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I. SUMMARY

The second all-titanium loop, 100A Loop H, was placed in operation during the past quarter and has operated satisfactorily for more than 400 hr with uranyl sulfate solution at 250°C and approximately 1000 psi.

Loop I has been modified to provide better control of the oxygen concentration in the circulating solution in order to study the effect on corrosion of various oxygen concentrations under dynamic conditions.

A fourth test of the mockup of the Zircaloy-2 - stainless steel transition joint used in the HRT reactor vessel was completed. No additional mechanical deflections of the bellows were made, but fifty additional thermal cycles of the unit were carried out. The joint and bellows functioned properly and were leaktight. Pitted areas on the bellows, which developed during the first runs, filmed over and stopped corroding.

The series of long-term runs at 200, 250, and 300°C with solution proposed for use in the HRT was concluded. The tests had continued for roughly 20,000 hr at each temperature. It was shown that once the oxide film formed on the pins during the first test, no measurable corrosion occurred during subsequent exposures. Stainless steel and titanium stress specimens also exposed during about the latter 13,000 hr of these tests gave no evidence of stress-corrosion cracking.

In a study of the effect of heat treatment on corrosion of type 347 stainless steel, it was found that areas heated above 1950°F have somewhat lower critical velocities and lose more weight during film formation than those annealed at 1950°F.

Pretreatment of stainless steel specimens for 100 hr at 250°C with oxygenated water containing 100 or 200 ppm chromium (VI) as chromium trioxide decreased initial weight losses on subsequent exposure to uranyl sulfate solutions at lower temperatures but could not be depended on to increase the critical velocities.

Oxygen exhaustion in runs at 200, 250, and 280°C with 0.17 m UO_2SO_4 containing less than 3 ppm chloride did not produce stress-corrosion cracking of stressed type 347 stainless steel specimens in short exposures.

Increasing sulfuric acid concentrations in 0.17 m UO_2SO_4 at 250°C increased the corrosion rate of type 347 stainless steel linearly at 6 and 12 fps, but more than linearly at 70 fps.

Failure of a 1/2-in. type 347 stainless steel pipe in 0.04 m UO_2SO_4 containing 0.02 m D_2SO_4 and 0.005 m CuSO_4 in heavy water was observed when the solution was heated above the two-liquid-phase separation temperature. The pipe was severely corroded when small quantities of the heavy phase apparently came in contact with the steel.

Studies of the stress-corrosion cracking of type 347 stainless steel in boiling, halide-containing uranyl sulfate solutions have shown that chloride concentrations between 25 to 500 ppm produced cracking of type 347 stainless steel during exposure times of 25 to 500 hr. Under the same conditions, bromide ions did not produce cracking, although severe subsurface attack was found in highly stressed areas. Studies have also shown that uranyl ions conjointly with chloride ions influence the susceptibility to cracking.

Stress-corrosion tests in high-temperature water have shown that cracking will occur with chloride concentrations between 25 and 100 ppm, with either high or low oxygen concentrations, at starting pH values between 2.8 and 10.5 and at temperatures between 200 and 300°C. At 200 and 250°C, cracking seemed to occur faster and more frequently than at 300°C.

A number of alloys of zirconium were corrosion tested in simulated HRT core solution at 300°C. The following alloys exhibited very good corrosion resistance: 5 Pt - 95 Zr, 10 Pt - 90 Zr, and 5 Pd - 95 Zr. Other alloys tested were considerably less resistant than Zircaloy-2.

Type 347 stainless steel, surface hardened either by Malcomizing or Thermospray 16-C corroded excessively in uranyl sulfate solutions even at 80°C. Hastelloy R-235, Multimet and Timken 16-25-6 demonstrated a high degree of corrosion resistance to simulated core solution at 300°C. Under the same conditions,

types 431 and 414 stainless steel corroded excessively; even at boiling temperatures, the latter two alloys corroded at rates as high as 7 mpy. Type 202 stainless steel has shown a high corrosion resistance to most reactor-associated environments. In tests run to date, its corrosion resistance has been equal to that of type 347 stainless steel.

Type 420 stainless steel hardened at 50 to 52 Rockwell C corroded badly in 90°C uranyl sulfate solution of the composition used in in-pile loops. At 25°C, the corrosion rate was much less. In similar environments, both 17-4 PH and Stellite No. 6 corroded at negligible rates.

II. INTRODUCTION.

The data presented in the following sections represent the detailed results obtained during the past quarter (April 30, 1957 to July 31, 1957) by the out-of-pile 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 July 31, 1957.

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, W. C. Ulrich, T. H. Mauney, H. C. Savage, and J. C. Griess.)

A. LOOP ENGINEERING

- (1) 100A Loop H. -- The second all-titanium loop, 100A loop H, was placed in operation during the past quarter and has operated satisfactorily for more than 400 hr with uranyl sulfate solutions at 250°C and approximately 1000 psi.

Loop H was constructed of titanium for the purpose of eliminating the contamination of the circulating solution by corrosion products which originate from type 347 stainless steel loops. This is desirable in studies of the mechanism of corrosion of stainless steels. In addition, solutions that are highly corrosive to stainless steel

can be circulated in the titanium loop to determine corrosion resistance of materials other than stainless steels which are of interest to the HR program. The loop consists essentially of a model 100A Westinghouse circulating pump, three horizontal sample barrels, a pressurizer, a pressurizer mixing line, and associated loop piping. Sample barrels can be arranged in any combination as required to expose a number of corrosion specimens to various solution flow rates. Figure 1 is a photograph of the completed loop.

The sample barrels and loop piping were constructed from 1.90-in.-OD x 1.34-in.-ID titanium tubing and 1-1/2 in. schedule 80 forged titanium welding fittings. The pressurizer was made from 3-1/2-in.-OD x 2-3/4-in.-ID titanium tubing and has an over-all length of 82 in. The pressurizer mixing line is 7/8-in.-OD x 1/2-in.-ID titanium tubing. Commercially pure titanium metal (yield strength < 55,000 psi; tensile strength < 75,000 psi) was used throughout.

- (2) 100A Loop I. -- Loop I has been modified to provide close control of the oxygen concentration in the circulating solution, particularly at low concentrations (< 100 ppm). The loop is operated completely full of solution at temperatures up to 300°C. Overpressures up to 1500 psig are maintained by a Pulsafeeder feed pump and a let-down valve. The Pulsafeeder pump is a Model CPS-1, manufactured by the Lapp Insulator Company, and is rated at 1 gph at 1500 psi. The let-down valve is an air-controlled Hammel-Dahl. The valve trim consists of a spline-type plug (Hammel-Dahl size 13) fabricated of Stellite 6 and a replaceable Stellite 12 seat. The valve flow coefficient (C_v) is 0.0025 and let-down is from loop pressure to atmospheric. A stainless steel porous metal filter protects the valve by removing loop solids from the let-down stream.

Oxygen addition to the loop circulating solution is on a continuous basis and may be added to the solution in a low-pressure oxygen addition tank at low pressure, or directly into the loop. Figure 2 is a schematic drawing of the loop showing the oxygen addition and let-down system.

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Fig. 1. All Titanium 100A Loop H

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Fig. 2 Schematic Drawing of 100A LOOP I Showing Let-Down Valve and Oxygen Addition Systems

When a low oxygen concentration (< 200 ppm) in the loop is desired, the oxygen addition is made by bubbling oxygen through the loop solution in the oxygen addition tank at relatively low temperature and pressure before it is pumped back into the pressurized loop. By varying the temperature and/or oxygen partial pressure in the dump tank where the oxygen addition is made, the concentration of oxygen in the loop may be varied.

For higher oxygen concentration (> 200 ppm) in the circulating solution, the oxygen may be added directly to the pressurized loop. The rate of addition is controlled by a calibrated thermal valve.

The dissolved oxygen in the circulating solution is removed after passing through the let-down valve. A gas separator tank is provided for this purpose. The temperature of solution in the gas separator is maintained at 70 to 90°C for minimum gas solubility. The oxygen removed from the solution in the gas separator tank is collected and measured as a check of the dissolved oxygen concentration in the loop circulating solution.

Analyses of solution samples removed from the loop while operating at 290°C and 1500 psig with water (run I-47) showed dissolved oxygen concentrations of 5 to 10 ppm. Values of oxygen concentration obtained from measurements of the oxygen removed from solution in the gas separator were also in the range of 5 to 10 ppm, which was the desired concentration. This concentration of oxygen was obtained by bubbling oxygen through the solution in the oxygen addition tank at $\sim 40^{\circ}\text{C}$ and atmospheric pressure. Oxygen was then removed from the loop let-down stream in the gas separator tank at $\sim 85^{\circ}\text{C}$ and atmospheric pressure.

B. FOURTH TEST OF THE HRT CORE - PRESSURE VESSEL FLANGE AND TRANSITION JOINT MOCKUP.

A fourth 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 LOCA dynamic loop F. The first three tests were mentioned previously,^{1,2,3} and detailed reports were published elsewhere.^{4,5}

The test lasted 1201 hr, 143 hr on water and 1058 hr on fuel solution ($0.04 \text{ } m \text{ } \text{UO}_2\text{SO}_4$, $0.02 \text{ } m \text{ } \text{H}_2\text{SO}_4$, $0.005 \text{ } m \text{ } \text{CuSO}_4$). The system was checked out on water and concentrated fuel solution was added while the loop was at 100°C and 100 psi. Fifty thermal cycles were made, one per day, between 300 and 100°C . Steady state operation was at 300°C . No mechanical deflections of the bellows were made. Operation of the loop and test unit was trouble-free and routine.

Prior to disassembly, the 10-in. IPS, 1500-lb test vessel oval-ring joint was leak tested at 200 psig of helium with a mass-spectrograph-type leak detector. No leakage was observed. After disassembly of the joint and removal of the oval-ring gasket, examination of the flange grooves showed that no leakage of fuel solution into the grooves had occurred.

No leakage of fuel solution through the bellows or past the transition joint was detected during the run. After disassembly of the flanged joint, the bellows and transition joint were leak tested with 50 psig of helium and a mass-spectrograph-type leak detector and no leakage was detected. Therefore, during the four tests, the bellows and transition joint have remained sound and leaktight for 4118 hr total operating time, 3617 hr exposure to fuel solution, 166 thermal cycles, and 148 mechanical deflections.

The pitted areas on the bellows⁶ were examined closely by moving the reinforcing rings to reveal the entire crevice area between the rings and the bellows. A microscope-dial gauge indicator assembly was used again to measure the pit depths. No significant increase in pit depths was observed. Also, the pitted areas were covered with the same adherent, black film observed on other areas of the bellows, in contrast to the loose, red oxide observed in the pits after the previous tests. Therefore, since no mechanical deflections were made during this fourth test, it appears that the pitting attack was in some way caused by the mechanical deflections made during the first and second tests. X-ray diffraction analysis of the loose oxide collected from the crevice between the reinforcing rings and the bellows indicated 10 to 40% UO_2 .

The presence of reduced uranium oxide in the crevice has been observed before⁷ and indicates the absence of oxygen in the crevice. However, no excessive attack due to oxygen exhaustion was found.

The corrosion specimens in the loop were removed, scrubbed, and weighed. They were not defilmed, but were replaced in the loop for further testing. The type 304L and 347 stainless steel pins at 17 fps and the type 347 stainless steel coupons at 7 to 50 fps exposed in the loop by-pass lost small amounts of weight as did the titanium alloy pins (Ti - 6Al 4V, Ti - 3Al 5Cr, Ti - 5Al 2-1/2Sn, Ti - 4Al 4Mn) exposed at 68 fps in the loop main line. The coupon exposed at 50 to 64 fps corroded at a high rate. The Incoloy and type 309 Ssb stainless steel pins at 17 fps and the titanium RC-55, crystal-bar zirconium, and Zircaloy-2 pins at both 17 and 68 fps gained small amounts of weight.

The solution remained stable throughout the test. The increase in nickel ion concentration corresponded to a generalized corrosion rate of about 0.1 mpy. This is in good agreement with a previous isothermal test made under similar conditions⁸ and is lower than previously observed in this series of tests with mechanical deflection of the bellows.^{4,5} Further testing of the unit is in progress.

C. LONG-TERM RUNS WITH 0.04 m UO_2SO_4 CONTAINING 0.025 m H_2SO_4 and 0.005 m CuSO_4 .

Long-term runs with 0.04 m UO_2SO_4 containing 0.025 m H_2SO_4 and 0.005 m CuSO_4 at 200, 250, and 300°C were terminated after 3630, 4411, and 3611 hr, respectively. The runs were made to determine the effect of the acid concentration on corrosion and solution stability. Previous runs made with less acid are discussed below. (See Section D) Table I lists the conditions of the runs.

The solution in the present series of runs with 0.025 m H_2SO_4 was entirely stable at 200 and 250°C. At 300°C, however, during the first 1832 hr, a gradual decrease in cupric ion concentration from 360 ± 20 ppm to 270 ± 20 ppm was observed. After 1832 hr, the run was restarted with fresh solution and continued for 1078 hr. A third part of the run was made for 701 hr, also with fresh solution. Within 20 ppm, no cupric ion was lost from

TABLE I

Conditions of Long-Term Runs with 0.04 m UO_2SO_4
Containing 0.025 m H_2SO_4 and 0.005 m CuSO_4

Run No.	Temp. (°C)	Time (hr)	Average Uranium Conc. (gm U/l)	Average Copper Conc. (ppm)	Average Oxygen Conc. (ppm)	Gen. Corrosion Rate (mpv)
L-37	200°C					
1st part		1081	10.2 ± 0.3	320 ± 20	670 ± 100	0.4
2nd part		2549 (a) (3630 Total)	9.4 ± 0.4	290 ± 20	640 ± 100	0.1
M-30	250°C					
1st part		1614	10.6 ± 0.4	340 ± 20	730 ± 350	0.1
2nd part		2797 (a) (4411 Total)	10.0 ± 0.4	300 ± 30	800 ± 400	0.1
K-18	300°C					
1st part		1832	10.6 ± 1.0	360 → 270(c)	1300 ± 300	0.2
2nd part		1078 (b)	11.0 ± 1.0	320 ± 20	1300 ± 300	0.2
3rd part		701 (b) (3611 Total)	11.4 ± 0.6	340 ± 20	900 ± 400	0.2

(a) Solution from previous part of the run plus makeup.

(b) New solution used for this part of run.

(c) A 1% nitric acid rinsed 9 hr at 250°C after the first part of the run recovered 80 ppm copper.

solution during the latter two parts of the run. Examination of the analytical data showed that the pH in the first part of the run, 1.5 to 1.6, was slightly higher than in the second and third part of the test, 1.4 to 1.5; although it seems unlikely, it is possible that the precipitation of copper may have been due to the acid concentration being slightly low during the first part of the run.

Table II lists the corrosion rates of the pins exposed only in the present runs with 0.025 M H_2SO_4 determined both from the final defilmed weight loss averaged over the entire run (over-all corrosion rate) and from the difference between the intermediate and final scrubbed weight (continuing corrosion rate after film formation). The table shows that there was substantial attack on the stainless steel pins at all velocities at 200 and 250°C, but that only those pins at 20 to 42 fps at 200°C were exposed above their critical velocity and continued to corrode. Niobium generally showed continuing corrosion, particularly at the higher flow rates.

A variety of titanium and zirconium alloys were exposed in these tests after having been carried over undefilmed from previous tests (see Section D below). In the scrubbed condition, the commercially pure titanium pins showed weight gains at all temperatures. The high strength titanium alloys showed weight gains at 200 and 250°C, but corroded at 0.3 to 0.5 mpy at 300°C. With one exception Zircaloy-2 and zirconium - 2-1/2Sn pins gained weight at all temperatures. Crystal-bar zirconium pins gained weight at 200°C, but at 250 and 300°C they showed perceptible attack under the Teflon insulation. One Zircaloy-2 pin at 300°C also showed attack under the Teflon. A possible reason for this attack is discussed in Section D below. The pins so attacked showed corrosion rates of 0.03 to 0.2 mpy at 250°C and 0.8 to 1.7 mpy at 300°C.

The critical velocity of type 347 stainless steel coupons was 10 to 20 fps at 200°C, 35 to 45 fps at 250°C, and greater than 45 fps at 300°C. All coupon weight losses were greater than in runs with less acid, and weight losses at 30 to 45 fps at 250°C were severe, 100 to 300 mg/cm². However, all of this weight was lost during the first part of the runs at the end of which time, the specimens were completely filmed over.

TABLE II

Corrosion Rates in Long-Term Runs with 0.04 m UO_2SO_4
 + 0.025 m H_2SO_4 + 0.005 m CuSO_4 , 500-1500 ppm O_2

Material	Flow Rate (fps)	Over-All Corrosion Rate (mpy)			Continuing Corrosion Rates Based on Scrubbed Weights (mpy)		
		200°C (3630 hr)	250°C (4411 hr)	300°C (3611 hr)	200°C (1081 to 3630 hr)	250°C (1614 to 4411 hr)	300°C (1832 to 3611 hr)
Stainless	8	3.3	-	-	0	-	-
Steels	12	-	1.2	0.32	-	0	0
(new pins) ^a	20	5.8	2.0	0.38	1.3	0	0
	26	-	3.0	0.40	-	0	0
	34	13	6.6	0.40	14	0	0
	42	23	0	0	20	-	-
Niobium	8	0.03	-	-	0	-	-
	12	-	0.40	0	-	0.28	0
	34	-	1.8	10	-	1.9	13
	42	12	-	-	9.9	-	-

(a) Includes types 202, 304, 304 cast, 304 sensitized, 304L, 309 SCB, 347, 347 cast, 347 sensitized, 430, and 446 (defilmed).

D. CONCLUSION OF LONG-TERM RUNS WITH HRT SOLUTION.

The series of runs at 200, 250, and 300°C with the solution proposed for use in the HRT, 0.04 m UO_2SO_4 , containing various amounts of sulfuric acid and 0.005 m $CuSO_4$, were concluded. The runs with solution containing 0.006,⁹ 0.010,¹⁰ 0.015,¹¹ and 0.020¹² m H_2SO_4 have been reported previously. The present runs with a solution containing 0.025 m H_2SO_4 were discussed above. Table III gives the conditions of all of the runs. Pins of a variety of alloys were carried over from run to run throughout the test. Also, in each run, new pins were exposed.

The runs were made with increasing amounts of acid at each temperature in order to attain a solution stable with regard to hydrolytic precipitation of copper and uranium. All solutions were stable at 200°C. At 250°C, only the solutions containing 0.020 and 0.025 m H_2SO_4 were stable. At 300°C, none of the solutions were entirely stable, but as noted previously, the solution containing 0.025 m H_2SO_4 was stable for 1779 hr when the room temperature pH was 1.4 to 1.5.

All of the pins that had been exposed at 200 and 250°C for 19,342 and 20,657 hr, respectively, were defilmed. The pins that had been exposed at 300°C for 20,143 hr were carried over to another test. Table IV lists the defilmed weight losses of the stainless steel pins carried over from run to run at 200 and 250°C and compares them with the defilmed weight losses of the pins exposed in the first run only.

The very significant result of the tests is apparent in Table IV; viz., weight losses of the pins carried over for roughly 20,000 hr were, at most, only slightly greater than weight losses of pins exposed in the first test only. That is, once the oxide films formed on the pins in the first test, corrosion rates of less than 0.1 mpy occurred in subsequent exposures. This result is significant also in that the pins exposed at 19 to 42 fps at 200°C were above the critical velocity (measured on new stainless steel pins) during the last two or three runs. In other words, the oxide film that formed below the critical velocity in the HRT solution containing 0.006 m H_2SO_4 was protective for the duration of the test above the critical velocity in the HRT solution containing 0.015 to 0.025 m H_2SO_4 .

TABLE III

CONDITIONS OF RUNS WITH HRT SOLUTION

 $0.04 \text{ m } \text{UO}_2\text{SO}_4 + 0.005 \text{ m } \text{CuSO}_4 + \text{Various Amounts of } \text{H}_2\text{SO}_4$

<u>Acid Concentration m</u>	<u>L Loop 200°C</u>	<u>M Loop 250°C</u>	<u>K Loop 300°C</u>
0.006	6799	7272	8515
0.010	1139	1163	945
0.015	4093	4151	3231
0.020	3681	3660	3841
0.025	<u>3630</u>	<u>4411</u>	<u>3611</u>
Total Hours	19,342	20,657	20,143

TABLE IV

Comparison of Weight Losses of Stainless Steel Pins Exposed 20,000 hr to HMT Solution at 200 and 250°C With Pins Exposed 7000 Hr.

6799 hr at 200°C (L-32 Only)			19,342 hr at 200°C (L-32, 33, 34, 35, 36)		
Material	Flow Rate fps	Defilmed Weight Loss mg/cm ²	Material	Flow Rate fps	Defilmed Weight Loss mg/cm ²
304L	10	3.4	304 Cast	10	3.7
309SCb	10	4.9	304L	10	3.9
347	10	3.4	309SCb	10	6.2
304L	19	5.6	347 Cast	10	4.4
309SCb	19	2.1	347	10	4.0
347	19	4.2	304 Cast	19	3.9
309SCb	34	1.5	304L	19	5.4
347	34	3.9	309SCb	19	2.1
309SCb	42	3.1	347	19	5.5
			309SCb	34	3.0
			347	34	4.0
			309SCb	42	11.0

7272 hr at 250°C (M-26 Only)			20,657 hr at 250°C (M-26, 27, 28, 29, 30)		
Material	Flow Rate fps	Defilmed Weight Loss mg/cm ²	Material	Flow Rate fps	Defilmed Weight Loss mg/cm ²
304L	10	1.0	304 Cast	10	1.0
309SCb	10	1.9	304L	10	1.0
347	10	1.0	309SCb	10	5.7
304L	19	1.1	347 Cast	10	0.7
309SCb	19	2.2	347	10	1.0
347	19	1.3	304L	19	1.1
304L	38	1.2	309SCb	19	2.9
309SCb	35	3.5	347	19	1.2
347	38	1.6	304 Cast	38	1.3
			304L	38	1.3
			309SCb	35	3.1
			347	38	1.9

Various zirconium and titanium alloys, also carried over from run to run at 200 and 250°C, were defilmed. Crystal bar zirconium, Zircaloy-2, and commercially pure titanium showed zero weight losses. The high strength titanium alloys showed corrosion rates of 0.01 to 0.12 mpy.

Although the specimens exposed 20,143 hr at 300°C were not defilmed, the scrubbed weight losses and visual appearances of the specimens indicated that very little corrosion occurred after the first run. However, the high strength titanium alloys continued to lose weight throughout the series of tests corresponding to corrosion rates of 0.1 to 0.5 mpy. The zirconium specimens formed a white oxide under the Teflon insulation in the first test at 300°C. The oxide did not change appreciably in appearance during subsequent tests except on the crystal bar zirconium pins and on one Zircaloy-2 pin where it thickened slightly. During the final test (described in Section C above) the oxide on those pins thickened appreciably more and flaked off during scrubbing. The other zirconium pins gained weight throughout the series of tests.

The thick oxide was shown to be monoclinic ZrO_2 by x-ray diffraction analysis. Its formation was undoubtedly due to thermal decomposition of the Teflon at 300°C with production of fluoride ions which attacked the zirconium. Evidently crystal bar zirconium is slightly less resistant to this form of attack than Zircaloy-2 (with one exception, the reason for which is unknown) and zirconium - 2-1/2 Sn, and after 20,000 hr, the oxide became thick enough to crack and slough off.

Stress specimens of the following alloys were exposed in vapor and liquid regions during all but the first runs in this series: types 309 SCB, 347, 17-4 PH (partially hardened to Rockwell C-37), AM-350 (precipitation hardened to Rockwell C-39), and AM-350 (refrigeration hardened to Rockwell C-38) stainless steel and titanium alloys 110AM and 130AM. The specimens exposed for 12,543 hr at 200°C and for 13,385 hr at 250°C were defilmed and examined microscopically. The specimens exposed for 11,628 hr at 300°C were examined microscopically without defilming. No cracks or significantly greater corrosion due to the applied stress was observed.

A number of new stainless steel pins were exposed in each run and defilmed at the completion of the run. The weight losses of the pins are shown in

Table V. The data substantiate the generally known effects of three variables on corrosion. With few exceptions Table V shows the following: With other conditions constant, increasing the acid concentration of the solution increases the amount of metal dissolved during film formation; increasing the flow rate at a fixed temperature, and acidity has a similar effect; and at a given flow rate and acidity, increasing the temperature decreases the amount of metal dissolved during the initial period of corrosion. Also listed in Table V are the critical velocities observed in each run. At 250°C the critical velocity was greater than 35 fps and at 300°C greater than 45 fps at all acid concentrations, although initial weight losses in the solutions containing 0.020 and 0.025 m H_2SO_4 at 250°C were considerable. On the other hand, at 200°C, the critical velocity decreased significantly with increasing acid concentration. The corrosion rates for the pins exposed above their critical velocities are listed in parenthesis in Table V and also show increases with increasing acid concentration.

As has been stated, a variety of alloys was exposed in these runs. There were no significant differences in behavior between alloys within the following groups:

- (1) Types 202, 302B, 304, 304 cast, 304 sensitized, 304L, 304L sensitized, 309 SCb, 316, 316 cast, 316L, 321, 321 sensitized, 347, 347 cast, 347 sensitized, 416, 430, and 446 stainless steel, and Incoloy.
- (2) Titanium RC-55, 75A, 100A, and 150A.
- (3) Titanium - 3Al, 5Cr; Titanium - 4Al, 4Mn; Titanium - 5Al, 2-1/2Sn; Titanium - 6Al, 4V.
- (4) Zirconium (crystal bar), zirconium - 2-1/2Sn; Zircaloy-2 (except as noted above).

Carpenter 20 and stainless steel 1515-N gave significantly higher rates than group (1). Niobium was included only in the runs with 0.020 and 0.025 m H_2SO_4 and showed constant corrosion rates as noted in Table II and reference 12, Table II.

Six type-347-to-type-347 stainless steel welded pins, three exposed as-machined and three exposed after a heat treatment for six hours at 1000°F,

TABLE V

Average Weight Losses Observed on New Stainless Steel Pins^a
Exposed to 0.04 M UO_2SO_4 Containing 0.005 M CuSO_4
and Different Concentrations of Sulfuric Acid

Temp. (°C)	Time (hr)	H_2SO_4 M	Defilmed Weight Loss (mg/cm ²)						Critical Velocity (fps)
			8 fps	12 fps	20 fps	26 fps	34 fps	42 fps	
200	6799	0.006	3.7	-----	3.0	-----	3.3	2.5	65 - 75
	1139	0.010	12	-----	18	-----	40	41	N. D.*
	4093	0.015	17	-----	31	-----	120(1.5) ^b	160(11) ^b	25 - 35
	3681	0.020	15	42	-----	-----	100(5.4) ^b	140(8.0) ^b	20 - 30
	3630	0.025	28	-----	49(1.3) ^b	-----	110(14) ^b	190(20) ^b	10 - 20
250	7272	0.006	1.1	-----	1.5	-----	2.0	1.8	> 75
	1163	0.010	-----	1.7	2.1	3.5	4.8	-----	N. D.*
	4151	0.015	-----	3.5	6.4	4.8	6.6	-----	> 45
	3660	0.020	-----	6.4	9.4	7.9	11	-----	35 - 45
	4411	0.025	-----	12	20	31	68	-----	35 - 45
300	8515	0.006	2.0	-----	2.4	-----	2.5	2.8	> 45
	945	0.010	-----	0.54	0.50	0.64	-----	0.53	N. D.*
	3231	0.015	-----	1.8	1.5	2.0	2.8	-----	> 45
	3841	0.020	-----	2.0	2.8	3.7	4.2	-----	> 45
	3611	0.025	-----	2.7	3.2	3.4	---	3.4	> 45

a. Includes types 304, 304 Cast, 304 Sensitized, 304L, 309SCb, 347, 347 Cast, 347 Sensitized, 430 and 446.

b. Number in parentheses gives the continuing corrosion rate for those pins exposed above their critical velocity.

* Not determined.

were carried over undefilmed in all runs at 250 and 300°C. No difference in behavior from group (1) was noticed. Six similar pins were exposed defilmed in the first three runs at 200°C and again no difference from group (1) was found. However, two type-347-to-type-304 stainless steel pins welded with type 347 weld rod were exposed in the "as-welded" and machined condition in the last two runs at 200°C, at 12 fps in L-35 and at 18 fps in L-36, and the weld metal was selectively attacked.

E. EFFECT OF HEAT TREATMENT AND SURFACE PREPARATION ON CORROSION OF TYPE 347 STAINLESS STEEL.

The effects of various heat treatments and surface preparations on the corrosion rates and critical velocity of type 347 stainless steel were investigated in five runs. All runs were for 200 hr with 0.17 M UO_2SO_4 at 250°C. The heat treatments and surface preparations given the specimens are listed in Table VI.

Table VII gives the weight losses observed on the type 347 stainless steel specimens at velocities from 10 to 80 fps. Consideration of these data lead to the following conclusions:

- (1) The heat treatment of 1 hr at 1250°F did not affect either the weight losses or the critical velocity.
- (2) The heat treatment of 1 hr at 1650°F with slow cooling and subsequent pickling gave slightly lower weight losses up to 35 fps than pickled control specimens. The effect was more marked on the pins than on the coupons. No difference in critical velocity was observed, however.
- (3) The heat treatment of 1 hr at 1950°F did not affect weight losses of coupons except between 20 and 40 fps where weight losses were slightly higher. The critical velocity of the electro-polished heat-treated coupons was 5 to 10 fps lower than the electro-polished control coupons. However, heat treated pin weight losses were lower than control pin weight losses. The pin results were in agreement with data given previously¹³ where it was stated that 1 hr at 1950°F was beneficial at 15 fps. The reason for the different coupon results is not known.

TABLE VI

Heat Treatment and Surface Preparation of Type 347 Stainless Steel Specimens

Run No.	Heat Treatment			Surface Treatment Prior to Run
	Time (hr)	Temp. (°F)	Cooling Method	
A-109	1	1650	Furnace cool at 50° per hr to 800°F, air cool	Cathodically defilmed
A-110	1	1650	Furnace cool at 50° per hr to 800°F, air cool	Pickled
A-111	1	1250	Air Cool	Electropolished
A-112	1	1950	Air Cool	Electropolished
A-113	2-1/2	2200	Furnace cool to 1950°F	Pickled and buffed to remove scale. Then electropolished.
	1	1950	Then water quench.	

TABLE VII

Effect of Heat Treatment on Weight Losses of Type 347 Stainless Steel Specimens Exposed to 0.17 M UO₂SO₄ at 250 C for 200 Hr.

Weight Loss (mg/cm ²)										
	A-109		A-110		A-111		A-112		A-113	
	1 hr at 1650	Control As-Defilmed Surface	1 hr at 1650	Control Pickled Surface	1 hr at 1250	Control Electro-polished Surface	1 hr at 1950	Control Electro-polished Surface	1 hr at 2200	Control Electro-polished Surface
Solution Velocity (fps)										
10-11	6.5	14	6.3	17	7.9	6.6	9.6	8.3	25	7.1
11-14	3.5	12	5.1	13	7.1	6.4	8.0	7.7	-	-
14-17	5.0	13	6.3	16	6.6	6.8	8.6	7.6	33	7.3
17-22	5.9	17	17	19	8.1	7.7	9.7	8.5	46	8.8
22-35	6.8	27	26	32	12	11	20	13	58	12
35-39	8.7	46	40	64	20	27	42	25	57	17
39-45	9.6	62	59	62	61	58	70	65	60	25
45-53	16	66	63	66	64	63	76	70	66	43
53-64	67	72	69	78	69	67	76	75	74	68
64-81	88	84	88	79	76	76	86	85	81	73
Pins at 17 fps	6.6 ^a	19	7.9	32	9.6	11	9.1	17	38 ^b 39 ^c	14

a. Pickled surface.

b. Heat treated 2-1/2 hr at 2200°F, followed by 1 hr at 1950°F. Water quenched.

c. Heat treated 2-1/2 hr at 2200°F. Water quenched.

- (4) The heat treatment of 2-1/2 hr at 2200°F followed by 1 hr at 1950°F was deleterious to corrosion resistance at flow rates up to roughly 50 fps. The critical velocity of the heat-treated coupons also was lowered to 15 to 20 fps. This result was observed previously.¹³ No difference was observed between pins heat treated only at 2200°F and pins heat treated at 2200°F followed by 1 hr at 1900°F.
- (5) Control (not heat-treated) specimens pickled prior to exposure gave slightly higher weight losses below the critical velocity (30 to 35 fps) than specimens used as-machined. However, control specimens electropolished prior to exposure gave considerably lower weight losses below the critical velocity than specimens used as machined. No significant difference in critical velocity was observed. It may be that electropolishing removes surface strains and imperfections and thus decreases the initial weight loss, or it may be that electropolishing reduces the true surface area of the specimens.
- (6) Specimens heat treated for 1 hr at 1650°F with slow cooling and which were electrolytically defilmed to remove the oxide scale prior to exposure gave considerably lower weight losses below the critical velocity and a higher critical velocity (40 to 45 fps) than similar specimens pickled to remove the oxide scale. It is believed that the defilming actually was incomplete so that the coupons started the run already partially filmed over. As the next section will show, a pretreatment film can at least temporarily protect the surface and increase the critical velocity.
- (7) Above the critical velocity, all coupons corroded at essentially the same rate.

The above results are relevant to the question of the corrosion resistance of welds, the heat-affected zone adjacent to welds, and other heat-treated areas. It can be seen that areas heated above 1950°F may have somewhat lower critical velocities and may lose more weight during film formation than parent metal. However, as long as the solution velocity is below the critical velocity, the areas will film over and be protected.

P. EFFECT OF CHROMIC ACID PRETREATMENT ON CORROSION OF TYPE 347 STAINLESS STEEL.

It was found previously that type 347 stainless steel specimens pretreated at 250°C with a solution containing 100 ppm chromium (VI) as chromium

trioxide and 1000 to 2000 ppm oxygen was effective in extending the critical velocity upon subsequent exposure of the specimens to 0.17 and 1.3 m UO_2SO_4 at 250°C.¹⁴ Further experimentation has been carried out to determine whether the pretreatment film formed at 250°C would be protective during subsequent exposure to uranyl sulfate solutions at lower temperatures.

- (1) Pretreatment at 250°C; Exposure to 1.3 m UO_2SO_4 at 200°C.-- The 100-ppm chromium(VI) as chromium trioxide pretreatment for 100 hr at 250°C was found to decrease weight losses of type 347 stainless steel specimens considerably during a 200-hr exposure to 1.3 m UO_2SO_4 at 200°C in comparison with a previous run made without pretreatment. However, the critical velocity was not significantly affected. The previous run without pretreatment, J-37,¹⁵ gave weight losses 3 to 4 times greater than the run with pretreatment, D-72. The critical velocity in these runs was not sharply defined but appeared to be about the same, 20 to 30 fps.

Run D-72 was continued, after an initial shutdown at 200 hr, for a total of 505 hr with a second shutdown after 300 hr. The critical velocity became more pronounced at 20 to 25 fps after a total of 300 hr. A new 1.3 m UO_2SO_4 solution was used for the final 205 hr of the run and for an unknown reason seemed to increase the critical velocity to 30 to 35 fps. Above the critical velocity, the pretreatment delayed onset of rapid attack for perhaps 50 to 100 hr as evidenced by the increase in corrosion rate (about double) during the second part of the run above that for the first part. Below the critical velocity, no further weight loss occurred after the first 200 hr.

- (2) Pretreatment at 250°C; Exposure to 0.04 m UO_2SO_4 Containing 0.02 m H_2SO_4 and 0.005 m $CuSO_4$ at 225°C.-- It was of interest to determine whether a pretreatment at 250°C would give protection to type 347 stainless steel exposed at 225°C in HRT solution, since corrosion is most severe at 225°C in the HRT fuel solution. In run E-73, a 100-hr pretreatment with 100 ppm chromium (VI) as chromium trioxide was made at 250°C followed by a 194- and a 72-hr exposure to HRT fuel solution at 225°C. The results are shown in Fig. 3. Run N-7, a 200-hr run made under similar conditions without pretreatment, is shown for comparison. It can be seen that the pretreatment significantly

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Fig. 3. Weight Losses of Type 347 Stainless Steel Coupons in
0.04m UO₂SO₄ + 0.02m H₂SO₄ + 0.005m CuSO₄ at 225°C

decreased weight losses, but that the critical velocity was little, if at all, affected.

In order to see if a pretreatment with a more concentrated chromic acid solution would give more of an effect, run E-74 was made under conditions rather similar to those of E-73. However, the pretreatment was made with 200 ppm Chromium (VI) for 100 hr at 250°C instead of 100 ppm, and was followed by a 200- and 400-hr exposure to HRT fuel solution at 225°C. It was found that the results were similar except the critical velocity in E-74 was slightly higher than in E-73. Run E-74 was repeated as E-75, and the results were the same.

The major effect of the pretreatments discussed in paragraphs (1) and (2) was to decrease the amount of weight lost by the specimens below the critical velocity. A secondary effect was to delay for several hours the onset of rapid attack above the critical velocity. The critical velocity was affected to only a small extent, 5 to 10 fps, under certain conditions. Increasing the chromium (VI) concentration from 100 to 200 ppm in the pretreatment solution appeared to be beneficial in this regard. It is not known whether higher chromium (VI) concentrations would be more beneficial. It was concluded that pretreatment was in general beneficial in decreasing initial weight loss but could not be depended on to increase the critical velocity.

G. RUNS WITH 0.17 M URANYL SULFATE IN THE ABSENCE OF OXYGEN.

In the previous report, a series of runs was reported in which stress-corrosion cracking of type 347 stainless steel occurred in 0.17 M UO_2SO_4 solution containing 50 ppm chloride when oxygen exhaustion occurred.¹⁶ It was of significance to determine whether stress-corrosion cracking would occur in 0.17 M UO_2SO_4 in the absence of oxygen if no chloride were present. Therefore, type 347 stainless steel specimens stressed to 25,600 psi (75% of room temperature yield strength) were exposed at 200, 250, and 280°C to 0.17 M UO_2SO_4 containing less than 3 ppm chloride in the absence of oxygen. Table VIII gives the conditions and the results of the runs. Soon after start-up of each run, the trace of oxygen remaining in the solution was used up by the corrosion process and then the uranyl ion began to be reduced and precipitated. As the uranium precipitated (as U_3O_8), the pH decreased. The run was stopped when the room temperature pH of the

TABLE VIII

Conditions and Results of Runs in 0.17 m UO_2SO_4 Without Oxygen

<u>Run No.</u>	<u>UO_2SO_4 Conc. m</u>	<u>Time hr</u>	<u>Temp. °C</u>	<u>Initial pH</u>	<u>Final pH</u>	<u>Chloride Conc. ppm</u>	<u>Results</u>
E-76	0.17	30	250	2.4	1.3	< 2	No stress corrosion cracks observed.
E-77	0.17	84	200	2.4	1.4	< 2	No stress corrosion cracks observed. Numerous pits 2 to 4 mils deep found.
E-78	0.17	7	280	2.4	1.2	2	No stress corrosion cracks observed.

solution had fallen from 2.4 to 1.4 or less. This process took a shorter time the higher the temperature.

Metallographic examination of the stress specimens showed no stress-corrosion cracking. However, the specimens were pitted, particularly at 200°C. Since the runs were terminated after such short times, it was not possible to determine whether cracks would have developed at the base of the pits. However, it was concluded that for short periods of time, oxygen exhaustion does not lead to stress-corrosion cracking in the absence (less than 3 ppm) of chloride.

H. THE COMBINED EFFECT OF COPPER SULFATE AND POTASSIUM DICHROMATE ON THE CORROSION OF TYPE 347 STAINLESS STEEL.

Previous reports have discussed the effect on the corrosion of type 347 stainless steel of potassium dichromate^{17,18,19} and of copper sulfate²⁰ added separately to 0.17 M UO_2SO_4 . To determine whether there was a synergistic effect when both were present, several runs were made in the all-titanium loop, loop G. Conditions of the runs are given in Table IX.

The results are illustrated in Fig. 4. The previously obtained results with copper sulfate are included for comparison. It can be seen that the increase in corrosion rate at 13 and 68 fps with increasing copper sulfate concentration gives roughly the same slope in the presence of 200 ppm chromium (VI) (top-most and bottom-most curves) as in the presence of only 3 to 4 ppm chromium (VI) (middle curves). Therefore, there is little or no synergistic effect.

I. EFFECT OF SULFURIC ACID CONCENTRATION ON THE CORROSION OF TYPE 347 STAINLESS STEEL.

To determine the effect of adding sulfuric acid to 0.17 M UO_2SO_4 on the corrosion of type 347 stainless steel, the all-titanium loop, loop G, was used to minimize interference from corrosion products from the loop piping. Conditions of the runs are listed in Table X.

The results of the runs are shown in Fig. 5. The results at 70 fps were quite erratic as indicated by the length of the vertical line at each acid concentration used. The reason for the error was probably due to the build-up of corrosion products as a result of the high corrosion rates.

TABLE IX

Conditions and Results of Runs with 0.17 m UO_2SO_4
Containing CuSO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ at 250°C.

Run No.	Time hr	Average Cu (II) Conc. ppm	Average Cr (VI) Conc. ppm	Average Oxygen Conc. ppm	Average Corrosion Rate at 13 fps (mpy)	Average Corrosion Rate at 70 fps (mpy)
G-44	100	0	3	1900	84	150
G-65	100	49	4	5000*	81	150
G-67	100	2290	3	940	79	180
G-68	100	1150	4	2000	98	260
G-78	100	0	200	1600	32	370
G-80	100	300	200	1400	42	430

* Supersaturated with oxygen.

TABLE X

Conditions and Results of Runs with 0.17 m UO_2SO_4
Containing Various Amounts of Sulfuric Acid at 250°C.

Run No.	Time hr	H_2SO_4 Conc. m	Average Cr (VI) Conc. ppm	Average Oxygen Conc. ppm	Average Corrosion Rate		
					6 fps	12 fps	70 fps
G-75	200	0	16	1500	30	--	320
G-44	100	0	3	1900	--	84	150
G-69	200	0.017	6	500	--	140	290
G-72	200	0.025	14	1900	--	225	495
G-73	200	0.025	12	1500	60	--	400
G-70	200	0.040	24	1600	--	280	710
G-71	200	0.040	19	1300	--	245	690
G-74	200	0.040	20	1700	80	--	930

Fig. 4. Effect of Copper Sulfate Addition to 0.17m UO_2SO_4 Containing Chromium (VI) on Corrosion of Type 347 Stainless Steel Pins at 250°C (100 hr. runs)

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Fig. 5

EFFECT OF SULFURIC ACID ON CORROSION OF
TYPE 347SS PINS IN 0.17M UO₂SO₄ AT 250°C

It can be seen that corrosion rates increased linearly with acid concentration at 6 and 12 fps, but at 70 fps, corrosion rates increased more sharply with acid concentration. Due to the scatter in the data, no quantitative treatment has been attempted.

These results are in agreement with previous experience with additions of sulfuric acid to uranyl sulfate (see Section C above). However, the extremely high rates observed at 70 fps with 0.04 m H_2SO_4 added to 0.17 m UO_2SO_4 are much higher than observed in stainless steel loops. The reason for this difference is not known.

J. SECOND-LIQUID-PHASE TEMPERATURE OF HRT CORE SOLUTION IN HEAVY WATER: FAILURE OF A TYPE 347 STAINLESS STEEL PIPE.

An attempt was made to determine the second-liquid-phase separation temperature of 0.04 m UO_2SO_4 containing 0.02 m H_2SO_4 and 0.005 m $CuSO_4$ in heavy water by circulating the solution in loop J and raising the temperature gradually. Solution samples were taken every five degrees up to 330°C and at 333 and 335°C. No phase separation was indicated by uranium and copper analyses up to 333°C. A slight decrease in uranium and copper analyses in the 335°C sample indicated possibly that the second-liquid-phase temperature had been reached in parts of the system slightly warmer than the bulk solution temperature. The loop temperature was not increased above 335°C because the pressure was 2000 psi at that temperature (design pressure of the loop). After the solution sample was taken at 335°C, the loop was cooled to 300°C. The loop had been at 330°C or above roughly 1/2 hr.

About 15 hr after cooling the loop to 300°C, the 1/2 in. type 347 stainless steel mixing line was observed to be leaking and the run was terminated. The piping was removed and sectioned for detailed examination. It was apparent that the inside of the pipe had corroded severely in several localized areas under the cast-on aluminum heater (1500 watts).

The cast-on heater had been used in the two previous tests during which time 0.17 m UO_2SO_4 had been circulated at 250°C with the pressurizer maintained at 280°C for 400 hr. It is probable that during any or all three of the tests, the mixing line heater was set so high that the slowly

flowing (1 gpm) solution became heated above the second-liquid-phase separation temperature. The appearance of the interior of the pipe indicated that the heavy phase collected in small areas on the piping wall and caused localized corrosion severe enough to penetrate the wall (about 1/8 in.). This failure illustrates the necessity for preventing two-liquid-phase separation even in dilute solution.

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

A. STRESS CORROSION CRACKING OF TYPE 347 STAINLESS STEEL.

- (1) Effect of Halides in Uranyl Sulfate Solutions.---Tests to determine the stress-corrosion cracking behavior of type 347 stainless steel in boiling and aerated 0.04 M UO_2SO_4 solution containing 0.02 M H_2SO_4 , 0.005 M CuSO_4 , and various concentrations of halide species have continued during the past quarter. The halides (added as the potassium salts) included in the tests are: (a) chloride in concentrations of 0, 5, 10, 25, 50, 100, 200, and 500 ppm; (b) bromide in concentrations of 50, 100, and 200 ppm; and, (c) iodide in a single concentration of 100 ppm.

Chloride Tests.---Cracking occurred on simple-beam specimens stressed at 15,000 and at 30,000 psi in the uranyl sulfate environment containing chloride concentrations of 25, 50, 200, and 500 ppm during exposure intervals from 100 to 500 hr.^{21,22} In solutions containing 100 ppm chloride, cracking did not take place until the 2000 to 2500-hr exposure interval and occurred on the specimen stressed at 15,000 psi. No cracking took place during 2500 hr in the environment on the specimen stressed at 30,000 psi. Likewise, no cracking has been observed on stressed specimens after 2500 hr in uranyl sulfate solutions containing 0, 5, and 10 ppm chloride.

The orientation of the crack on the 15,000 psi stress specimen exposed in the 100-ppm chloride environment was unusual in that the crack appeared to propagate in a direction parallel with the direction of applied stress. A photograph of the crack is shown in Fig. 6. The crack was the only one found on the specimen.

Photo No. 12579

Test P-14

Fig. 6. Crack on Type 347 Stainless Steel Specimen at 15,000 psi After 2500 Hr in Boiling and Aerated Uranyl Sulfate Solution Containing 100 ppm Chloride. Magnification 6X.

Upon sectioning, the area beneath the crack was found to be badly pitted as shown in Fig. 7. The sub-surface attack was much the same as was observed on the specimens exposed to bromide-containing uranyl sulfate solutions which will be discussed later. Metallographic examination of the attacked areas disclosed no signs of cracks beneath the surface. An unstressed control specimen which exhibited a fine network of cracks originating from the edge surface of a hole drilled in the specimen was sectioned. In addition to severe sub-surface attack, cracks were found which appeared to be more inter-granular than transgranular in nature. A photograph of the attacked area is shown in Fig. 8. When cracking has been observed in other chloride-containing uranyl sulfate solutions, the cracks were transgranular in nature as shown in the photomicrograph of Fig. 9. The stress-corrosion cracking tests in uranyl sulfate solution containing 100 ppm chloride are being repeated.

The effect of applied stress on the generalized corrosion behavior of type 347 stainless steel in chloride-containing uranyl sulfate solutions is summarized in Table XI. Data for bromide and iodide-containing solutions are included also. With the noted exceptions, the corrosion rates were determined from defilmed weight losses on the unstressed control specimens and on the stress specimens of the dismantled stress assemblies. In cases where the tests are being continued, the corrosion rates are based upon the as-removed weight losses for the entire stress assembly. No particular effect of stress on the generalized corrosion rates of types 347 stainless steel is evident from the data in Table XI. In a few cases, the corrosion rates for stressed specimens were slightly higher than the observed rates for unstressed specimens; but more generally, the opposite was true. One consistency in the data was evident - at chloride concentrations of 0, 5, and 10 ppm, applied stresses of 15,000 or 30,000 psi had no effect on the generalized corrosion rates; in all cases the rates were less than 0.1 mpy - the same as for the unstressed control specimens.

The results of the single iodide-containing test were negative with respect to the incidence of stress-corrosion cracking during the 2500-hr exposure period. There appeared to be no effect of stress

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Photo No. T-12573

Test P-14

Fig. 7. Sub-Surface Attack on Type 347 Stainless Steel Specimen at 15,000 psi After 2500 Hr in Boiling and Aerated Uranyl Sulfate Solution Containing 100 ppm Chloride. Magnification 50X.

Photo No. T-12575

Test P-14

Fig. 8. Suspected Cracking in Unstressed Type 347 Stainless Steel Specimen After 2500 Hr in Boiling and Aerated Uranyl Sulfate Solution Containing 100 ppm Chloride. Magnification 100X.

Photo No. T-12572

Test P-12

Fig. 9. Cracking in Type 347 Stainless Steel Specimen at 30,000 psi After 1000 Hr in Boiling and Aerated Uranyl Sulfate Solution Containing 25 ppm Chloride. Magnification 250 X.

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TABLE XI

The Effect of Applied Stress on the Generalized Corrosion Behavior of Type 304 Stainless Steel After 2500 Hr in Halide-Containing Boiling and Aerated 0.04 M H_2SO_4 - 0.02 M H_2SO_4 - 0.005 M CuSO_4 Solution

No.	Species	Halide Additive Concentration (ppm)	Generalized Corrosion Rate (mpy)		
			Unstressed ^a	15,000 psi	30,000 psi
P-9	None		< 0.1	< 0.1	< 0.1
P-10	Cl^-	5	< 0.1	< 0.1	< 0.1
P-11	Cl^-	10	< 0.1	< 0.1	< 0.1
P-12	Cl^-	25	10.0	5.1 ^b	13.2 ^b
P-13	Cl^-	50	16.0	22.4 ^b	11.8 ^b
P-14	Cl^-	100	3.7	6.1	6.2
S-25	Cl^-	200	16.1	7.6 ^c	12.9 ^c
S-26	Cl^-	500	8.7	3.3 ^d	5.4 ^d
S-27	Br^-	50	< 0.1	< 0.1	< 0.1
P-15	Br^-	100	9.3	2.4	3.4
S-28	Br^-	200	5.5	6.1 ^e	11.1 ^e
P-16	I^-	100	0.5	1.4	0.3

a. Average corrosion rate for duplicate specimens.

b. Exposure time, 1000 hr.

c. Exposure time, 1500 hr; corrosion rate based on "as-removed" weight loss on stress assembly.

d. Corrosion rate based on "as-removed" weight loss on stress assembly.

e. Exposure time, 2214 hr.

on the generalized corrosion rate of the type 347 stainless steel.

Bromide Tests.-- The behavior of stressed type 347 stainless steel exposed in bromide-containing uranyl sulfate solution was unusual. No cracks appeared on specimens exposed in the 50-ppm bromide environment during a 2500-hr test. In a solution containing 100 ppm bromide, a suspected area of cracking was noted on a specimen stressed at 15,000 psi upon completion of the 2000 to 2500-hr exposure interval; no indication of cracking was noted on the 30,000-psi specimen in the environment. A similar occurrence of suspected cracking was found on specimens stressed at 15,000 and 30,000 psi after completion of the 1000 to 1500-hr exposure interval in uranyl sulfate solution containing 200 ppm bromide. In all three of the above cases, the apparent cracking was located in areas of maximum or near-maximum stress and the cracks were oriented in a direction normal to the direction of applied stress. A photograph showing the appearance of the surface cracks on the 15,000-psi specimen after 2500 hr in the 100-ppm bromide-containing uranyl sulfate solution is included in Fig. 10. The cracks were discontinuous in nature and extended across the full width of the specimen, approximately 5/8 in. Other than a few randomly-oriented pits, the surface of the specimen was free from localized corrosion attack. The appearance of cracks observed on specimens exposed in the 200-ppm bromide solution was similar to that shown by the photograph in Fig. 10.

The stress specimen at 15,000 psi in the 100-ppm bromide test was submitted for metallographic examination of the surface cracks. Several sections were made normal to the direction of the cracks. A severe sub-surface attack was disclosed. The attack consisted of extremely intense pitting with penetration in a direction parallel with the direction of the applied stress. Three cross-sectioned areas showing the sub-surface attack appear in Fig. 11. Both white and dark-colored areas are indicative of pit sites. The white-colored areas contain a plastic mounting material which flowed into the pits during the preparation of the sections for metallographic study. A few of the deeper pits in the sections were estimated to be in excess of 125 mils in depth. Examination

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Photo No. T-12539

Test P-15

Fig. 10. Surface Cracks on Type 347 Stainless Steel Specimen at 15,000 psi After 2500 Hr in Boiling and Aerated Sulfate Solution Containing 100 ppm Bromide. Magnification 5X.

Photo No. T-12567

Test P-15

Fig. 11. Sub-Surface Attack on Type 347 Stainless Steel Specimen at 15,000 psi After 2500 Hr in Boiling and Aerated Uranyl Sulfate Solution Containing 100 ppm Bromide. Magnification 5X.

of the stress specimens from the 200-ppm bromide test disclosed a similar sub-surface attack.

None of the sections from the stress specimens exhibited any evidence of a susceptibility to cracking. A photomicrograph showing a typical appearance of an attacked area is included in Fig. 12. Corrosion attack on the walls of the pits was relatively uniform and there were no indications of intergranular attack.

In summary, the experimental evidence is not clear that bromide in uranyl sulfate solution will promote stress-corrosion cracking in type 347 stainless steel. Although outward appearances of the specimens strongly suggested a susceptibility to stress cracking in the presence of bromide, careful metallographic examination of cross-sectional areas revealed no signs of cracks. There is the possibility, however, that the severe sub-surface attack observed was the result of an accelerated corrosion due to the applied stress in the presence of bromide ions. No similar sub-surface attack was observed on the unstressed control specimens, although a random and shallow pitting attack was in evidence. In the case of the 100-ppm bromide test, however, there was no acceleration of the over-all corrosion rate arising from the presence of an applied stress. In fact, the unstressed control specimens were corroded at an average defilmed corrosion rate of 9.3 mpy in 2500 hr as compared with an average defilmed rate of 2.9 mpy for the stress specimens. The situation was different in the 200-ppm bromide test, however. The average defilmed corrosion rate for the stress specimens in 2214 hr was 8.6 mpy as compared with a slightly lower rate of 5.5 mpy for the unstressed control specimens in 2500 hr. No significance was attached to the slight differences in the corrosion rate values.

The effect of bromide additions in uranyl sulfate solutions on the corrosion behavior of stressed type 347 stainless steel is undergoing further examination. Also included in the study is a series of tests to determine the effect of degree of cold working on the generalized corrosion of type 347 stainless steel in bromide-containing solutions.

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Photo No. T-12646

Fig. 12. Photomicrograph of Sub-Surface Attack on Type 304 Stainless Steel Stressed at 15,000 psi After 1500 Hr in Boiling-Aerated Uranyl Sulfate Solution Containing 200 ppm Bromide. Magnification 250X.

- (2) Effect of Various Cations in HRT Core Solution.-- It has been demonstrated that in the presence of chloride concentrations between 25 and 500 ppm, stress-corrosion cracking can be induced in stressed type 347 stainless steel with a fair degree of reproducibility in boiling simulated HRT core solution (0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , and 0.005 m CuSO_4 .) It was of interest to conduct a number of experiments to determine the effect singly or in combination of the specific cations in the HRT core solution on the stress-corrosion cracking process. This was accomplished in two ways: substitution of a particular cation by another cation, and, removal of the particular cation or cations from the environment. Each test environment contained 50 ppm chloride as potassium chloride.

A U-bend type of stress specimen was employed for the tests in preference to the simple-beam specimens used in the preceding study. The U-bends were more easily assembled and more economical than the conventional simple-beam type stress assemblies. The U-bends were prepared from annealed and pickled 0.019-in.-thick type 347 stainless steel strip, the edges of which were mechanically abraded to remove sheared surface effects. After cold-forming into a U-bend, the specimens were elastically stressed by means of a type 347 stainless steel tie-bolt through the legs of the U. No quantitative measurement of the applied stress was made.

Control tests with the U-bend stress specimens were run initially in the boiling and aerated HRT core solution consisting of 0.04 m UO_2SO_4 with 0.02 m H_2SO_4 , 0.005 m CuSO_4 , and 50 ppm chloride.

Three out of four of the specimens cracked during the 400-hr of exposure. The fourth specimen has exhibited no tendency toward cracking after 2000 hr. The results of the control tests and the tests to determine specific cation effects are shown in Table XII.

In two of the test solutions - one containing potassium and cupric ions and sulfuric acid and the other containing potassium ions and sulfuric acid only - the stressed specimens did not crack after 2000 hr. The generalized corrosion rates with one exception were

TABLE XII

The Effect of Various Cations in Boiling and Aerated Solutions on the Stress-Corrosion Cracking Behavior of Type 347 Stainless Steel
(All Solutions Contained 50 ppm Cl and KCl)

Lab No.	Solution Composition	Specimen Number	Total Time(hr)	Corrosion Rate(mpy)	Observations
U-68	0.04 m UO_2SO_4	1	2000	0.4	Cracked during 300-400 hr interval.
	0.02 m H_2SO_4	2	2000	3.7	No cracking.
	0.005 m CuSO_4				
V-97	Same as above	1	200	0.3	Cracked during 25-50 hr interval.
		2	200	0.6	Cracked during 25-50 hr interval.
U-79	0.04 m K_2SO_4	1	2000	0.3*	No cracking.
	0.02 m H_2SO_4	2	2000		No cracking.
	0.005 m CuSO_4				
U-80	0.04 m K_2SO_4	1	2000	0.2*	No cracking.
	0.02 m H_2SO_4	2	2000		No cracking.
W-21	0.04 m UO_2SO_4	1	150	0.1	No cracking.
	0.02 m H_2SO_4	2	150	0.2	No cracking.
W-22	0.02 m H_2SO_4	1	150	0.1	No cracking.
		2	150	0.2	No cracking.
W-25	0.04 m UO_2SO_4	1	150	0.1	No cracking.
		2	150	0.1	No cracking.

* Corrosion rate determined from dissolved nickel content in test solution.

in good agreement with rates of 0.3 to 0.6 mpy for the control specimens which cracked during the initial 400 hr of test. The corrosion rate for the control specimen which did not exhibit cracking was considerably higher, 3.7 mpy. The remaining three environments in Table XII (tests W-21, W-22, W-25) have accumulated only 150 hr of test time thus far; no cracking has occurred on any of the stressed specimens during this period. The tests will be continued.

Although the data in Table XII are very preliminary, there appears to be some indication that the uranyl ion is an important factor in the stress-corrosion cracking mechanism. This indication is based upon the two tests in Table XII (U-79 and U-80) in which the uranyl ions were replaced with potassium ions. No cracking has occurred on the stress specimens after 2000 hr in the two media, whereas experience has shown that in the presence of uranyl ions with chloride, cracking has rather consistently occurred during periods of 400 hr or less. Further testing will be required, however, to resolve conclusively the effect of the uranyl ion.

It was previously reported that the presence of platinum ions in a chloride-containing boiling simulated HRT core solution shortened the time required for crack initiation in stressed U-bends of type 347 stainless steel.²³ Cracking occurred on duplicate specimens exposed in solutions with and without dissolved oxygen during the initial 25 hr of exposure. Presumably, platinum metal selectively plated at cathodic sites should present a cathode with a low hydrogen overvoltage, thus allowing for an increased corrosion current. The increased current flow should thereby favor an acceleration in the stress-corrosion cracking rate. The fact that cracking consistently took place during the first 25 hr as compared with cracking times of 100 to 500 hr for simple-beam stress specimens in the absence of platinum appeared to substantiate the hypothesis on the platinum effect. However, during the past quarter, a number of control tests in platinum-free HRT core solution with 50 ppm chloride were repeated with U-bend type specimens in place of the simple-beam type specimens. As shown in Table XII, two

U-bend specimens cracked during the interval between 25 and 50 hr. In other similar tests, cracks appeared on specimens during the first 25 hr of exposure - the same period of time in which cracking occurred on the specimens exposed in HRT core solution containing platinum and chloride ions. In view of the recent experimental results, it appears that the presence of platinum ions in chloride-containing HRT core solution does not have the accelerating effect on the cracking process as was first intimated.

- (3) Behavior in Distilled Water at Elevated Temperatures. The susceptibility of the austenitic stainless steels to stress-corrosion cracking presents a serious obstacle to the operation of the HRT leak-detector and steam-generator systems and, in fact, to the operation of any reactor when austenitic stainless steels are exposed to high-temperature chloride-bearing solutions. A study has been undertaken to examine the factors which influence stress-corrosion cracking in water solutions. A knowledge of these factors and their effects will aid in prescribing conditions that will minimize the possibility of cracking in the HRT. A summary of the preliminary test results follows:

- (a) Effect of pH and Chloride Concentration.-- A series of tests in water to determine the effect of such variables as pH, chloride concentration, temperature, and oxygen concentration on time to cracking of stressed type 347 stainless steel is being run. The majority of the tests are conducted in stainless steel autoclaves at temperatures of 200 to 300°C using duplicate U-bend specimens in each test; the remaining tests are conducted at the atmospheric boiling temperature of the solutions. Low pH was achieved through the addition of part of the chloride as hydrochloric acid, the balance being sodium chloride. High pH was obtained by the addition of sodium hydroxide; sodium chloride was the source of chloride ion.

Chloride concentrations of 25, 50, and 100 ppm at initial pH levels of 2.8, 6.5, and 10.5, and oxygen concentrations of approximately 1200 and 10 ppm were examined in the tests at

300°C. At 100, 200, and 250°C, only 100 ppm chloride at pH 2.8 was run. A summary of the test results is included in Table XIII. The "time-to-cracking" refers to the first appearance of a visible crack, not to the time of complete fracture. In nearly all cases, the pH changed during a run so that after 200 to 300 hr, the pH was between 4 and 6 regardless of the initial pH.

Examination of the data obtained at 300°C shows that the difference in the time to cracking between two different environments is no greater than the maximum difference in time to cracking between duplicate samples in a single experiment. Thus, it appears that any combination of variables within the ranges studied will produce stress-corrosion cracking in type 347 stainless steel in 100 to 700 hr at 300°C.

The use of U-bend type specimens in the tests led to some inconsistent results due to the lack of uniformity in the applied elastic stresses. As an example, superficial cracks were observed on the surfaces of the specimens exposed at 300°C in pH 2.8 water containing 25 ppm chloride at the end of 400 hr (test U-99). These cracks failed to propagate during an additional 300 hr of testing. At this time, an examination of the specimens showed that there was no elastic stress being applied by the tie-bolt. Tightening the bolts resulted in deep cracks during the next 100 hr. It is almost certain that these specimens would have cracked much earlier if a constant stress had been applied throughout the entire exposure.

Additional experiments are planned to examine the effect of chloride concentrations down to 5 ppm, and oxygen concentrations down to zero.

- (b) Effect of Temperature.-- U-bend specimens were exposed to distilled water containing 100 ppm chloride at a pH of 2.8 and approximately 10 ppm dissolved oxygen. At 300°C, the environment produced severe cracking in 200 to 400 hr. At 100°C, a total of 16 specimens exposed to 25, 50, 100, and 500 ppm chloride at a pH of 2.8 have accumulated 1500 hr of

TABLE XIII

Stress-Corrosion Cracking of Type 347 Stainless Steels in
Distilled Water Containing Chlorides

Test No.	Temp. (°C)	Cl (ppm)	Initial pH	Dissolved Oxygen (ppm)	Time to Cracking (hr)	
					1st Specimen	2nd Specimen
U-95	300	100	2.8	1200	300	400
U-96	300	100	10.5	1200	400	400
V-2	300	100	2.8	10	200	200
V-5	300	100	10.5	10	200	300
V-53	300	100	2.8	10	400	400
V-83	300	100	6.5	1200	200	300
V-84	300	100	6.5	10	> 300 Not Completed	
V-97	300	50	2.8	1200	600	700
U-98	300	50	10.5	1200	400	400
V-3	300	50	2.8	10	200	200
V-6	300	50	10.5	10	700	800
V-52	300	50	6.5	10	500	500
V-85	300	50	6.5	1200	> 100 Not Completed	
V-86	300	50	6.5	10	100	100
U-99	300	25	2.8	1200	800	800
V-1	300	25	10.5	1200	200	700
V-4	300	25	2.8	10	300	400
V-7	300	25	10.5	10	300	300
V-88	300	25	6.5	10	> 400 Not Completed	
V-92	250	100	2.8	10	100	100
V-93	250	100	2.8	10	300	300
V-94	200	100	2.8	10	100	100
V-95	200	100	2.8	10	100	100

testing without cracking. At 200°C, all four specimens tested developed numerous cracks in less than 100 hr. Two of four specimens exposed at 250°C cracked in less than 100 hr; a third cracked in the interval between 100 to 200 hr, and the fourth cracked between 200 to 300 hr.

These data point strongly to the existence of a threshold of temperature for rapid crack initiation, and a region of maximum rate of cracking between 100 to 200°C. A detailed examination of this temperature range will be made to verify these indications.

- (4) Effect of Additives in Boiling 42% MgCl₂.-- As previously discussed, coupling stainless steel to a metal having a lower hydrogen overvoltage should accelerate cracking, if the reduction of hydrogen is the rate limiting reaction at the cathode. Conversely, a metal having a higher hydrogen overvoltage, if plated on the cathodic sites, should possibly inhibit stress-corrosion cracking.

Tests were set up using boiling 42% MgCl₂ as the cracking medium. Platinum as PtCl₄ was added to provide an easily reducible metal having a low hydrogen overvoltage, and mercury as HgCl₂ was added to another test to provide the metal having a high hydrogen overvoltage. Concentrations of 50 ppm of each metallic ion were added.

Two U-bend specimens were exposed in each solution. In both tests, one specimen cracked in less than one hour, and the second one cracked in the interval between 2 and 3 hr. Four control specimens in pure, boiling 42% MgCl₂ cracked in 1 to 4 hr, so that little influence can be attributed to the effect of either platinum or of mercury.

Losses of the metallic ions from solution were 72% of the initial platinum concentration, and 50% of the initial mercury concentration. Since narrow black strips were observed along

the edges of the cracks, it is assumed that the metals plated out in these areas. No similar deposits have been observed in any experiment where easily reducible ions were absent.

In a similar test, platinum-black was electroplated on U-bend specimens. One was covered completely, and three others were plated so that narrow strips of bare 347 stainless steel were left in various positions on the surface. All four specimens cracked in the interval between 2 and 3 hr. All cracked completely across the region of maximum stress at right angles to the applied stress, regardless of the location of the bare metal areas.

Additional testing will be done along this line, using three-point loaded specimens with low applied stresses in an attempt to magnify any differences resulting from the difference in hydrogen overvoltages at the cathodes.

B. CORROSION OF ZIRCONIUM ALLOYS BY URANYL SULFATE SOLUTION.

The corrosion test program for the evaluation of zirconium-base alloys has continued. The purpose of the program which is a cooperative effort with the HRP Metallurgy Group is to determine the corrosion behavior of a number of binary, ternary, and quaternary alloys of zirconium and to supply corrosion specimens for study of the oxide film structures. Corrosion results from other zirconium alloys tested in this program have been reported previously.^{24,25}

The corrosion environment for the present and for the previous tests consisted of oxygenated 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m $CuSO_4$ at 300°C. If corrosion attack was not excessive, the tests were run for 1000 hr. Otherwise, the tests were of shorter duration. The present series of tests included zirconium specimens alloyed with platinum, tin, silver, uranium, palladium, iron, niobium, molybdenum, and manganese in various combinations. All the alloys were prepared from high-purity iodide-process zirconium. Prior to test, the alloy specimens were mechanically abraded on 80 and 120 grit papers, respectively. The results of the corrosion tests are included in Table XIV.

TABLE XIV

CORROSION OF CAST ZIRCONIUM-BASE ALLOYS BY OXYGENATED
 0.04 M UO_2SO_4 - 0.02 M H_2SO_4 - 0.005 M CuSO_4 SOLUTION AT 300°C

Lab No.	Material Identity	Alloy Composition (wt%)	Specimen Treatment	Spec. No.	Total Hr.	Corrosion Rate (mpy)
T-62	Zr-55	5Pt-95Zr	Abraded	1	1000	(+0.2 mg/cm ²)
				2	1000	(+0.1 mg/cm ²)
T-62	Zr-56	10Pt-90Zr	Abraded	3	1000	(+0.1 mg/cm ²)
				4	1000	Negligible
T-63	Zr-76	2Sn-7.5Ag-90.5Zr	Abraded	1	1000	11.3
				2	1000	45.8
T-64	Zr-43	10U-90Zr	Abraded	1	1000	(+6.4 mg/cm ²)
				2	1000	(+10.4 mg/cm ²)
T-80	Zr-24	5Pd-95Zr	Hot rolled at 500°C; ground to 0.094-in.-thick; abraded	1	1000	Negligible
				2	1000	(+0.2 mg/cm ²)
T-81	Zr-31	10Pd-90Zr	Hot rolled at 700°C; ground to 0.098-in.-thick; abraded	1	1000	45.7
T-83	Zr-19	1Fe-10Nb-89Zr	Abraded	1	1000	(+22.6 mg/cm ²)
T-84	Zr-23	5Mo-95Zr	Abraded	1	1000	(+8.8 mg/cm ²)
				2	1000	(+10.0 mg/cm ²)
T-96	Zr-39	2Mo-98Zr	Abraded	1	200	58.7
				2	200	53.7
T-98	Zr-78	2Sn-2Mo-96Zr	Abraded	1	1000	(+2.1 mg/cm ²)
				2	1000	(+2.5 mg/cm ²)
T-99	Zr-79	2Sn-7.5Nb-90.5Zr	Abraded	1	1000	(+6.5 mg/cm ²)
				2	1000	(7.6 mg/cm ²)

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Three of the alloys exhibited very good corrosion resistance; the alloy compositions were 5 Pt - 95 Zr, 10 Pt - 90 Zr, and 5 Pd - 95 Zr. In all three cases, the 1000-hr exposure period produced very slight weight increases on the specimens which were not in excess of 0.2 mg/cm^2 . The appearance of the specimens was characterized by very thin, adherent, and highly lustrous dark black films. A single alloy in the same composition series, 10 Pd - 90 Zr alloy, was severely attacked; the corrosion rate was 45.7 mpy in 1000 hr.

Other alloys that corroded excessively included: (1) a 2 Sn - 7.5 Ag - 90.5 Zr alloy which corroded at rates of 11 and 46 mpy for duplicate specimens, and (2) a 2 Mn - 98 Zr alloy which corroded at rates of 54 and 59 mpy on duplicate specimens after 200 hr. The remaining alloys, 10 U - 90 Zr, 1 Fe - 10 Nb - 89 Zr, 5 Mo - 95 Zr, 2 Sn - 2 Mo - 96 Zr, and 2 Sn - 7.5 Nb - 90.5 Zr, exhibited appreciable weight increases ranging between 2 and 10 mg/cm^2 . In these cases, the corrosion films generally were non-uniform, bulky, and relatively non-adherent.

The effect of high-temperature air-formed films on the corrosion behavior of a number of zirconium alloys will be examined during the next quarter. The films on the specimens were produced by heating in air for 3 to 5 min at 1100°C .

C. MISCELLANEOUS CORROSION TESTS.

- (1) Corrosion of Types 202, 414, and 431 Stainless Steel. -- Types 202, 414, and 431 stainless steel were tested in several reactor-associated environments to determine their applicability in parts of reactor systems. The compositions of the alloys are shown in Table XV. Two different compositions of type 431 stainless steel were tested; the main difference between the two heats is the nickel content.

The conditions of the tests, as well as the results, are shown in Table XVI. The results show that type 414 stainless steel corroded at such excessive rates that no test was continued for more than 100 hr. Type 431 stainless steel had considerably better corrosion resistance than type 414 stainless steel but the rates were fairly

TABLE XV
THE COMPOSITIONS OF SEVERAL STAINLESS STEELS

Element	Type Steel			
	414	431 (Lot 1)	431 (Lot 2)	202
C	0.11	0.166	0.154	0.094
Mn	0.48	0.60	0.57	7.85
Si	0.38	0.50	0.33	0.51
Ni	1.90	2.30	1.56	5.18
Cr	12.06	16.24	16.00	18.00
Mo	0.11	0.06	0.06	0.31
P	0.018	0.014	0.017	0.019
S	0.010	0.012	0.020	0.009
Fe	Balance	Balance	Balance	Balance

TABLE XVI
CORROSION BEHAVIOR OF VARIOUS STAINLESS STEELS
UPON EXPOSURE TO SEVERAL DIFFERENT ENVIRONMENTS

Type	Time (hr)	5 wt% HNO ₃ Boiling	Corrosion Rate (mpy) MRT Core Solution*			1.33 m UO ₂ SO ₄ Boiling
			Boiling	200°C	300°C	
414	100	1490	700	250	141	480
431(2.3% Ni)	100	35	2.5	14	134	3.7
	500	11	6.8	3.1		9.6
	1000			1.7		
431(1.6% Ni)	100	2.0	1.0	**	103	1.4
	500	4.0	2.5			4.4
	1000		3.7			9.1
202	100	< 0.1		3.5	0.3	< 0.1
	500	< 0.1		0.9	0.2	< 0.1
	1000	0.1		0.9	0.4	< 0.1

* 0.04 m UO₂SO₄, 0.02 m H₂SO₄, 0.005 m CuSO₄.

** Each specimen gained ~ 550 mg; after defilming twice, each specimen still showed an average weight gain of 200 mg.

high in all solutions. On the other hand, type 202 stainless steel corroded at low rates in all environments. In fact, its corrosion resistance was practically the same as that of type 347 stainless steel in the environments used. In view of its corrosion resistance, further experiments will be performed, particularly with welded and sensitized specimens. No further testing is planned with types 431 or 414 stainless steel.

- (2) Corrosion of Special Nickel-Molybdenum Alloys. -- Four specimens of special nickel-molybdenum alloys were submitted by the HRT Metallurgy Group for corrosion testing in boiling HRT core solution in order to evaluate their possible usefulness in HRT applications. The compositions of the alloys are given in Table XVII.

TABLE XVII
Chemical Composition of Four Nickel-Molybdenum Alloys

Heat No.	Element (wt%)								
	Mo	Ti	Al	C	Nb	Cr	Mn	Fe	Ni
30-14	16.5	1.52	2.45	0.08					Bal
30-21	16.4			0.07	4.71				Bal
30-24	17.31		0.69	0.09		6.19	0.27		Bal
30-45	16.64		0.77			7.97	0.30	7.15	Bal

The tests were conducted on coupons which were obtained from rolled stock prepared from 36-lb induction melts and which, after cutting, were fired for 1/2 hr at 1093°C (2000°F) in a hydrogen atmosphere. The tests were terminated after 200 hr because by this time, it was apparent that the materials were unsuitable in uranyl sulfate solutions. The corrosion rates based on the weight losses of the defilmed specimens are given in Table XVIII.

TABLE XVIII
Corrosion of Special Nickel-Molybdenum Alloys
by Boiling HRT Core Solution After 200 Hr

Heat No.	Corrosion Rate (mpy)
30-14	146
30-21	81
30-24	121
30-45	29

- (3) Corrosion of Alternate HRT Bolt Materials. -- Several alloys have been considered as replacement materials for the types 17-4 and 17-7 PH stainless steel presently used for bolting applications in the HRT pumps. The alloys are Hastelloy R-235, wrought Multimet, and Timken 16-25-6, supplied as 1/16, 1/8, and 1/2-in. rod, respectively. The compositions of the alloys are presented in Table XIX.

TABLE XIX

Chemical Compositions of Prospective HRT Bolt Materials
Composition (wt%)

<u>Hastelloy R-235</u>	<u>Multimet</u>	<u>Timken 16-25-6</u>
< 2.50 Co	0.08-0.16 C	16 Cr
14-17 Cr	20.0-22.5 Cr	25 Ni
4.5-6.5 Mo	19.0-21.0 Ni	6 Mo
9-11 Fe	2.5-3.5 Mo	0.08-0.10 C
< 1.00 Si	0.75-1.25 Cb-Ta	< 2 Mn
< 1.00 Mn	2.0-3.0 W	< 1 Si
< 0.16 C	18.5-21.0 Co	0.15 N
1.75-2.25 Al	0.10-0.20 N	Balance Fe
2.25-2.75 Ti	Balance Fe	
Balance Ni		

The Hastelloy and Multimet were reported as having been bright-annealed (solution treated and air cooled) in a hydrogen atmosphere. The Timken alloy was reported to be in the hot-swaged condition with a 32-Rockwell-C hardness. The Hastelloy and Multimet were heat treated for 6 hr at 871°C (1600°F) and air-cooled in order to increase their hardness; however, no increase in hardness occurred. The Hastelloy alloy had an initial hardness of 92 Rockwell B, and the Multimet had a 28.5-Rockwell-C hardness. After the heat treatment, the hardnesses were 90.5 Rockwell B and 22.5 Rockwell C, respectively. Although a Haynes Stellite Company representative was consulted, the reason for the failure to harden was never resolved. The suggested recommendation was that alloys of the desired hardness should be ordered directly from Haynes Stellite Company. In spite of not having improved the hardnesses of the two alloys, it was decided, in view of the preliminary nature of this investigation, to proceed with the corrosion tests. The Timken alloy was tested in the as-received condition.

The tests consisted of exposing 1-in. lengths of the materials to HRT core solution at 300°C with an over-pressure of ~ 50 psi of oxygen. The corrosion rates for various elapsed time intervals

are shown in Table XX.

On the basis of the described tests, any one of the three alloys would be satisfactorily corrosion-resistant for use in a bolt material. The Timken alloy exhibited superior corrosion resistance to the other two alloys.

(4) Corrosion of Hardened Surface Coatings on Type 347 Stainless Steel.

Surface-hardened type 347 stainless steel could be of practical use in homogeneous reactor systems and as a result, type 347 stainless steel specimens surface hardened by two different methods were subjected to test in HRT core solution at 80°C. One set of specimens was Malcomized by the Lindberg Steel Treating Company of Melrose Park, Illinois. Another set was treated by the Thermospray 16C process by the Metallizing Engineering Company, Inc. of Westbury, New York. The Malcomized specimens were heated to 1010 to 1038°C (1850 to 1900°F) and then given the Malcomizing treatment to a case depth of 0.006 to 0.007 in. The Rockwell hardness was 92 on the 15N scale (65 Rockwell C). The coating on the Thermospray specimen was 0.062-in. thick and had a composition of 2 Fe, 16 Cr, 4 Si, 4 B, 3 Cu, 3 Mo and the balance Ni. The hardness was between 85 and 92 Rockwell C.

The Malcomized sample deteriorated very rapidly. It was removed from solution after 3 hr of exposure since it was evident that the material was undergoing very severe corrosion attack. Upon removing the sample from solution and brushing off the loose flocculent material that surrounded it, the weight loss was determined to be almost 1 g, which corresponds to a corrosion rate of ~ 860 mpy. The corrosion rate of the Thermospray C sample was determined to be ~ 70 mpy after the first 50 hr, ~ 60 mpy after 150 hr, and the coating began to disintegrate and fall off after 300 hr.

In view of the above results, it can be concluded that neither of the two surface-hardening processes for type 347 stainless steel is satisfactory in uranyl sulfate solutions.

TABLE XX

RATES OF ATTACK ON BOLT MATERIALS BY OXYGENATED
 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 SOLUTION AT 300°C.

Time (hr)	Corrosion Rate (mpy)		
	Hastelloy R-234	Wrought Multimet	Tinken 16-25-6
50	5.6	2.9	1.5
150	3.2	2.3	1.1
310	2.3	1.6	1.1
614	1.6	1.1	0.6
1014	1.5	1.0	0.4
1014	1.5*	1.0*	0.4*

* Rate calculated from weight loss of defilmed specimens at conclusion of test.

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(5) Corrosion of Types 420 and 17-4 PH Stainless Steel and Stellite 6.

Twelve valve stems of hardened type 420 stainless steel were subjected to a rather extensive series of tests in order to evaluate their stability under the conditions and in the environments to which they would most likely be subjected when used in valves for the in-pile corrosion test loops. The stem portions of the valves were in a polished condition; the shank portions were covered with a black, heat-treatment film which was removed prior to testing by means of a fine-grit emery cloth. The steel had a hardness of 50 to 52 Rockwell C. The compositions of the test solutions, test temperatures, and observed corrosion rates are shown in Table XXI. Four of the specimens were given a solution pretreatment to induce preformation of a protective film. It was intended that each specimen be exposed to its respective solution for two weeks, at the end of which time the solution would be replaced and the test continued for an additional two weeks with fresh solution. However at 90°C, the attack was so excessive that all tests were terminated before two weeks had elapsed. In some cases, after as little as 50 to 78 hr, the specimens were so badly corroded that the tests were terminated. Other tests at this temperature were carried out for longer periods only because initially the specimens did not visually appear to be undergoing severe attack; the attack seemed to accelerate with time. Only the tests at 25°C were conducted for the full four weeks.

Some unusual effects were observed in the course of the tests. During the pretreatment, large quantities of shiny crystals accumulated and almost surrounded the specimens; however, the crystals re-dissolved within the next 24 hr. In the 90°C tests, similar crystals deposited on the specimens. In addition, appreciable amounts of sediment formed. The sediment from two experiments and the crystals from one were submitted for spectroscopic analysis; the results appear in Table XXII. From the data in Table XXII, it is apparent that the crystals were copper (or copper-containing) formed by reduction of the copper sulfate. Similarly, it can be seen that the sediment is composed essentially of the constituents of the steel; the fact that nickel was found is

TABLE XXI

CORROSION OF TYPE 420 STAINLESS STEEL VALVE STEMS
UNDER A VARIETY OF ENVIRONMENTAL CONDITIONS

Test No.	Temperature (°C)	Solution Composition (m)			Exposure Time (hr)	Corrosion Rate (mpy)
		UO ₂ SO ₄	H ₂ SO ₄	CuSO ₄		
1	25	0.04	0.04	0.03	672	0.3*
2	90	0.04	0.04	0.03	78	1080
3	25	0.17	0.04	0.03	672	0.5*
4	90	0.17	0.04	0.03	50	1320
5	25	0.05	0.4	0.03	672	9.1*
6	90	0.04	0.4	0.03	78	1760
7	25	0.17	0.4	0.03	672	0.6*
8	90	0.17	0.4	0.03	198	1640
Pretreated for 24 hr in 0.17 m UO ₂ SO ₄ , 0.4 m H ₂ SO ₄ , 0.03 m CuSO ₄ at 25°C.						
9	90	0.04	0.04	0.03	198	187
10	90	0.17	0.04	0.03	50	1410
11	90	0.04	0.4	0.03	78	2300
12	90	0.17	0.4	0.03	198	1510

* Based on weight loss of defilmed specimen.

TABLE XXII

SPECTROSCOPIC ANALYSES OF RECOVERED RESIDUES AND CRYSTALS
FROM CORRODED TYPE 420 STAINLESS STEEL VALVE STEMS

Element	Test No. 2		Test No. 6	Test No. 11
	Crystals	Precipitate	Precipitate	Precipitate
Ag	T			
Cr	0.1	2	5	5
Cu	> 10	2	0.02	0.01
Fe	0.1	10	> 10	> 10
Mo	0.02	0.15	0.05	0.5
Si	0.05	0.1	1	
V		0.1	0.2	0.3
Al			0.3	0.2
Ca			0.3	0.3
Co			0.1	0.1
Mn			0.2	0.2
Ni			1	7

not explainable, since iron and chromium are the only major components of this steel.

From the corrosion data, it can be seen that type 420 stainless steel is resistant in most of the test solutions only at 25°C, and even at this temperature it is quite reactive in 0.04 m UO_2SO_4 , 0.4 m H_2SO_4 , 0.03 m CuSO_4 solution. It is improbable that this material would be suitable for use as a valve-stem material in in-pile loops at temperatures of 25°C and above.

In view of the poor performance of the type 420 stainless steel in the in-pile-loop solutions, two 17-4 PH stainless steel valve stems and four Stellite No. 6 pins (machined from as-received weld rod) with hardness of 28.5 and 48.5 Rockwell C, respectively, were tested in the environments that were most aggressive toward the type 420 stainless steel: (1) pretreatment for 24 hr in 0.17 m UO_2SO_4 , 0.4 m H_2SO_4 , 0.03 m CuSO_4 solution at room temperature and subsequent exposure to 0.04 m UO_2SO_4 , 0.4 m H_2SO_4 , 0.03 m CuSO_4 solution at 90°C; and (2) no pretreatment, merely exposure to the latter solution at 90°C. The total time at 90°C was four weeks (672 hr). At the end of two weeks, the solution was discarded and the experiment was continued for two additional weeks with a fresh solution. The results, given in Table XXIII, show very low corrosion rates for both materials.

The 17-4 PH valve stems had smooth, adherent, uniform black films, whereas the Stellite specimens retained their original polished appearance, although some slight etching was evident along the fine grooves left by the machine-polishing operation.

The attack on both materials was relatively slight, and from a corrosion standpoint, either one would appear to be suitable for in-pile loop applications in the described environment at temperatures of 90°C and lower.

- (6) Corrosion of AlSiMag 192 (TiO₂) and Gold Brazing Alloy. -- AlSiMag 192, essentially pure sintered titanium dioxide, and a brazing alloy containing 82Au-18Ni might find use in various phases of the Homogeneous

TABLE XXIII

CORROSION RATES OF TYPE 17-4 PH STAINLESS STEEL AND STELLITE NO. 6 IN
0.04 m UO_2SO_4 , 0.4 m H_2SO_4 , 0.03 m CuSO_4 SOLUTION AT 90°C FOR 672 HR

<u>Material</u>	<u>Specimen Number</u>	<u>No Pretreatment</u>	Pretreated at
			25°C for 24 hr in 0.17 m UO_2SO_4 0.4 m H_2SO_4 0.03 m CuSO_4
17-4 PH	1	0.75	0.63
Stellite No. 6	1	0.22	0.0
	2	0.10	0.07

* Corrosion rates calculated from weight losses of defilmed specimens.

Reactor Project if they were sufficiently resistant to uranyl sulfate solutions at high temperatures. Therefore, preliminary corrosion tests were carried out in 0.17 m UO_2SO_4 containing 0.02 m H_2SO_4 and 150 psi oxygen at 300°C.

The brazing alloy was fused on a small piece of platinum in a hydrogen atmosphere and tested in this condition. The AlSiMag 192 was tested in the form of two pins 1/8-in.-dia by 1-in. long. The duration of the test was 1000 hr.

If it is assumed that neither gold nor platinum corroded during the test, the weight loss of nickel from the brazing alloy corresponded to the leaching of nickel to a depth of 0.7 mil during the 1000-hr test period. The AlSiMag 192 specimens corroded at rates of about 4.5 mpy.

Thus both of the materials demonstrated a high degree of corrosion resistance to the rather severe conditions of test.

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