and 518 mechanical deflections. It is felt that the design has been proven insofar as an out-of-reactor mockup can test it.

E. Corrosion Resistance of York Mesh in an Iodine-Containing Uranyl Sulfate Solution at 100°C.

In the HRT, fuel solution at 100°C containing various amounts of radiolytic gases and fission product iodine could very likely come in contact with the type 304 stainless steel York mesh used as an entrainment separator above the fuel dump tank. To investigate the possibility of severe corrosion of the York mesh under these conditions, specimens of the mesh were exposed in both the liquid and vapor phases to 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4 circulated at 100°C under a 2:1 hydrogen-oxygen atmosphere. Two samples of the mesh were exposed in the annealed condition and two samples were exposed after sensitizing by heating 1 hr in air at 1250°F followed by pickling to remove the scale. No severe corrosion was evident on any of the samples after a 60-hr exposure during which the system was depleted in oxygen for about 40-hr (due to severe wear in the pump).

The specimens of the mesh were replaced in the loop without defilming for a second test under the same conditions except two additions of potassium iodide were made to the solution to simulate the appearance of fission product iodine in the HRT. The amount of iodide added each time, 300 mg KI, was equivalent to the total amount of iodine generated during HRT

run No. 13. No iodide appeared in solution after the first addition, but 20 to 30 ppm iodide was detected in solution throughout the run after the second addition. No deleterious effect of the iodine in solution or in the vapor phase was detected on the mesh after 240-hr exposure at 100°C.

F. Stability and Corrosiveness of 0.04 *m* UO_2SO_4 Containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ at 280°C.

In a previous report[9] it was observed that 0.04 *m* UO_2SO_4 containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ was less corrosive to stainless steel than 0.04 *m* UO_2SO_4 containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$, but that the beryllium - containing solution was unstable at 300°C. Since it was intended that the HRT operate at temperatures of 280°C and below, it was of interest to determine whether the beryllium - containing solution would be phase stable at 280°C. Accordingly, a 500-hr run was made in a stainless steel loop with 0.04 *m* UO_2SO_4 containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ at 280°C. The corrosion results for the type 347 stainless steel coupons are plotted in Figure 9. Comparison curves are shown for similar runs at 200 and 250°C.

Table III shows the composition of the solution at the beginning and end of the run. There was a definite decrease in pH and uranium, beryllium, and copper concentrations also decreased as the loop was brought to temperature. During the run the concentrations fluctuated widely around fairly constant median values except the copper concentration increased to its original value. It was concluded that the solution was unstable at 280°C but that if the pH of the solution had been originally adjusted to about 2.5 with sulfuric acid, the solution might have been stable. The loss of uranium as well as beryllium was not expected since a previous run at 300°C had shown only a loss of beryllium.[9] The reason for the loss of uranium in this run is not known.

TABLE III

The Concentrations of Various Ions in a Solution Containing 0.04 *m* UO_2SO_4, 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ at the Beginning and End of a 500-hr Run

	pH	U g/l	Ni ppm	Cr ppm	Cu ppm	Be g/l
Initial Conc.	3.0	11.6	0	0	300	0.44
Final Conc.	2.7	9.5	53	34	300	0.36

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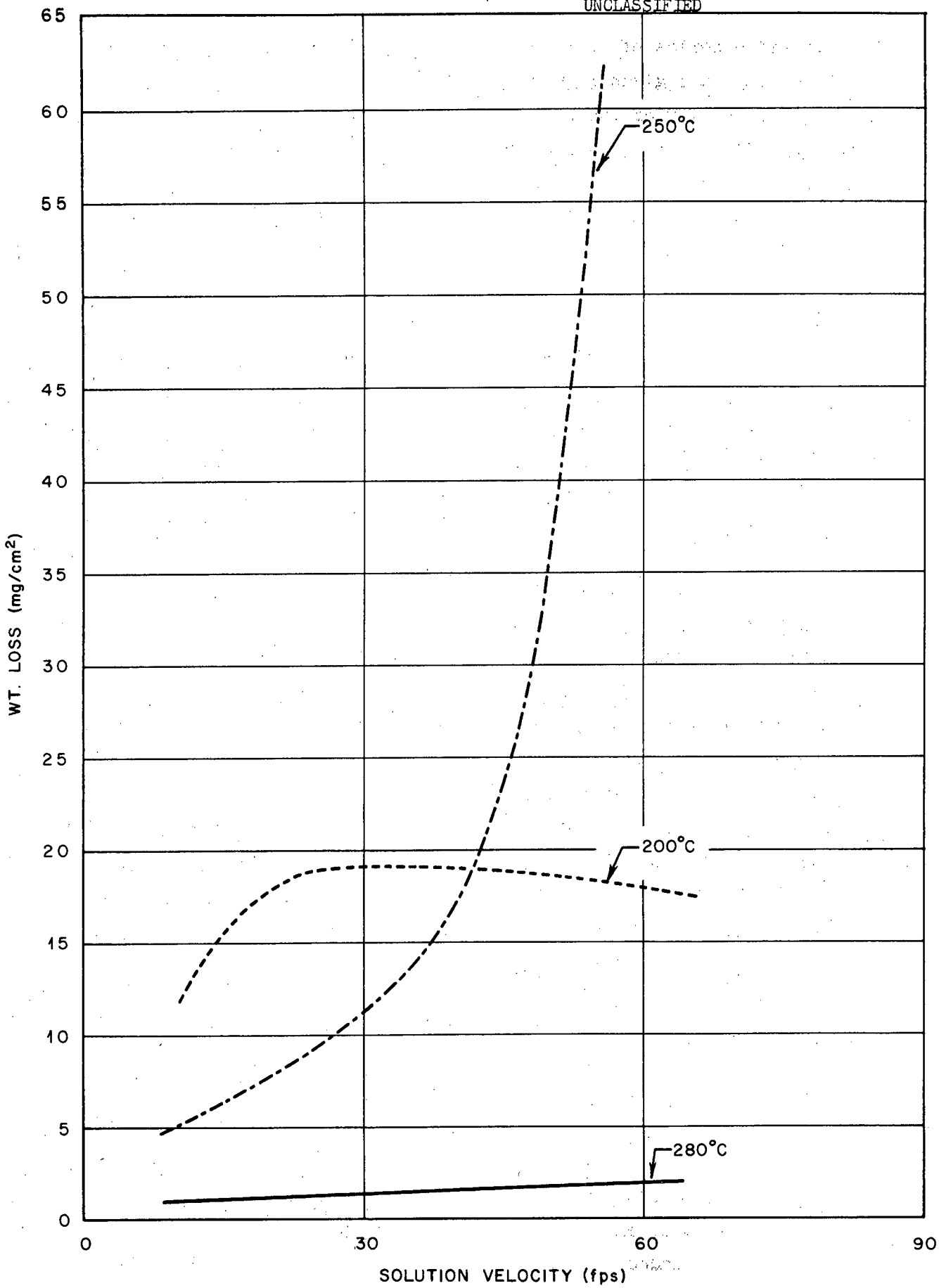

Fig. 9. Weight Losses of Type 347 Stainless Steel Coupons in 0.04m UO_2SO_4 Containing 0.04m $BeSO_4$ and 0.005m $CuSO_4$ for 500 hr

The extensive series of tests with 0.04 *m* UO_2SO_4 containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ have given promising results from a corrosion standpoint but the phase stability of the solution is definitely limited to about 250°C. Although addition of a small concentration of sulfuric acid could possibly increase the stability of the solution without greatly impairing its corrosiveness, work presently in progress with 0.04 *m* UO_2SO_4 containing magnesium sulfate and sulfuric acid appears more promising..

G. Miscellaneous Tests with Sulfate Additives.

1) Ruthenium Nitroso Sulfate.

The relatively stable ruthenium nitroso sulfate has been tested for its corrosion inhibition properties in 0.17 *m* UO_2SO_4.[10] It was found that the complex was not stable at 250°C, that ruthenium precipitated from solution as a mixture of the metal and ruthenium dioxide, and that a large increase in the hexavalent chromium concentration in solution occurred. Corrosion of stainless steel was markedly inhibited at low velocities, presumably by the chromium (VI).

In order to be sure that these observations were correct, another run was made at 250°C in a different stainless steel loop with 0.04 *m* UO_2SO_4 containing 0.025 *m* H_2SO_4, 0.01 *m* $CuSO_4$, 100 ppm Ru as ruthenium nitroso sulfate, and about 1000 ppm O_2. As in the previous run, all but about 10 ppm ruthenium precipitated from solution within 24 hrs. Chemical analysis of the scale on the type 347 stainless steel coupons after the run confirmed the previous X-ray data that the ruthenium precipitated as a mixture of the metal (roughly 2/3) and the dioxide (roughly 1/3). As before, the chromium (VI) concentration in solution increased rapidly, reaching 600 ppm within 50 hr. Normally at 250°C in this solution the chromium (VI) concentration reaches only about 5 ppm in 50 hr. Apparently the ruthenium catalyzes the oxidation of chromium either from the metal or the film to the hexavalent state.

Figure 10 is a plot of the weight losses <u>versus</u> velocity of the type 347 stainless steel coupons in this run and in an identical run with no ruthenium added. As can be seen, marked inhibition of corrosion

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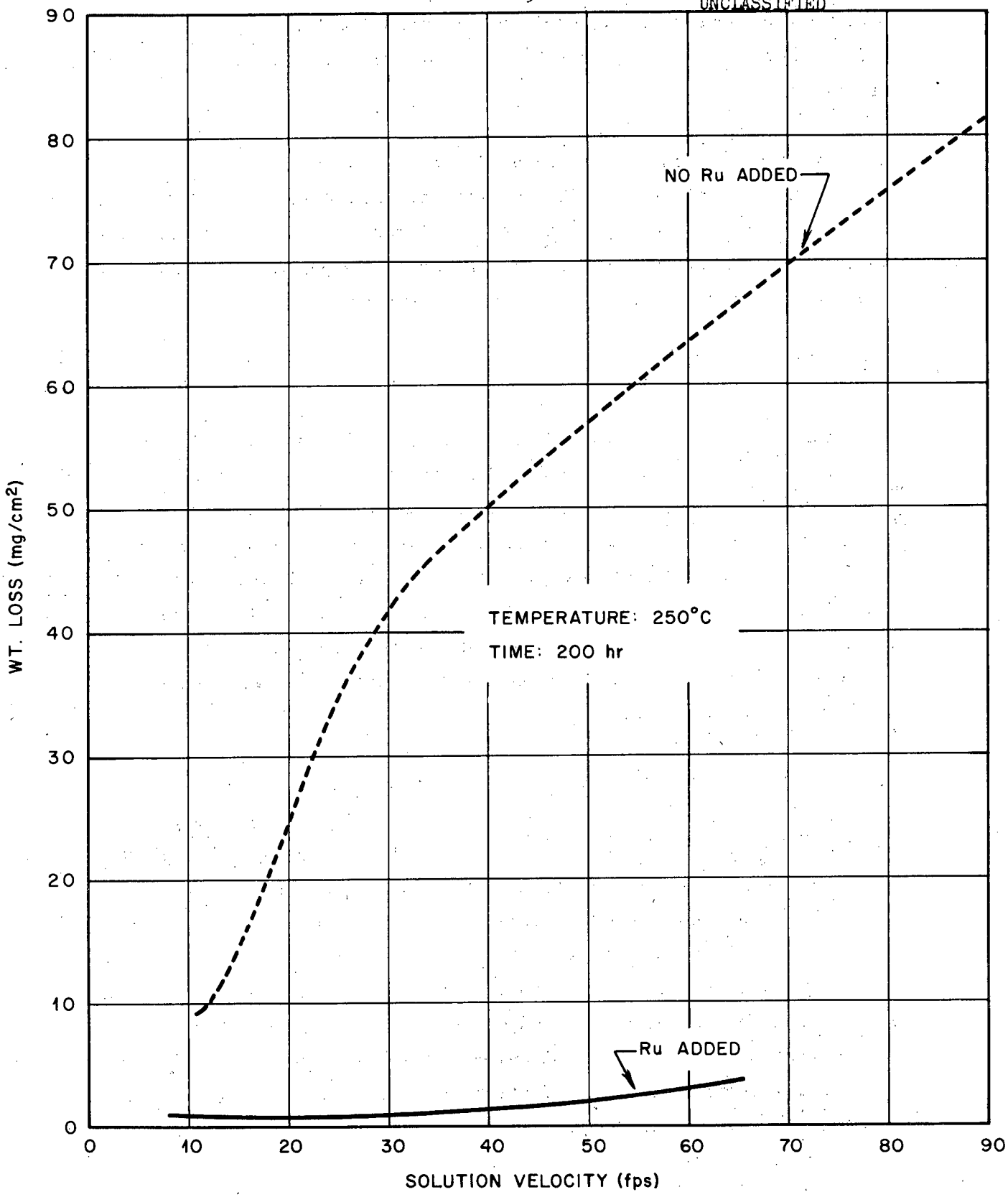

Fig. 10. Weight Losses of Type 347 Stainless Steel Coupons in 0.04 m UO_2SO_4 Containing 0.025 m H_2SO_4, 0.01 m $CuSO_4$ and 100 ppm Ruthenium as $(RuNO)_2(SO_4)_3$

occurred, presumably as a result of the chromium (VI). Thus, any direct effect that the ruthenium may have on corrosion is masked by the secondary effect.

In view of the rapid rate of oxidation of chromium to the hexavalent state, it is possible that the addition of ruthenium to in-pile solutions may result in a residual concentration of chromium (VI) which presumably would be an effective corrosion inhibitor. As a result, further tests are planned to verify and extend the present results.

2) Lithium Sulfate.

The inhibition of corrosion of stainless steel by lithium sulfate added to 0.17 *m* UO_2SO_4 [11] was deemed sufficient to warrant in-reactor investigation. For several reactor-related reasons and for comparison with previous in-reactor runs, the solution chosen was 0.17 *m* UO_2SO_4 containing 0.20 *m* Li_2SO_4, 0.10 *m* H_2SO_4, and 0.02 *m* $CuSO_4$. Quartz tube tests showed the solution to be phase stable to at least 295°C. Prior to making the in-reactor test, two out-of-reactor tests were made, one at 280 and 295°C to check further the solution stability, and one at 250°C to investigate corrosion.

The results of the out-of-reactor tests are shown in Figure 11 as a plot of the weight losses of the type 347 stainless steel coupons against velocity. For comparison, the results of tests with 0.17 *m* UO_2SO_4 without additives are also shown. As can be seen, corrosion of stainless steel was somewhat greater in the solution containing the lithium sulfate, copper sulfate, and sulfuric acid than in the solution without additives. The increased corrosion was undoubtedly due to the large amount of sulfuric acid added. However, the in-reactor test showed that the corrosion of Zircaloy-2 was inhibited by the additives and the in-reactor corrosion of stainless steel was not significantly greater.[12] The solution was phase stable in both the in-reactor and out-of-reactor tests.

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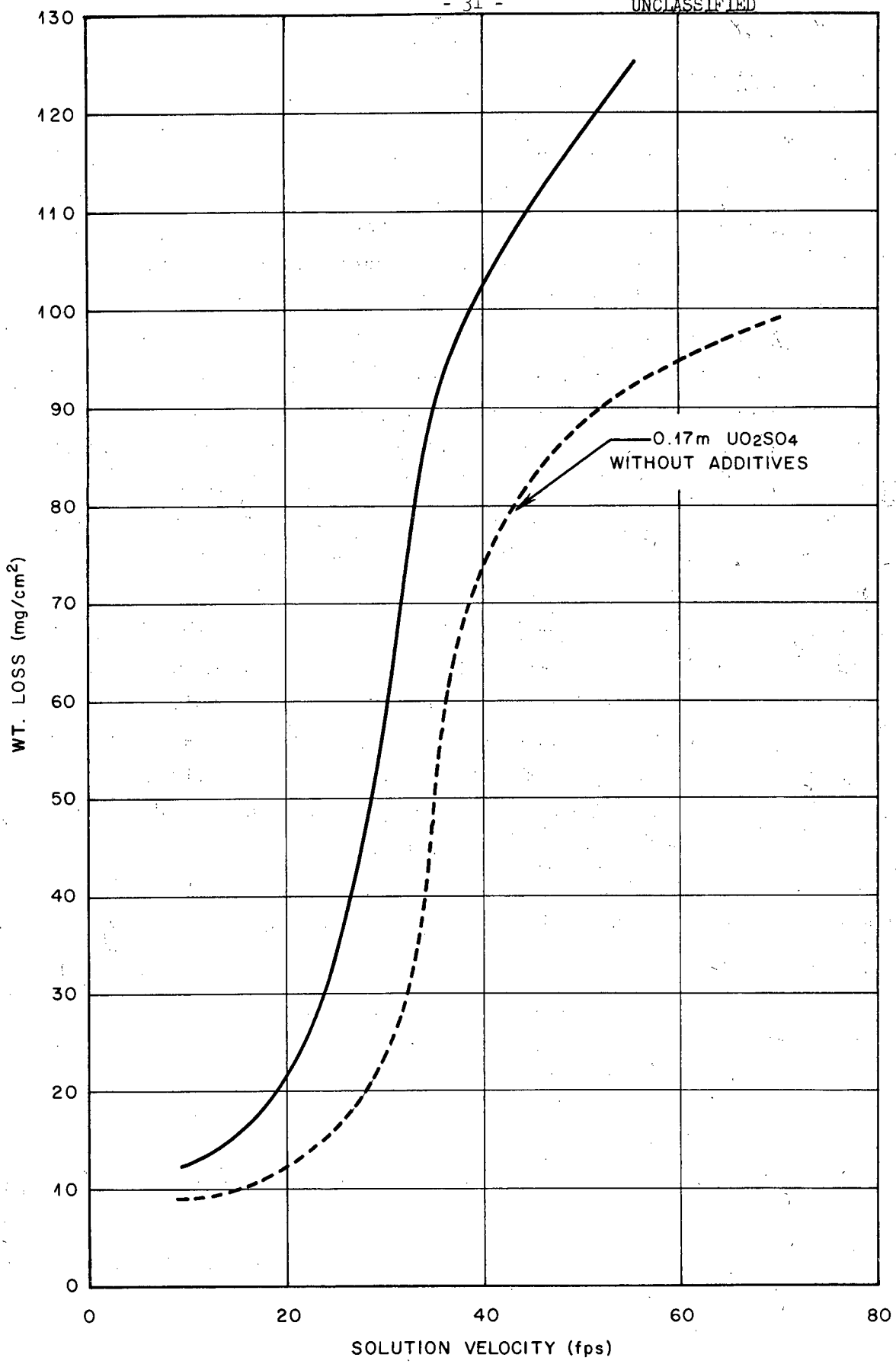

Fig. 11. Weight Losses of Type 347 Stainless Steel Coupons in 0.17m UO_2SO_4 Containing 0.2m Li_2SO_4, 0.1m H_2SO_4 and 0.02 m $CuSO_4$ at 250°C for 200 hr

H. Tests of Inhibitors in Sulfuric Acid.

The corrosion of stainless steel by sulfuric acid in a titanium system relatively free from corrosion products was reported last quarter to have a linear relationship with the pH of the solution calculated for 250°C.[13] This quarter the effects of several inhibitors were investigated for the purpose of similarly relating the degree of inhibition to the pH or some other property of the solution. The inhibitors used were $K_2Cr_2O_7$, $MgSO_4$, Li_2SO_4, and UO_2SO_4. The conditions of the runs and the results are listed in Table IV. As expected, chromium (VI) as potassium dichromate was very effective as an inhibitor. Since the small amount added would not affect the pH or ionic strength significantly, its effect was more likely due to a catalytic effect, perhaps by an adsorption process as postulated elsewhere.[14] The magnesium sulfate at the 0.02 *m* level gave very erratic and anomalously high corrosion at 13 fps and a corrosion rate at 68 fps higher than that predicted from the pH vs log corrosion rate curve given previously.[13] At the 0.05 *m* level both magnesium sulfate and lithium sulfate gave substantial inhibition but again the corrosion rates were greater than predicted. The failure of the prediction possibly means that magnesium sulfate and lithium sulfate are not completely ionized at 250°C. Uranyl sulfate at the 0.02 *m* level had little effect and gave rates higher than predicted which very likely indicated that hydrolysis, complex formation, and incomplete ionization should be taken into account for a full understanding of corrosion at 250°C in such solutions.

TABLE IV

Conditions of Runs with 0.05 *m* H_2SO_4 Containing Various Inhibitors at 250°C in a Titanium System. (All Runs 200-hr)

Run No.	Additive	Concentration *m*	Calculated pH at 250°C	Flow Rate fps	Weight Change mg/cm²	Defilmed Corr'n Rate mpy	Predicted Corr'n Rate* mpy
G-92	none	-	1.46	13	13	27	-
					14	30	-
				68	210	450	-
					210	450	-
G-97	$K_2Cr_2O_7$	0.002 (200 ppm Cr VI)	1.46	13	0.4	0.8	-
					0.6	1.4	-
				68	38	**	450
					46	**	450
G-98	$MgSO_4$	0.02	1.69	13	200	410	-
					250	520	-
				68	150	320	150
G-99	$MgSO_4$	0.05	3.13	13	9.5	20	-
					8.3	18	-
				68	38	80	0.3
					41	86	0.3
G-100	Li_2SO_4	0.05	3.16	13	2.3	4.9	-
					2.4	5.1	-
				68	11	24	0.2
					12	26	0.2
G-101	UO_2SO_4	0.02 (assuming no complexing or hydrolysis of the uranyl ion)	1.69	13	10	22	-
					12	26	-
				68	210	450	150
					280	600	150

* Corrosion rate predicted from pH vs log corrosion rate curve given previously.[14]

** Pins were filmed over except for small areas at top and bottom of pin where turbulence occurs. Corrosion rate was calculated from weight loss and the measured area of corroded metal.

IV. LABORATORY CORROSION STUDIES (J. L. English, D. N. Hess, P. D. Neumann, and J. C. Griess)

A. Stress-Corrosion Cracking.

1) Stress-Corrosion Cracking by Chloride-Containing Cooling Water.

The stress-corrosion cracking behavior of type 347 stainless steel and a number of other alloys of interest to the Homogeneous Reactor Project has been investigated under conditions in which pipe bends of the materials under consideration were heated internally with 60 psig steam at approximately 150°C and cooled on the external surfaces by chloride-containing potable water. The construction and operational characteristics of the pipe-bend test have been reported previously along with the results of initial tests.[15,16,17,18] Testing has been continued to determine the effects of annealing, surface condition, and cathodic protection on the cracking sensitivity of type 347 stainless steel and to examine the cracking behavior of other alloys. A test was also initiated to determine the cracking susceptibility of type 347 stainless steel under conditions in which chloride-containing potable water was allowed to drip on the surface of the heated pipe at a slow rate so that rapid vaporization of the water occurred. The type 347 stainless steel pipe bends were cold formed from 1/2-in Sch 40 welded pipe. When available, the same pipe size was used in forming bends from the other alloys included in the test. In a few cases, 1/2-in tubing was used for the latter.

Figure 12 is a photograph showing the typical appearance of the pipe bends in the spray test apparatus after completion of a 1000-hr run. Holes drilled in the copper cooling tubes mounted near the inner surface of the bends permitted the pipe surfaces to be continually and completely wetted by the chloride-containing water during test. Heavy accumulations of solids appeared on the pipe surfaces as a result of vaporization and drying of the cooling water. The initial chloride content of the potable water ranged between 3 and 6 ppm; at the end of 1000-hr runs, the chloride content in the deposited scale was 150 ppm or greater. The major constituents in the scale were carbonate and sulfate salts of calcium and magnesium.

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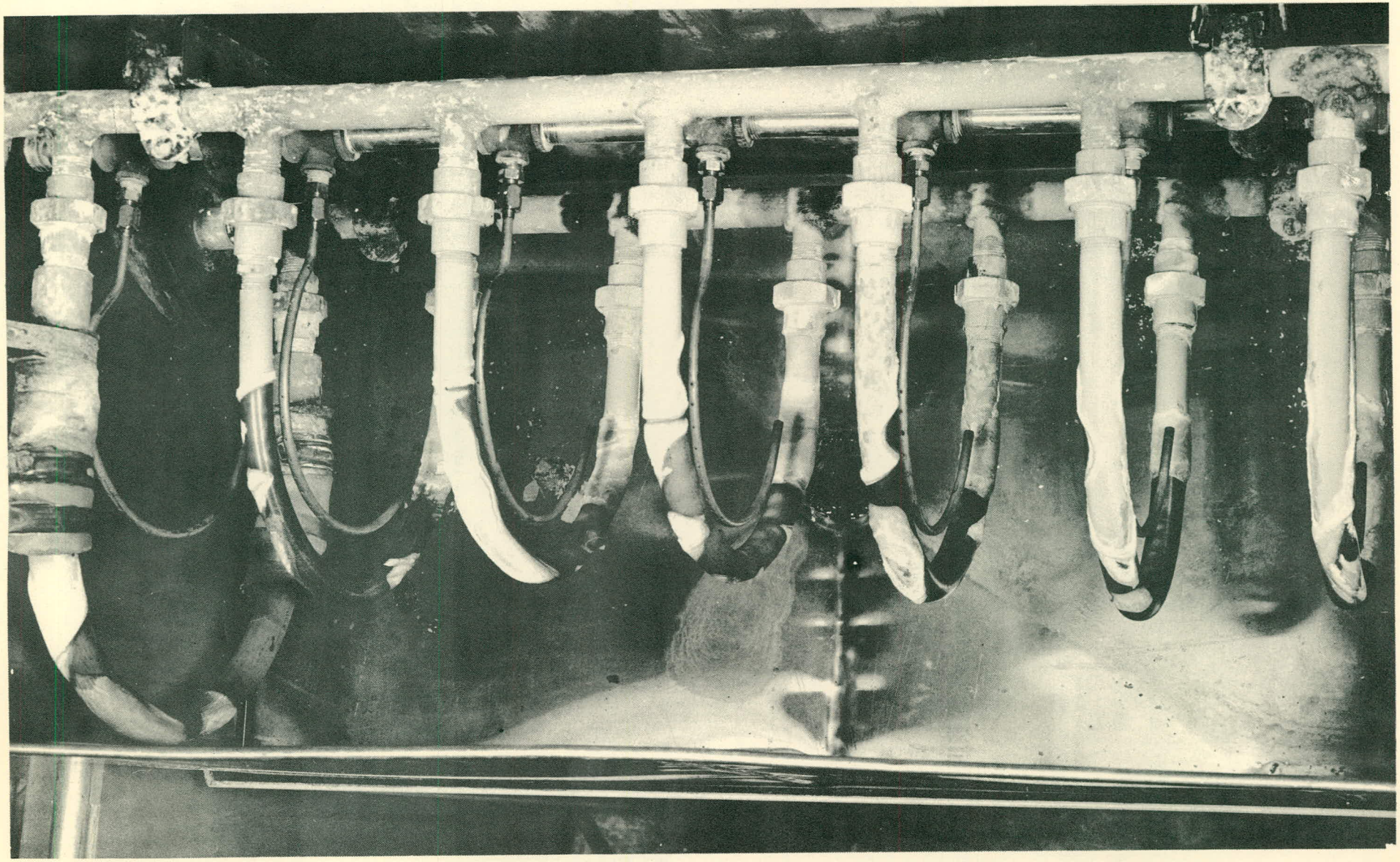

Figure 12. Typical Appearance of Steam-Heated Pipe Bends after 1000-hr of External Cooling by Chloride - Containing Potable Water.

Three approaches were studied to eliminate or minimize cracking in type 347 stainless steel. One approach consisted of annealing the pipe bend at 1950°F (1066°C) for 1/2 hr. In a second case, the cold-formed pipe was shot blasted to place the external surfaces under compressive stresses. And finally, an attempt was made to employ cathodic protection as a means for eliminating cracking. In the latter case, one-half of the surface of a cold-formed pipe was wrapped with 1/16-in dia aluminum wire placed on 1/2-in centers. The remaining half of the pipe was not wrapped. The results of the above tests with type 347 stainless steel and other alloys of interest appear in Table V. It should be noted that cold-formed type 347 stainless steel was cracked consistently during 1000-hr exposure times under the described conditions of test.

TABLE V

Stress-Corrosion Cracking of Steam-Heated Pipe Bends of Several Alloys Cooled with Chloride-Containing Potable Water

Material	Initial Treatment	Total Hr.	Observations
347 SS	Cold formed	1000	Many cracks
347 SS	Cold formed; annealed at 1950°F	1000	Several cracks
347 SS	Same as above	2000	No cracks
347 SS	Same as above	4990	No cracks
347 SS	Cold formed; shot blasted	4990	Crack in unblasted area extending into blasted area
347 SS	Cold formed; one-half of stressed area wrapped with aluminum wire; other half unwrapped	2000	No cracks on wrapped area; several cracks on unwrapped area
MST Gr 3 Titanium	Cold formed	4990	No cracks
Croloy 16-1 SS	Cold formed	4990	No cracks
Incoloy T	Cold formed	1990	Several cracks
Nionel	Cold formed	1990	No cracks
Inconel	Cold formed	990	No cracks

Annealing at 1950°F was not completely successful in eliminating cracking in type 347 stainless steel but a beneficial effect was evident. Cracking was eliminated on two pipe bends for periods of 2000 and 4990 hr, respectively. On a third annealed bend, cracking occurred during the first 1000 hr; the frequency of the cracks was appreciably lower than that observed on cold-formed pipes that were not subjected to the annealing treatment. A photomicrograph of one of the several cracks in the annealed pipe bend exposed for 1000 hr appears in Figure 13. Although it is not obvious from the photomicrograph of the unetched pipe cross section, the crack was of a transgranular nature. In this particular crack, the depth of penetration was approximately 90 mils into the 110-mil wall thickness during the 1000-hr test.

Placing the surfaces of a cold-formed type 347 stainless steel pipe bend under compressive stresses by shot blasting prevented cracking during a 4990-hr exposure to date. This behavior was expected since no case of chloride-induced stress-corrosion cracking of austenitic stainless steels involving compressive rather than tensive stresses has been reported in the literature. During the last 1000 hr of the present test, a small group of minor cracks developed on an unblasted surface where the pipe bend was connected to the steam manifold. From this group of cracks, a major crack extended for approximately 1/4-in into the adjacent shot blasted surface. Although it was not possible to determine the origin of the crack with certainty, the orientation suggested that it originated in the cluster of small cracks outside the blasted area. No cracks were found elsewhere on the shot-blasted surface.

The stressed area of a cold-formed pipe bend of type 347 stainless steel that was electrically coupled to an aluminum wire was resistant to cracking during a 2000-hr test. Presumably the aluminum cathodically protected the stainless steel. One-half of the surface of the bend was wrapped with 1/16-in dia aluminum wire placed on 1/2-in centers; the remaining half of the surface was left unwrapped. Cracks appeared on the unwrapped surface during the last 1000 hr of the 2000-hr test. A photomicrograph of several of the cracks appears in Figure 14.

Photo T14086

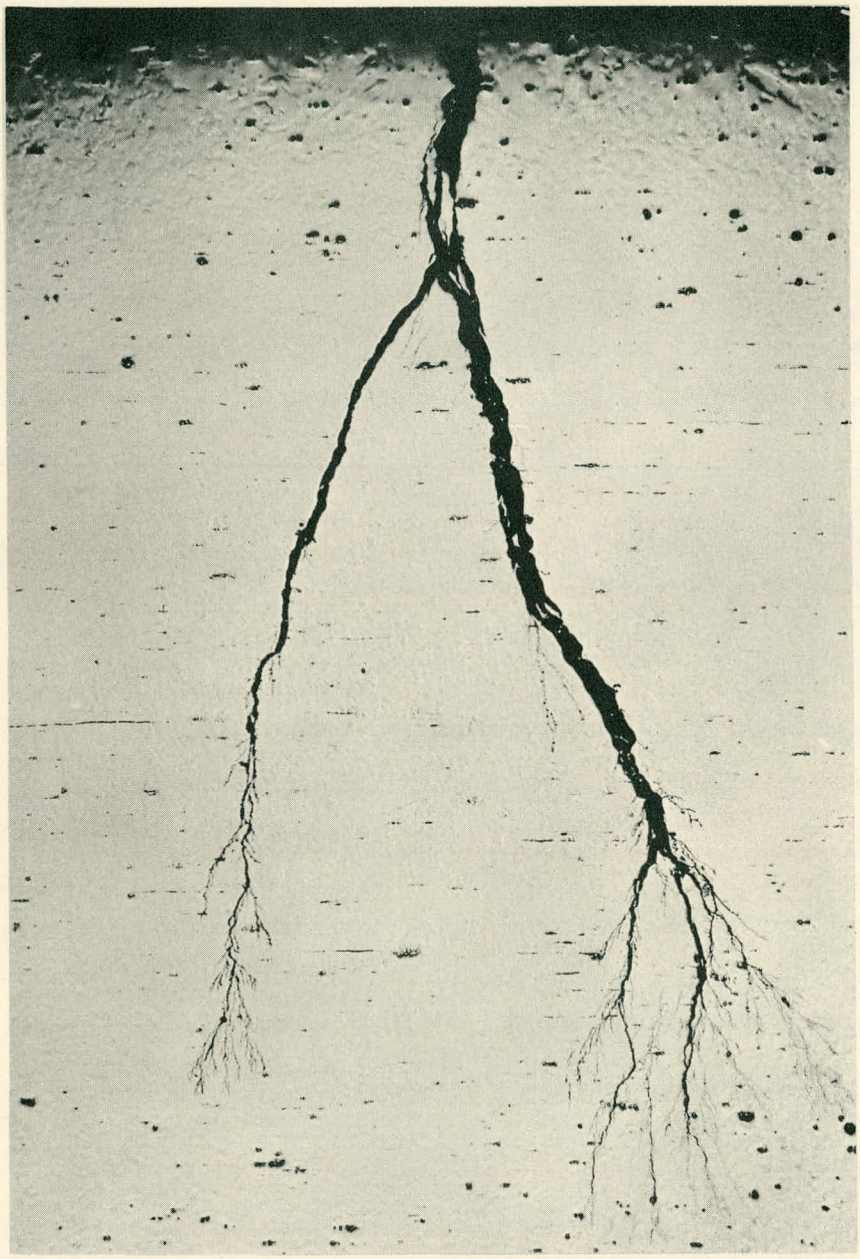

Figure 13. Crack in Annealed 1/2-in Dia Steam-Heated Type 347 Stainless Steel Pipe Externally Cooled by Chloride-Containing Potable Water for 1000-hr (Test S90-15). Unetched. Magnification 75X.

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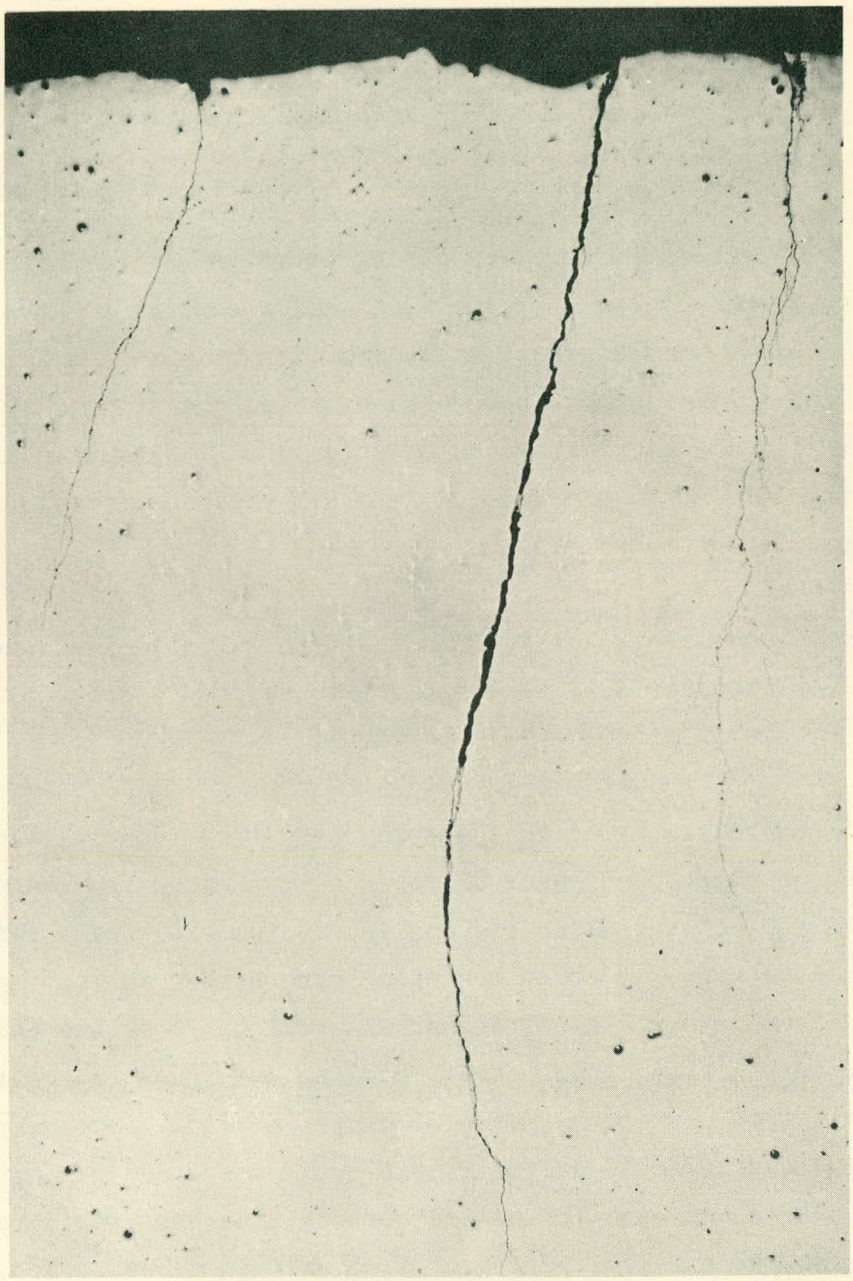

Figure 14. Cracks in a Steam-Heated Type 347 Stainless Steel Pipe Bend Not Protected by Aluminum Wire During 2000-hr of External Cooling by Chloride-Containing Potable Water. (The other half of the pipe cathodically protected by aluminum had no cracks.)
Unetched. Magnification 75X.

The stress-corrosion cracking behavior of four alloys with nickel contents ranging from 1% in Croloy 16-1 stainless steel to 80% in Inconel was examined in the spray-bend test. The four alloys - Croloy 16-1 stainless steel, Incoloy T, Nionel, and Inconel - were tested in the cold-formed condition. MST Gr 3 titanium was also tested in the cold-formed condition. The latter material and Croloy 16-1 stainless steel have resisted cracking for 5000 hr thus far. No cracking of Nionel or Inconel was observed during exposure periods of 2000 and 1000 hr, respectively. Incoloy T, an alloy similar to Incoloy in composition but containing a small addition of titanium for improved mechanical properties, cracked during the second 1000-hr run of a 2000-hr test. Photomicrographs of several of the cracked areas appear in Figure 15. As in the case of type 347 stainless steel, cracking occurred transgranularly.

The five alloys above, as well as the type 347 stainless steel pipe bends described earlier, were subject to varying degrees of pitting attack by the chloride-containing water.

A test, somewhat similar to the spray bend test, was started during the past quarter. The major difference in the new test was the rate at which the cooling water was applied to the external surface of steam-heated type 347 stainless steel pipe bends. In the spray test, continuous and complete wetting of external surfaces was maintained whereas in the present drip test, cooling water was restricted to one small area of pipe by means of drop-type flow. The drop rate was approximately 10 to 15 drops (2 to 2.5 ml, measured) per minute. Each drop upon contact with the heated surface underwent rapid vaporization so that for some finite period of time between drops no cooling water (electrolyte) remained on the surface.

Two cold-formed pipe bends of type 347 stainless steel were tested in the above manner for 1000-hr. Between 120 and 150 liters of chloride-containing cooling water contacted each pipe bend during the 1000-hr interval. A photograph of the drip-bend test after the run is included in Figure 16.

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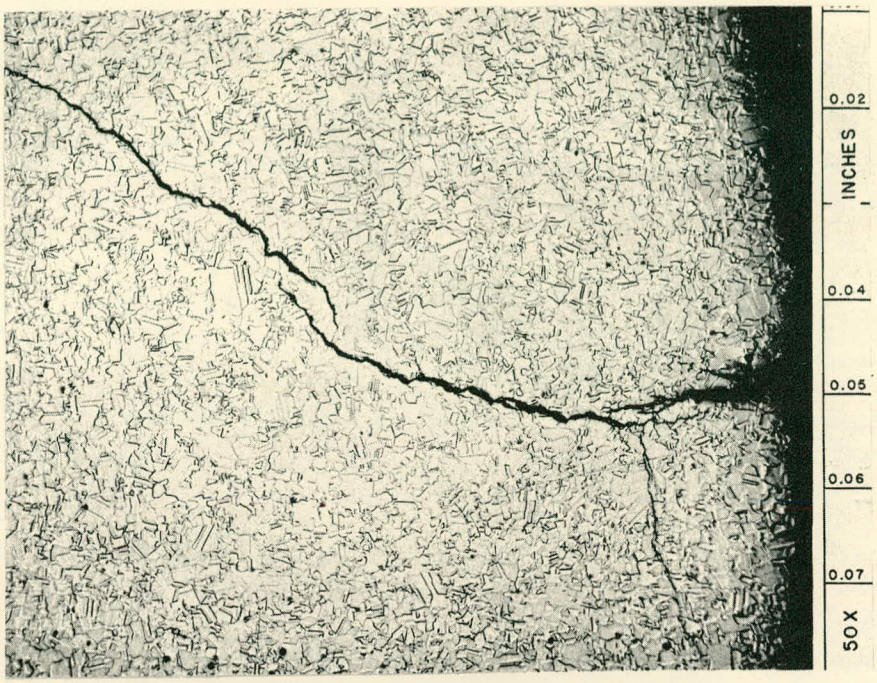

a. Magnification 50X.

Photo T14834

b. Magnification 250X.

Figure 15. Cracks in Steam-Heated Incoloy T Pipe Bend after 2000-hr of External Cooling by Chloride-Containing Potable Water. (Test S90-18). Etched in Glyceria-regia.

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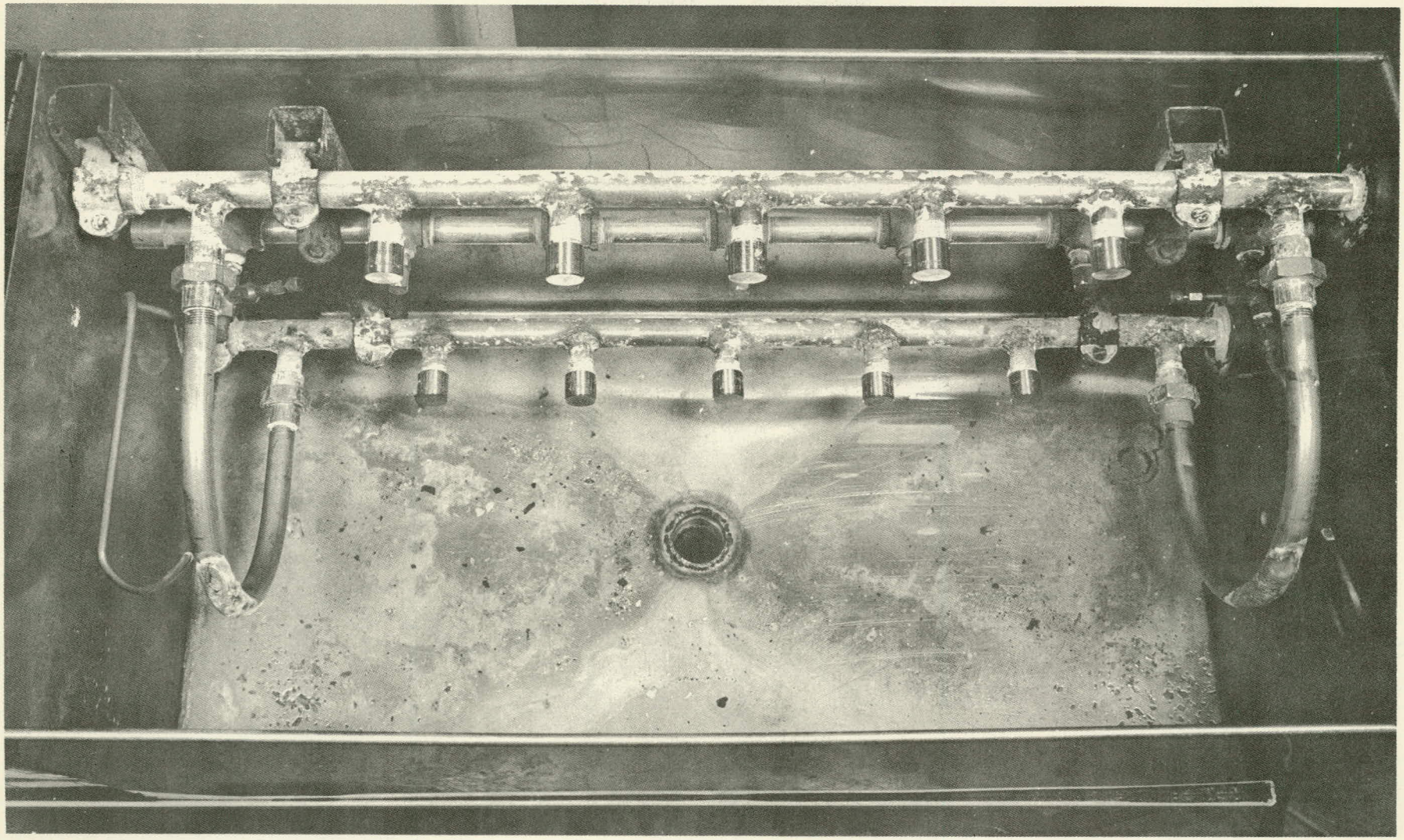

Figure 16. Type 347 Stainless Steel Drip-bend Test after 1000-hr of Contact by Chloride-Containing Potable Water.

Considerable quantities of scale formed on the surface contacted by the cooling water during the 1000-hr run. The chloride content of the scale removed from one of the pipe bends was 220 ppm; the scale from the second pipe bend contained 1250 ppm of chloride. After cleaning, the area contacted by the cooling water was carefully examined for cracks, visually, microscopically, and by dye penetrant. No cracks were found on either pipe; the test will be continued.

2) Stress-Corrosion Cracking by High-Temperature Chloride-Containing Water.

Corrosion tests have been continued to determine the stress-corrosion cracking behavior of a number of alloys at 300°C in distilled water containing oxygen and 100 ppm of chloride. The initial water pH was adjusted to values of 2.8, 6.5, and 10.5 using either sodium hydroxide or hydrochloric acid. Standard U-bend specimens were used. Among the alloys tested were a group of austenitic stainless steels, a ferritic stainless steel, and several high-nickel content alloys. The results of the tests appear in Table VI. Initial results have been reported previously.[19]

Generally, the austenitic stainless steels were found susceptible to cracking in most of the chloride-containing environments. The exceptions thus far include: (1) type 304L stainless steel after 500 hr in pH 2.8 water; (2) type 316 stainless steel after 500 hr in pH 2.8 water; and (3) type 321 stainless steel after 500 hr in pH 10.5 water. Extended exposure time for these alloys may produce cracking. With one exception, Carpenter 7-Mo stainless steel was resistant to cracking in the environments tested. The exception was the fully-hardened alloy in pH 2.8 water after 100-hr. Croloy 16-1 stainless steel exhibited cracks after 200-hr in pH 6.5 water but was not susceptible to cracking after 600-hr in pH 2.8 water nor after 1500-hr in pH 10.5 water. The pH 2.8 test was stopped after 600-hr because of excessive corrosion attack on the specimens. A photomicrograph of a crack formed in Croloy 16-1 stainless steel during 200-hr in pH 6.5 water appears in Figure 17. Incoloy developed cracks in pH 2.8 water during a 500-hr test but did not crack after 400 to 500 hr

TABLE VI

Stress-Corrosion Cracking Behavior of Various Alloys at 300°C in Air-Saturated* Distilled Water Containing 100 ppm of Chloride

Alloy Type	Condition Prior to Stressing	Initial Water pH	Total Hr	Observations
304 SS	Annealed	2.8	100	Cracks
	Annealed	10.5	100	Cracks
	Sensitized	2.8	200	Cracks
	Sensitized	10.5	400	Cracks
304L SS	Annealed	2.8	500	No cracks
309SCb SS	Annealed	2.8	500	Many cracks
316 SS	Annealed	2.8	500	No cracks
321 SS	Annealed	2.8	200	Cracks
	Annealed	10.5	500	No cracks
Carpenter 7-Mo SS	Annealed	2.8	1000	No cracks
	Annealed	10.5	600	No cracks
	Full-hard	2.8	100	Cracks
	Full-hard	10.5	400	No cracks
Croloy 16-1 SS	Annealed	2.8	600	No cracks
	Annealed	6.5	200	Cracks
	Annealed	10.5	1500	No cracks
Incoloy	Annealed	2.8	500	Cracks
	Annealed	6.5	400	No cracks
	Annealed	10.5	500	No cracks
Nionel	Annealed	2.8	300	Cracks
	Annealed	6.5	300	Cracks
	Annealed	10.5	300	No cracks

* Saturated with air at room temperature.

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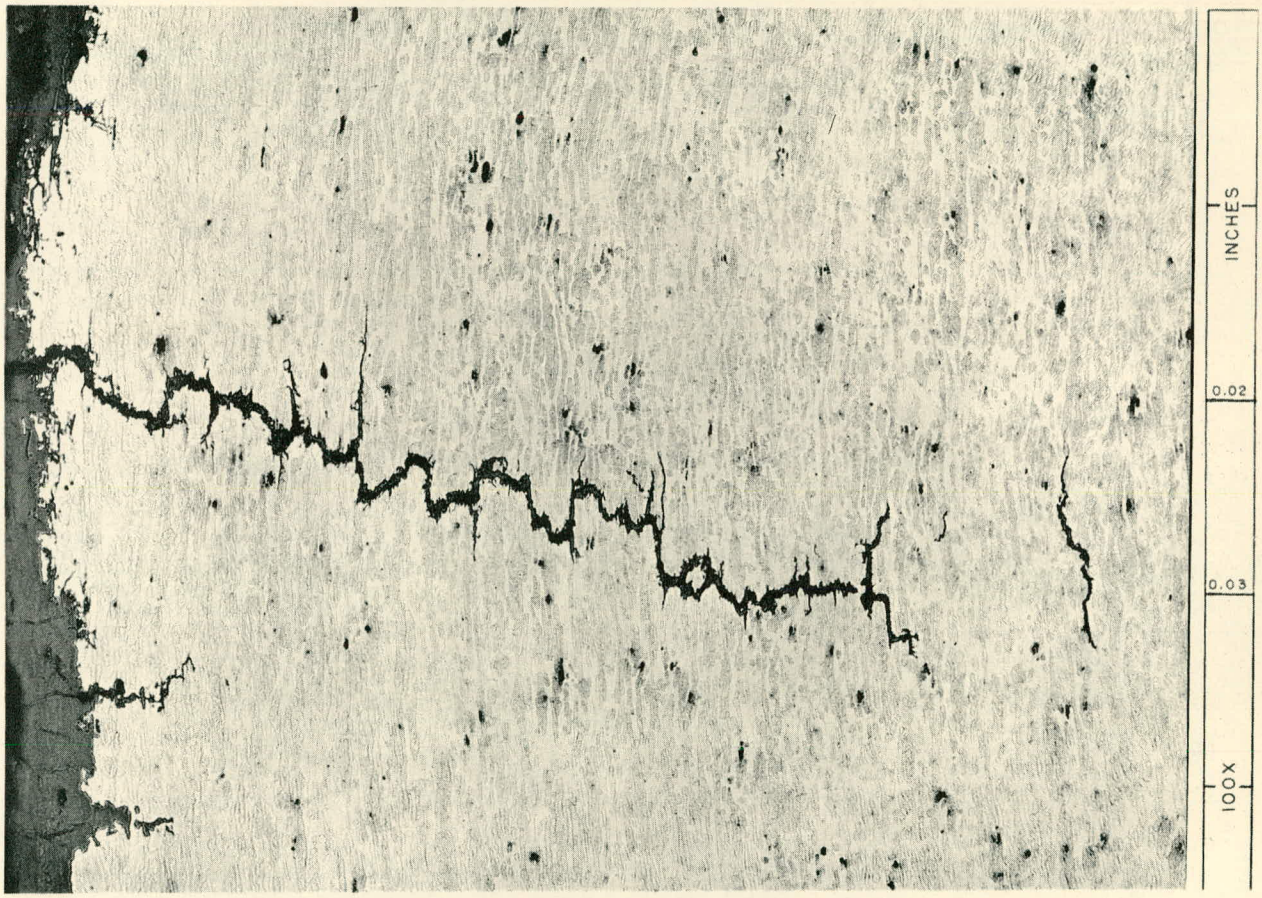

Figure 17. Crack in Croloy 16-1 Stainless Steel Exposed for 200-hr at 300°C in pH 6.5 Water Containing 100 ppm Chloride. Etched in glyceria-regia. Magnification 100X.

in pH 6.5 and 10.5 water. Nionel cracked after exposure periods of 300-hr in pH 2.8 and 6.5 water but was resistant to cracking after 300-hr in pH 10.5 water.

Thus far, the experimental data indicate that under conditions where both oxygen and chloride are present, the high-nickel alloys such as Nionel and Incoloy are more resistant to cracking in an alkaline environment (pH 10.5) than the austenitic stainless steels but are no more resistant to cracking than the austenitic stainless steels at pH values of 2.8 and pH 6.5. The tests are being continued in those cases where cracking has not been observed.

3) Stress-Corrosion Cracking by Boiling Chloride-Containing HRT Solution.

Studies are being continued on the stress-corrosion cracking behavior of type 347 stainless steel in boiling uranyl sulfate solution containing chloride ions. Tests this quarter have been concerned with resolving the effect of the individual components of a simulated HRT fuel solution on cracking behavior and with investigating the effect of pre-formed films on the prevention of cracking. Results of these tests will be included in a future report.

B. Miscellaneous Corrosion Tests.

As in the past, a number of corrosion tests were made on materials of possible interest to the Homogeneous Reactor Project. The materials include niobium, type 17-4 PH stainless steel, Croloy 16-1 stainless steel, Incoloy, and Rexalloy.

1) Niobium.

Niobium metal was supplied as 0.187-in thick plate by the Fansteel Corporation in Chicago, Illinois. The plate was cold-reduced further by the ORNL Metallurgy Division to 0.080-in thickness. Specimens prepared from the sheet were tested in two solutions: boiling 5% HNO_3 and 0.04 *m* UO_2SO_4 containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$.

Specimens were tested at atmospheric boiling, 200 and 300°C in the latter solution. A stress-corrosion cracking test was run also in the boiling uranyl sulfate solution containing 50 ppm of chloride as potassium chloride. A summary of the corrosion data appears in Table VII.

TABLE VII

Corrosion of Niobium Metal in Several Environments

Medium	Temp. (°C)	Atmosphere	Total Hr	Corrosion Rate (mpy)
UO_2SO_4 Solution*	Boiling	Air	1000	< 0.1
UO_2SO_4 Solution*	200	150 psi O_2	1000	Negligible
UO_2SO_4 Solution*	300	150 psi O_2	500	Unsatisfactory
UO_2SO_4 Solution* with 50 ppm chloride	Boiling	Air	1000	0.1; no cracks
5% HNO_3	Boiling	Air	1000	0.1

* 0.04 *m* UO_2SO_4 with 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$

In all cases except one, the observed corrosion rates were 0.1 mpy or less. The metal retained its original metallic luster in boiling solutions although some shallow pitting attack (< 0.5 mils) was noted. At 200°C, the specimens acquired a thin film and developed no pits. At 300°C in the oxygenated uranyl sulfate solution, specimens underwent catastrophic attack as shown in Figure 18 during a 500-hr exposure. Severe exfoliation of the specimens occurred.

Although not expected to crack, a stress-corrosion cracking test was run in the boiling uranyl sulfate solution containing 50 ppm of chloride. No cracking was observed during a 1000-hr test.

On the basis of the catastrophic type of corrosion attack encountered, niobium could not be used in uranyl sulfate solution at 300°C and

Photo 3078

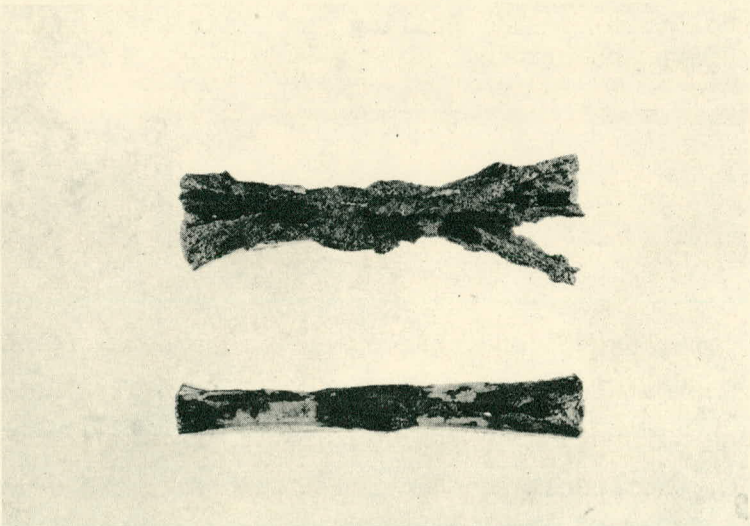

Figure 18. Catastrophic Attack on Niobium Specimens Exposed for 1000-hr at 300°C in Oxygenated 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ Solution. Magnification 2X.

probably somewhat lower. In addition, its tendency toward pitting attack in the environments tested would cause some hesitancy in advocating its use for reactor-related applications.

2) Type 17-4 PH Stainless Steel.

Type 17-4 PH stainless steel, a precipitation-hardening alloy, has been of considerable interest to the Homogeneous Reactor Project during the past several years because of its favorable mechanical properties which make it a promising material for use in bolts, valve stems and trim, etc. Corrosion tests have been completed with the alloy in various heat-treated conditions in a number of reactor-related environments. The test conditions and results are summarized in Table VIII.

The corrosion resistance of the alloy was excellent under all conditions of test and was independent of the hardness. Observed corrosion rates were 1 mpy or less. The attack on specimens in all environments resulted in uniform metal removal. No cracking in the fully-hardened condition (44 Rockwell C) was noted as has been found in earlier work in similar environments.[20]

Recently, a test was run with type 17-4 PH stainless steel bolts partially hardened to a value of 37 Rockwell C. The bolts were stressed to a room-temperature value of approximately 40,000 psi. A graphite-vaseline lubricant was used during the stressing operation; after stressing, the excess lubricant was removed by carefully wiping with a cloth. Single specimens of the stressed bolts were exposed at 280°C in the solution and vapor phases of a 0.04 *m* UO_2SO_4 - 0.02 *m* H_2SO_4 - 0.005 *m* $CuSO_4$ solution; no detectable chloride was present. The initial examination of specimens was made at the end of 500-hr at which time a crack was found in the root of a thread of the vapor-exposed bolt. Metallographic examination disclosed the crack to be approximately 70 mils in length. Numerous other small cracks were found in thread roots. Figure 19 shows photomicrographs of the 70-mil crack and other smaller cracks. Indications were that

TABLE VIII

Corrosion of Type 17-4 PH Stainless Steel in Several Reactor-Related Environments

Medium	Temp. (°C)	Atmosphere	Metal Hardness (Rockwell C)	Corrosion Rate (mpy)(1)
Distilled Water	80	Oxygen	44	< 0.1
Distilled Water	Boiling	Air	32	0.1
UO_2SO_4 Solution(2)	80	Oxygen	44	0.2
UO_2SO_4 Solution(2)	Boiling	Air	32	0.3
UO_2SO_4 Solution(2)	Boiling	Air	44	0.2
UO_2SO_4 Solution(2)	300	Oxygen	32	0.3
UO_2SO_4 Solution(3)	90	Oxygen	28.5	0.8
UO_2SO_4 Solution(3)	90	Oxygen	28.5	0.6(4)
5% HNO_3 Solution	Boiling	Air	32	1.0

(1) Test time 1000-hr except 672-hr for tests in solution (3) below.

(2) 0.04 *m* UO_2SO_4 - 0.02 *m* H_2SO_4 - 0.005 *m* $CuSO_4$.

(3) 0.04 *m* UO_2SO_4 - 0.4 *m* H_2SO_4 - 0.03 *m* $CuSO_4$.

(4) Specimens pretreated 24-hr in a 0.17 *m* UO_2SO_4 - 0.4 *m* H_2SO_4 - 0.03 *m* $CuSO_4$ solution at room temperature before start of test.

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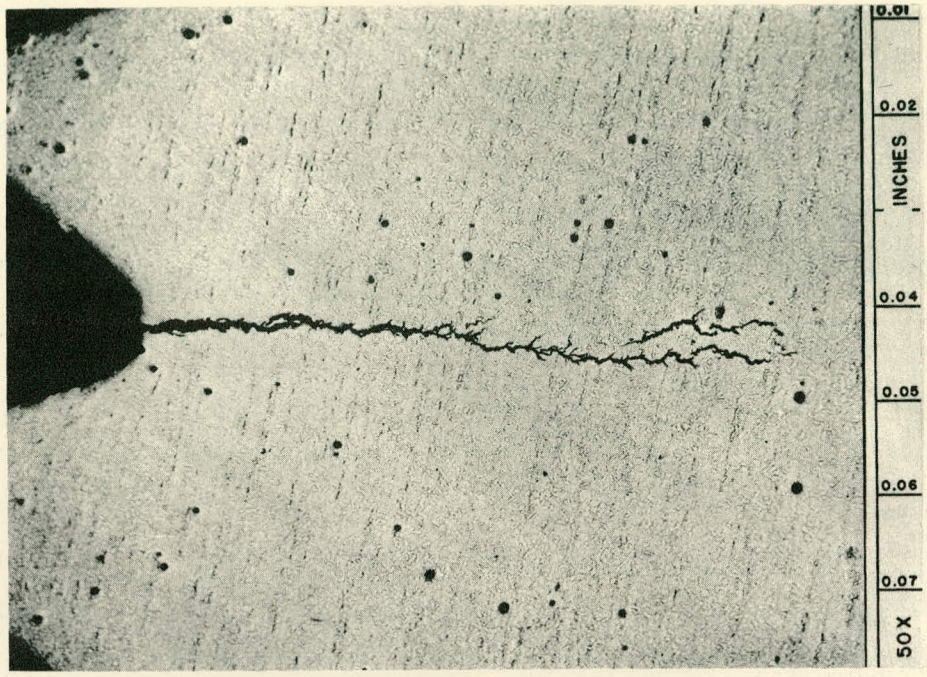
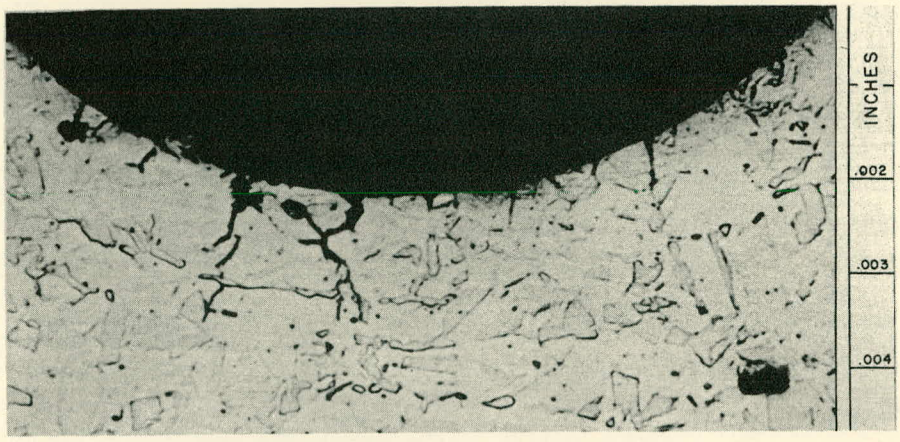


a. Major crack in thread root. Magnification 50X.



b. Small cracks in thread root. Magnification 500X.

Figure 19. Cracking in Partially-Hardened and Stressed Type 17-4 PH Stainless Steel after 500-hr at 280°C in the Vapor above 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ Solution.

the initial formation of the cracks occurred along grain boundaries. With propagation of the cracks, a transgranular path was followed. A more detailed report on the metallographic examination of the type 17-4 pH bolt has been issued.[21]

The corrosion test was continued with the original solution-exposed bolt and a newly-stressed bolt suspended in the vapor phase. After 500-hr, examination revealed complete fracture of the new vapor-exposed bolt and the existence of a large crack beneath the bolt head of the solution-exposed bolt. The total time on the latter was 1000 hr. The fracture on the vapor phase bolt occurred in a threaded area approximately 1/2-in from the bottom of the bolt.

The inconsistency of the above results regarding the cracking susceptibility of type 17-4 PH stainless steel demonstrates why the use of the alloy under tensive stresses in uranyl sulfate environments should be eliminated if possible. In cases where no substitute exists, thorough testing of the heat of steel to be used should be performed to demonstrate the adequacy of the alloy.

3) Croloy 16-1 Stainless Steel.

Croloy 16-1 stainless steel containing 16% chromium, 1% nickel, and 0.03% carbon maximum was one of several alloys considered for fabrication of heat exchanger tubes. In addition to a study on its stress-corrosion cracking behavior in high-temperature chloride-containing water, reported in a previous section, tests were run to determine the corrosion resistance of the alloy in a solution containing 0.04 *m* UO_2SO_4, 0.02 *m* H_2SO_4, and 0.005 *m* $CuSO_4$. The tests were run at atmospheric boiling, 200 and 300°C.

Corrosion specimens were prepared from two types of material, 1/8-in. thick plate and 1-in. Sch 80 pipe. Results of the tests appear in Table IX. Corrosion rates are based upon defilmed weight losses.

TABLE IX

Corrosion of Croloy 16-1 Stainless Steel by
0.04 *m* UO_2SO_4 - 0.02 *m* H_2SO_4 - 0.005 *m* $CuSO_4$ Solution

Material Type	Temp. (°C)	Total Hr	Atmosphere	Corrosion Rate (mpy)
Pipe	Boiling	200	Air	265
Pipe	Boiling	200	Air	82
Plate	Boiling	500	Air	83
Plate	Boiling	500	Air	69
Plate	Boiling	1000	Air	13
Plate	200	1000	Oxygen	4
Pipe	300	200	Oxygen	64
Plate	300	1000	Oxygen	9

The corrosion behavior of the 1-in. Sch 80 pipe was very erratic; rates of 82 and 265 mpy were obtained in duplicate boiling 200-hr tests. At boiling temperature and at 300°C, the pipe was subject to severe end-grain corrosion attack. Severe localized attack was also observed on the 1/8-in thick plate specimens at 300°C. Figure 20 shows the end-grain attack observed on the 1/8-in plate at 300°C.

In view of the poor corrosion resistance at all temperatures tested, Croloy 16-1 stainless steel is not considered an acceptable material for use in uranyl sulfate solutions.

4) Incoloy and Rexalloy 33.

Previous work with Incoloy, an alloy containing 20% chromium, 32% nickel and balance iron, showed the material to have excellent corrosion resistance to a 0.04 *m* UO_2SO_4 - 0.02 *m* H_2SO_4 - 0.005 *m* $CuSO_4$ solution at atmospheric boiling, 200 and 300°C.[22] The surface of a specimen exposed at 200°C, however, exhibited a crazed-type appearance. A photomicrograph of the surface appears in

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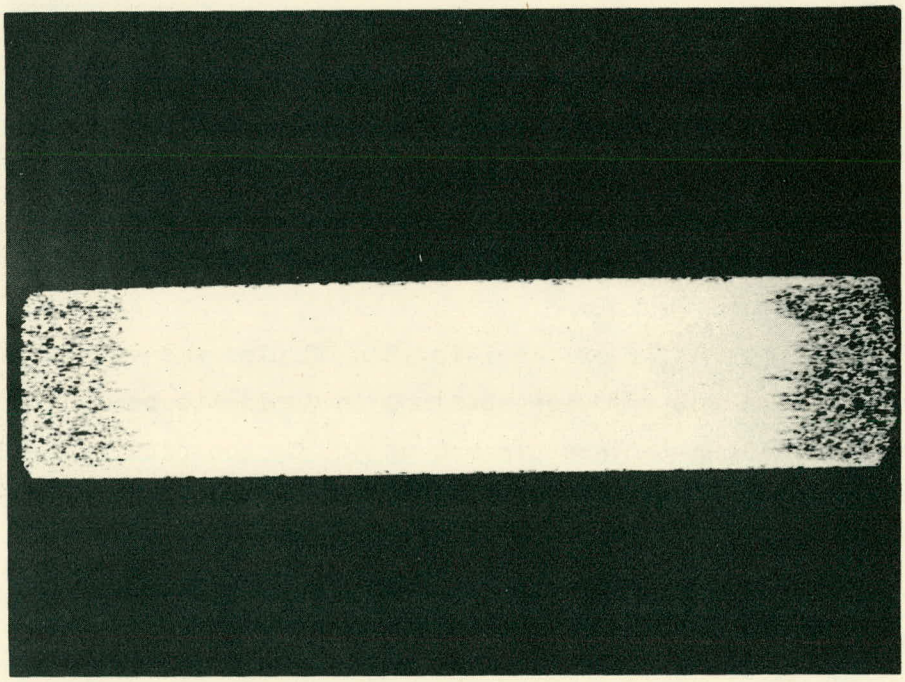

Figure 20. End-Grain Attack of Croloy 16-1 Stainless Steel Exposed to a Solution of 0.04 *m* UO_2SO_4 Containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$ for 1000-hr. As polished; Mag. 8X.

Figure 21. Recently, metallographic examination of the specimen was completed and a transverse-section photomicrograph appears in Figure 21 also. The crazing on the surface appeared to be the result of a very shallow preferential grain boundary attack. The depth of the attack was estimated to be 0.2 mil or less. No cracking was found. The observed corrosion rate on the specimen was less than 1 mpy.

Rexalloy 33, a high-carbon cobalt-base alloy containing tungsten and chromium, was found to corrode at a rate of less than 1 mpy after 1000-hr in boiling 0.04 *m* UO_2SO_4 solution containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$. Similarly, the average corrosion rate for a 1000 hr test in boiling 5% HNO_3 solution was 1 mpy. A third test environment consisted of distilled water at 300°C with an overpressure of approximately 375 psi of oxygen. The Rexalloy 33 specimen underwent severe corrosion attack in this environment; at the completion of a 300-hr test, the average corrosion rate was 37 mpy. A photograph showing the localized nature of the attack appears in Figure 22.

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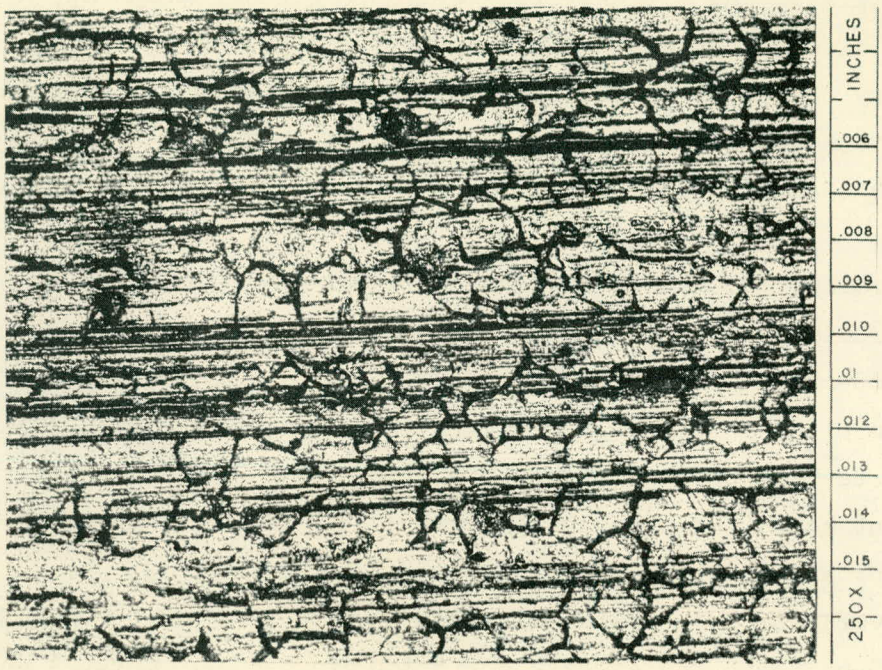

a. Surface View

b. Transverse Section

Figure 21. Attack on Incoloy after 1000-hr at 200°C by Oxygenated 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.002 *m* $CuSO_4$ Solution. Magnification 250X.

Photo 3045

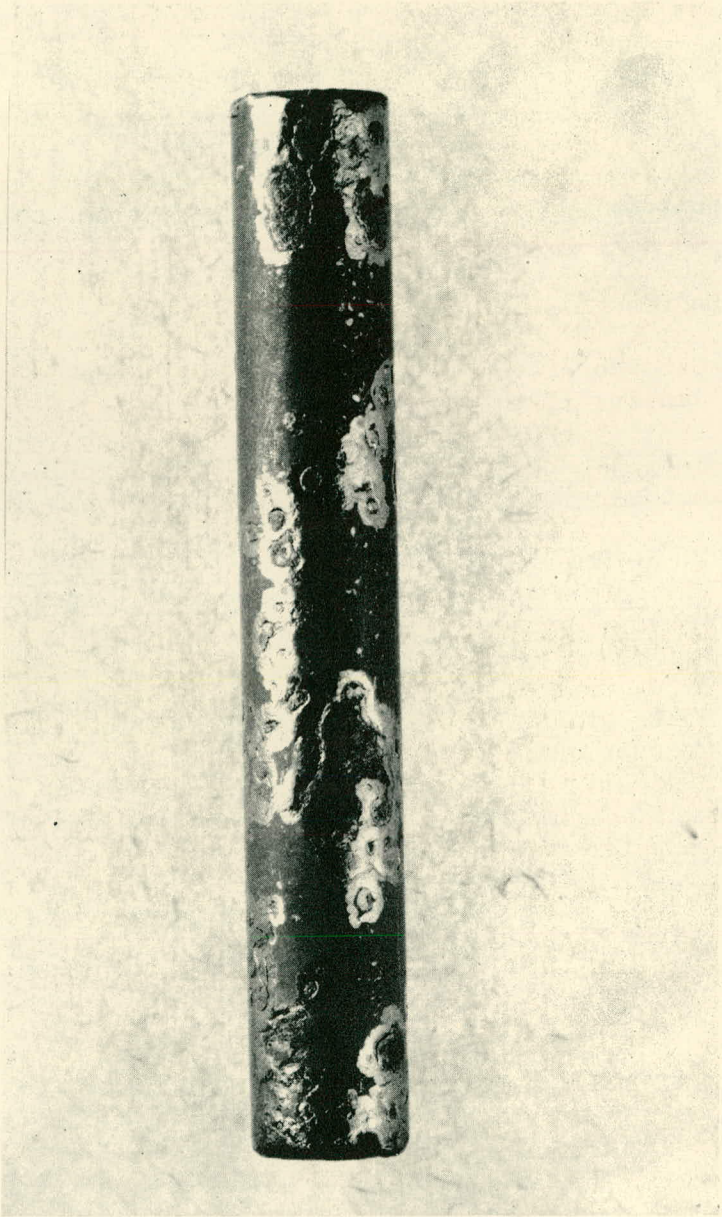

Figure 22. Rexalloy 33 Specimen after 300-hr at 300°C in Oxygenated Distilled Water. Magnification 3X.

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5. The half reaction for the oxidation of steel is not balanced since an odd number of electrons would be involved.

6. See previous reports in this series as follows:

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   January 31, 1957, ORNL CF-57-1-144, pp 5-9;
   April 30, 1957, ORNL CF-57-4-55, pp 5-9;
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