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I. SUMMARY

The mockup of the expansion joint and Zircaloy-stainless steel transition joint as used in the HRT reactor vessel has been exposed to circulating HRT fuel solution for 1240 hr in a 100A corrosion test loop (loop F). Fifty thermal cycles between 100°C and 300°C and fifty mechanical deflections of the bellows were imposed on the unit during this 1240-hr period. No leakage across the joint was observed. Several types of corrosion specimens of a number of alloys were subjected to a daily thermal cycle between 100 and 300°C during the testing of the Zircaloy-2-stainless-steel transition joint. None of the specimens showed unusually high corrosion rates as a result of the thermal cycling although the generalized corrosion rate of the entire system based on nickel analysis was somewhat higher than usual.

The 100A loop O, designed to circulate uranium solutions containing beryllium as an additive is now in operation. One preliminary run with a solution of uranium trioxide in beryllium sulfate has been made.

Loop runs were made at 200, 250 and 300°C with solutions containing 0.04 M UO_2SO_4 , 0.05 M CuSO_4 and 0.02 M H_2SO_4 . Each run lasted approximately 2000 hr and in each case the solution was completely stable. The critical velocities observed with type 347 stainless steel coupons were 15 to 20 fps at 200°C, 25 to 30 fps at 250°C and 40 to 45 fps at 300°C.

Further testing directed at determining the effect of chromium(VI) on the corrosion of stainless steel by uranyl sulfate solutions has been completed. At 275°C the effect of chromium(VI) additions was the same as at 250°C; that is, the film-free corrosion rate was increased and the amount of metal dissolved during the formation of a film was decreased.

An attempt was made to descale a 100A loop with a solution containing phosphorous acid and sodium hypophosphite. Very little scale was dissolved during the treatment, and further testing with this solution has been discontinued.

Additional testing of stressed type 347 stainless steel specimens showed that at 100°C in boiling 0.04 M UO_2SO_4 stress-corrosion cracking was not observed in the absence of chloride ions. In the presence of chloride ions new specimens developed pits and cracks in less than 500 hr but if the specimens had been exposed to the boiling uranyl sulfate solution for long periods before the addition of chloride ions, no pitting or cracking was observed for periods in excess of 2000 hr.

A series of tests has been completed in which different alloys and metals were exposed to 4.0 and 10.8 M H_2SO_4 solutions at their boiling points. In addition the same materials were tested in the acid solutions to which had been added rather large amounts of ferric, chromic and zirconium sulfates and lesser amounts of uranyl, copper and ruthenium sulfates. In the 10.8 M solution containing the additives only tantalum showed adequate corrosion resistance. In 4.0 M H_2SO_4 with the additives, tantalum, zirconium and

Zircaloy-2 had excellent corrosion resistance and Carpenter 20-Cb and types 316 and 347 stainless steel corroded between 1 and 3 mpy. In the absence of the additives types 316 and 347 stainless steel corroded at a rate of 2000 mpy and Carpenter 20-Cb at 30 mpy. In addition Carpenter 20-Cb showed a strong tendency toward stress corrosion cracking; in the presence of the additives cracking was not observed.

II. INTRODUCTION.

The data presented in the following sections represent the detailed results obtained during the past quarter (July 31, 1956 to October 31, 1956) by the out-of-pile solution corrosion group of the Homogeneous Reactor Project. A summary of the data has been given in the Homogeneous Reactor Project Quarterly Progress Report for the period ending July 31, 1956.

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

III. 100A LOOP PROGRAM. (H. C. Savage, J. C. Griess, R. S. Greeley, R. M. Pierce*,) (S. R. Buxton, T. H. Mauney, J. A. Russell, W. C. Ulrich.)

A. Loop Engineering.

Loop F - Mockup of HRT Core Vessel Expansion Joint and Zircaloy-Stainless Steel Gasket. The mockup of the Zircaloy-2 - stainless-steel transition and expansion joint, previously described¹, as used in the HRT reactor vessel was tested under conditions simulating reactor start-up, operation at temperature, and shut-down. Fifty thermal cycles and mechanical deflections during 1240 hr of operation in uranyl sulfate solution were completed and a preliminary examination of the unit was made.

After the transition joint and the expansion joint had been installed in 100A dynamic corrosion loop F, the loop was treated with 3% tri-sodium phosphate solution at 100°C for 7 hr, rinsed, and treated with 5% nitric acid solution at 100°C for 9 hr. A final treatment with 1000 ppm oxygen in water at 300°C for 28 hr was made. The loop was then filled with the desired volume of fuel solution containing 0.04 m UO_2SO_4 , 0.005 m CuSO_4 , 0.02 m H_2SO_4 .

During a complete test cycle of the expansion and transition joint the loop temperature was cycled between 100°C at 100 psig to 300°C at 1550 psig, and the expansion joint was extended 5/16 in. and compressed 5/16 in. for a total traverse of 5/8 in. Heating was accomplished in 4 hr, operation at 300°C and 1550 psig was for 16 hr and the cooling down to 100°C was accomplished in 4 hr. Expansion of the bellows joint was made during heat-up in 1/8-in. increments while compression was made during the cooling period in 1/8-in. increments. During the third test

* On loan from TVA.

cycle a faulty mechanical jack being used to extend and compress the bellows failed. This allowed the bellows to be compressed $\sim 3/8$ in. in excess of the design allowable.

The flow rate of the fuel solution from the main circulating loop through the pressure vessel in which the bellows and transition joint were housed was ~ 1 gpm. Flow was external to the expansion bellows, into the transition joint bore and then back into the main circulating loop. The differential pressure across the bellows from outside to inside and across the gasket in the transition joint was maintained at 45 to 55 psi throughout the run. The interior of the expansion joint was filled with distilled water throughout the run. Daily samples of the distilled water were taken and were analyzed for uranium to determine whether leakage across the test gasket or expansion joint had occurred.

After the 50-cycle test the loop was shut down and the outer pressure vessel removed. Visual examination failed to reveal any cracks or damage beyond a partial collapse of the uppermost convolution of the bellows. A leak test, in which 50 psig helium pressure was applied inside the expansion joint, failed to reveal any leakage as measured by a mass spectrograph type leak detector. Further examination of the bellows and transition joint to determine additional information relative to the mechanical reliability of this joint as presently installed in the HRT is being made.

Visual examination of the loop and bellows assembly after partial dismantling revealed one area of significant corrosion. The stainless steel bellows is prevented from flexing at the end welds by tightly fitting rings (see Fig. 1). Near the top and bottom of the crevice between the ring and the bellows several pits, one of which appeared to be 10 to 15 mils deep into the bellows, were observed. Further investigation is being made into the causes and extent of this attack. Over-all loop corrosion rate and corrosion specimen results are discussed under Loop Test Results of this report.

Photographs of the bellows and transition joint and of the test vessel flange are presented in Fig. 1 and 2.

Prior to disassembly, the 10-in. IPS test vessel oval-ring-gasketed joint was leak tested at 500 psig helium pressure with a mass spectrograph type leak detector without evidence of leakage. The flanges are 1500 lb, 10-in. IPS standard type with oval ring R-54 of type 304 stainless steel. Bolts are $1-7/8$ in. per ASTM-A193-52T, grade B-7, threads 8N8, class 3 fit. Nuts are per ASTM A194-53, grade 2H, threaded 8N8, class 2 fit. To assure a tight joint, the as-received flange grooves were remachined to remove tool chatter on mating surfaces and to mate pitch diameters to the gasket. The initial bolt stresses were $28-30 \times 10^3$ psi, with ~ 2500 ft-lb torque applied to obtain this stress.

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Examination of the 10-in. IPS flange groove and gasket after the 50 thermal cycles showed that leakage of fuel solution into the oval ring groove had occurred. A black deposit identified as uranium dioxide and ferric oxide was found in the bottom of the groove and on the curved surface of the gasket - probably resulting from oxygen depletion in the stagnant area between the inner and outer sealing surfaces. However, preliminary examination of the oval ring and groove revealed no pitting or other evidence of excessive corrosion attack.

Loop O - Beryllium Solution Loop. Loop O, designed to handle solutions of uranyl sulfate containing beryllium salts as additives was placed in operation during the past quarter, and in a preliminary run, a beryllium-containing solution was circulated at 250°C.

Prior to operation with the beryllium solution, the loop shielding was tested for adequate containment of toxic material in the event of a loop failure. This was done by charging the loop with a 0.17 M uranyl sulfate solution, bringing the loop up to 250°C and 1000 psia (partial pressure of oxygen was approximately 400 psi) and then opening three loop valves, thus discharging the loop contents into the shield. The area immediately surrounding the loop shielding and the filtered off-gas system was monitored by Health Physics Division personnel for escape of any uranium activity. Since no leakage of activity was observed, the shielding was considered adequate.

- B. Runs with Proposed HRT Solution. The long-term runs at 200, 250 and 300°C with proposed HRT solution (0.04 M UO_2SO_4 containing 0.02 M H_2SO_4 and 0.005 M CuSO_4) were shut down for examination of the corrosion specimens after 1876, 1854, and 2020 hr, respectively. The solutions contained more sulfuric acid, 50 mole%, than was added in previous runs² in order to prevent precipitation of copper and uranium at 250 and 300°C.

No loss of copper or uranium from solution was observed at 200, 250 or 300°C during the above runs. Moreover, the pH of the solutions was essentially constant at 1.6 to 1.7. However, the runs are being continued to insure that 50 mole% acid is sufficient to maintain a stable solution for long periods of time at temperatures as high as 300°C.

The corrosion specimens were scrubbed, weighed, and returned to the loop without being defilmed so that true corrosion rates were not determined; however, the following qualitative observations were made:

- (1) All of the pins that had been exposed in previous runs and that had not been defilmed gained weight. Most of these pins have been exposed to 0.04 M UO_2SO_4 containing 0.005 M CuSO_4 and various amounts of sulfuric acid for over 14,000 hr at velocities between 8 and 42 fps. All of these stainless steel pins retained a protective film under conditions where new stainless steel pins formed no film (e.g., 36 and 42 fps at 200°C and 34 fps at 250°C). This protection by a previously formed film has been observed and discussed before³.

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Fig 1 Photograph of Bellows and Transition Joint Assembly After 1250 Hours Operation

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Fig 2 Photograph of Interior of Transition Joint Assembly After 1250 Hours Operation.

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- (2) Those new stainless steel pins exposed at flow rates lower than the critical velocities listed below corroded more during the period of film formation than in previous runs with less acid. Those new pins exposed at flow rates above the critical velocity remained at least partially free of film and corroded at high rates.
- (3) New stainless steel coupons (exposed in these runs only) indicated critical velocities of 15 to 20 fps at 200°C, 25 to 30 fps at 250°C and 40 to 45 fps at 300°C.
- (4) Titanium and zirconium alloys showed excellent corrosion resistance under all conditions. Niobium pins exposed at low flow rates at 200 and 250°C lost little weight, but one pin at 42 fps at 200°C corroded at approximately 6 mpy.
- (5) Stress-corrosion specimens of types 347, 309 SCB, 17-4 PH (partially hardened), AM-350 (hardened) stainless steel, and titanium 110AT and 130 AM, all stressed to 75% of their room temperature yield strengths, were exposed in each run. No evidence of stress-corrosion cracking was found. These same specimens have now been exposed to 0.04 $\underline{m}$ UO_2SO_4 solution for over 7000 hr with no evidence of cracking.

Three relatively short runs were made in 0.04 $\underline{m}$ UO_2SO_4 at 280°C in order to gain out-of-pile data for comparison with proposed in-pile runs under such conditions. In the first run the solution contained 0.02 $\underline{m}$ H_2SO_4 and 0.0007 $\underline{m}$ CuSO_4 in addition to 0.04 $\underline{m}$ UO_2SO_4 . Stainless steel weight losses for the 200-hr run fell in between those for similar runs at 250 and 300°C as expected (see above). The copper concentration was lower than in previous runs but no effect of this difference was noted.

In the second run the 0.04 $\underline{m}$ UO_2SO_4 solution contained 0.024 $\underline{m}$ H_2SO_4 and 0.02 $\underline{m}$ CuSO_4 and a different loop was used. In this case, the chromium(VI) concentration increased rapidly during the run despite the high acid concentration. The chromium(VI) evidently was leached from the scale on the loop. This phenomenon probably occurred because previous runs in the loop had been at a lower temperature with very acid solutions and most of the chromium from extensive corrosion of the loop remained within the scale as Cr_2O_3 .

Since it was felt that the chromium(VI) had influenced the observed corrosion rates, the loop was washed with 0.17 $\underline{m}$ UO_2SO_4 at 280°C for 100 hr to remove some of the chromium from the scale. Then a third run was made under the same conditions as the second run. The chromium(VI) concentration increased about half as rapidly as before but corrosion rates were very similar to those obtained in the second run. Therefore, it was concluded that satisfactory data had been obtained for comparison with other out-of-pile runs; however, since the above runs were made in an old loop in the presence of chromium(VI), the results would probably not agree with in-pile data obtained in a new loop in the absence of chromium(VI). This difference has been discussed previously⁴.

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The corrosion rates in the latter two runs were slightly higher than in the first run at 280°C, presumably because of the higher acid concentration. Also, the critical velocities in the latter two runs, 25 to 30 fps, were lower than in the first run, 30 to 35 fps. The solutions in all three runs were stable. Of particular interest was the fact that neither uranium nor copper was lost from the 0.04 m UO_2SO_4 , 0.024 m H_2SO_4 , 0.02 m CuSO_4 solution at 280°C for 500 hr in the second run and 680 hr in the third.

- C. Effect of Thermal Cycling on Corrosion. The effect of thermal cycling on corrosion was investigated during the HRT bellows-flange mockup test. The solution circulated was 0.04 m UO_2SO_4 containing 0.02 m H_2SO_4 , 0.005 m CuSO_4 and 500 to 1000 ppm O_2 . The design of the mockup was presented previously⁵, and the experimental conditions and preliminary engineering results have been discussed above. The corrosion results are also preliminary since the specimens were not defilmed but were scrubbed, weighed, and returned to the loop for further testing.

The pins exposed at low flow rate (17 fps) all showed slight weight gains in the scrubbed condition, indicating essentially no corrosion after the initial film formed. Alloys exposed included titanium RC-55, Zircaloy-2, Incoloy, and types 347, 304L, and 309 SCb stainless steel.

The pins exposed at high velocity (70 fps) were all either titanium or zirconium alloys. Commercially pure titanium, crystal bar zirconium, and Zircaloy-2 showed insignificant weight losses, but the alloys of titanium with aluminum and tin, aluminum and vanadium, aluminum and manganese, and aluminum and chromium showed definite, though small, weight losses. The corrosion rates of the above-named alloys were between 0.4 and 1 mpy (scrubbed).

The type 347 stainless steel coupons indicated a critical velocity of 60 to 70 fps, a value substantially higher than normally found in the absence of the temperature cycling; however, the increased critical velocity could have resulted from the pretreatment which the system received before the run with uranyl sulfate began. Up to the critical velocity all coupons showed slight weight gains.

Specimens of the following alloys were suspended in the solution inside the bellows test unit: types 347, 304L, and 309 SCb stainless steel, titanium RC-55, titanium-8%-manganese, titanium-6%-aluminum-4%-vanadium, crystal bar zirconium, and Zircaloy-2. Coupons of the following alloys were mounted in contact with one another on a rod attached to the dip tube in the solution inside the test unit: type 347 stainless steel, titanium-75A, and Zircaloy-2. The latter coupons were used to investigate galvanic couple effects and crevice attack. Also attached to the dip tube in the solution inside the test unit were specimens of type 347 stainless steel, titanium-6%-aluminum-4%-vanadium, and Zircaloy-2, stressed to 80% of their 300°C yield strengths. The flow rate of solution past these specimens was very low.

All of these specimens inside the test unit were filmed over and none had suffered any significant attack perceptible under visual examination. None of the specimen assemblies were dismantled for weighing at this time.

No indication of accelerated attack caused by galvanic action, crevices, or stress was noted. All of the crystal bar zirconium and Zircaloy-2 specimens had a light coating of a loose, white scale on top of the dark adherent oxide. This white scale has been noticed before in some runs at 300°C and has not been associated with any increase in attack.

The increase in nickel ion concentration in solution indicated a generalized corrosion rate of nearly 1 mpy. A similar run at 300°C without thermal cycling had a generalized rate of about 0.1 mpy. Therefore, although the corrosion specimens indicated no effect of the thermal cycling, the generalized corrosion rate did indicate an increase in attack rate somewhere in the system.

- D. Effects of Steam Overpressure and Pretreatment. In a previous report⁷ data were presented on the effects of steam overpressure and pretreatment on corrosion of stainless steel in simulated "in-pile" solutions. It was reported that the results were not clear-cut due to experimental difficulties. Therefore, two additional runs, E-66 and E-67, were made this quarter. The conditions of the runs are listed in Table I.

TABLE I

THE EXPERIMENTAL CONDITIONS FOR RUNS E-66 AND E-67

Run No.	Time (hr)	UO ₂ SO ₄ <u>m</u>	H ₂ SO ₄ <u>m</u>	CuSO ₄ <u>m</u>	Pretreatment	Loop Temp. °C	Pressurizer Temp. °C	Steam Overpressure, psi
E-66	200	0.17	0.04	0.03	None	250	275	250
E-67	4	--	--	--	3% TSP	100	100	0
	12	--	--	--	5% HNO ₃	100	100	0
	24	--	--	--	H ₂ O + O ₂	250	275	250
	200	0.17	0.04	0.03		250	275	250

The results of run E-66, in which the pressurizer was maintained at 275°C to give about 250 psi steam overpressure, are shown in Fig. 3. They are compared with run E-62, in which the system was maintained isothermal, and run E-61 in which the pressurizer was maintained at 265°C to give about 150 psi steam overpressure. Both E-61 and E-62 had the same solution composition as E-66. The data show that with increasing steam overpressure the critical velocity was increased and weight losses were generally decreased. However, weight losses were still much higher in E-66 than those reported for in-pile runs in the absence of high-level radiation.

The result of run E-67, before which the loop and corrosion specimens were given a full pretreatment, is shown in Fig. 4. It is compared with run E-66, which had no pretreatment. Both runs were made with steam pressurization. The data show that the coupons in run E-67 had anomalously high weight losses, higher than the run without pretreatment. This effect of pretreatment was noted in a previous report for run E-64⁸ but is contrary to the results found with many other pretreatments in

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Fig. 3. Effect of Steam Overpressure on Corrosion of Type 347 SS Coupons in 0.17 $\underline{m}$ UO_2SO_4 + 0.04 $\underline{m}$ H_2SO_4 + 0.03 $\underline{m}$ CuSO_4 At 250°C - 200 Hours.

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Fig. 4. Effect of Pretreatment on Corrosion of Type 347 SS Coupons in 0.17 m UO_2SO_4 + 0.04 m H_2SO_4 + 0.03 m CuSO_4 At 250°C - 200 Hours.

similar solutions⁹.

Therefore, the effects of steam overpressure and pretreatment are still not fully understood and further testing must be carried out. However, it does appear that increasing the steam overpressure in a system does increase the critical velocity.

- E. Effect of Chromium(VI) on the Corrosion of Stainless Steel by Uranyl Sulfate Solutions. In a previous report¹⁰ the results of a study in which 0.17 M UO_2SO_4 containing definite concentrations of chromium(VI) were circulated in a titanium loop at 250°C were reported. During the past quarter a similar study was made at 275°C. The experimental conditions were the same as in the previous study; that is, all runs were made in loop G for 100 hr and the oxygen concentration was 1000 to 2000 ppm. Two stainless steel pins were exposed at 10 to 12 fps and two at 68 to 70 fps.

Figure 5 shows the results; for comparison, the data obtained previously at 250°C are also shown. The data show that the addition of chromium(VI) to 0.17 M UO_2SO_4 at 275°C has the same effect as at 250°C. That is, the higher the chromium(VI) concentration, the higher the film-free corrosion rate and the lower the average corrosion rate at low velocity. However, at 275°C at a given chromium(VI) concentration, the corrosion rate of the film-free stainless steel was higher and the filmed-over corrosion rate was lower than at 250°C. No more than 200 ppm chromium(VI) were added at 275°C because the critical velocity would have been in excess of 70 fps.

Since the data reported above show a trend identical to that obtained at 250°C, the same hypothesis previously reported¹⁰ seems to apply.

- F. Loop Decontamination with H_3PO_3 - NaH_2PO_2 . At the suggestion of the Chemical Technology Division an attempt was made to descale a stainless steel loop by use of a solution containing a 2 wt% phosphorous acid - 2 wt% sodium hypophosphite solution. The solution was circulated for 26 hr in Loop D at 170°C under helium pressurization. Loop D had previously been exposed for over 9000 hr to various uranyl sulfate solutions at temperatures between 200 and 350°C and was heavily coated with scale.

Solution samples taken during the run gave erratic results, presumably due to the insolubility of iron, nickel, and chromium phosphates. The final concentration of iron in solution corresponded to 54 g of Fe_2O_3 dissolved, although the iron concentration after 18 hr corresponded to 96 g of Fe_2O_3 dissolved.

However, visual examination of the loop after the run indicated that descaling was far from complete. All observable areas of piping were still covered with oxide scale. Also, four pins with scale on their surfaces from previous runs were exposed during the run, two at 17 fps and two at 68 fps. Each pin lost some weight but all retained a large fraction of their scale. Hence, the phosphorous acid-hypophosphite

Fig. 5. Corrosion of Type 347 SS Pins in 0.17 m UO_2SO_4 Containing Cr(VI) - Titanium Loop - Each Run 100 Hr.

solution was not as effective a descaling solution under the test conditions as the chromous sulfate solution tested previously¹¹.

IV. LABORATORY SERVICE CORROSION STUDIES. (J. L. English, E. F. House,
D. J. Krause, J. C. Griess)

- A. Stress Corrosion of Type 347 Stainless Steel. A small-scale, steam-heated stainless steel evaporator designed for study of stress-corrosion cracking susceptibility of type 347 stainless steel in boiling uranyl sulfate solutions has been operated for a total of 10,000 hr. The exposure time represents an increase of 1870 hr since corrosion data were last reported¹². Detailed information on the design of the evaporator experiment and preliminary corrosion data have been reported previously^{13, 14}.

No cracking was observed on three-point loading, constant-strain type 347 stainless steel specimens stressed at 20,000 psi after 7630 hr at 101 to 102°C in 0.04 M UO_2SO_4 solution containing 0.004 M H_2SO_4 and 0.005 M CuSO_4 . Corrosion rates determined from the as-removed weight loss on the total surface area of the stress assembly were less than 0.1 mpy for solution and vapor exposure. The initial 1500-hr exposure period was accumulated with with boiling 0.17 M UO_2SO_4 solution.

Upon completion of the 7630-hr period, the effect of chloride ion as a possible promoter of stress-corrosion cracking of type 347 stainless steel in boiling uranyl sulfate solution was examined. An addition of 60 ppm of chloride as sodium chloride was made to the 0.04 M UO_2SO_4 -0.004 M H_2SO_4 -0.005 M CuSO_4 test solution. The original stress assemblies remained in the evaporator; in addition, one new assembly of type 347 stainless steel stressed at 20,000 psi was placed in the solution phase and one in the vapor phase. All of the assemblies were examined after 500 hr of operation with the chloride-containing solution.

Several small cracks were found near the area of the maximum applied stress of 20,000 psi on the new solution-exposed specimen; random pitting and blistering were also observed on the stress specimen and on the welded base plate. The generalized corrosion rate for the complete stress assembly was 3.8 mpy as compared with the initial 500-hr rate of 0.1 mpy observed in the chloride-free uranyl sulfate solution at the start of the test. No cracks were found on the new vapor-exposed stress assembly nor on the solution and vapor-exposed assemblies that had been exposed previously for 7630 hr in chloride-free uranyl sulfate solution.

A total of 2380 hr of operation was accumulated on all of the stress assemblies with the chloride-containing 0.04 M UO_2SO_4 solution. During this period, the solution and vapor-exposed assemblies with 7630 hr of previous operation in chloride-free solution failed to show any tendency toward stress-corrosion cracking. Likewise, the vapor-exposed assembly included in the test at the start of the chloride-present phase of operation evinced no signs of cracking; the indicated corrosion rate for the assembly was 0.2 mpy after 2380 hr as compared

with negligible corrosion rates for vapor-exposed assemblies over a similar period of time with chloride-free uranyl sulfate solution present in the evaporator.

Four large cracks were present on the new solution-exposed stress specimen of type 347 stainless steel after 2380 hr of contact by the chloride-containing uranyl sulfate solution. Numerous pits and blisters appeared on the components of the assembly, namely, the stress specimen and the welded base plate. The generalized corrosion rate for the complete stress assembly was 4.1 mpy for the 2380-hr period.

The pre-corroded stress assemblies - both solution and vapor-exposed - exhibited slight weight increases at the completion of a total of 10,000 hr operation of which the last 2380 hr were accumulated in the chloride-present solution. The complete absence of cracks and pits on the stress specimens in these assemblies suggested that the film that formed on the specimens during the 7630 hr of chloride-free exposure possessed characteristics of uniformity and compactness that successfully prevented attack by chloride ions on the metal surfaces. Newly machined stainless steel surfaces were not endowed with a film of similar properties as was demonstrated by the development of cracks and pits on a stress specimen during the initial 500 hr of exposure in chloride-containing uranyl sulfate solution. Supporting laboratory corrosion studies with newly machined and stressed type 347 stainless steel specimens corroborated the results of the evaporator test with respect to the behavior of the new solution-exposed stress specimen. The laboratory results showed that cracking occurred on stress specimens during the exposure period between 100 and 200 hr in boiling and aerated $0.04 \text{ M } \text{UO}_2\text{SO}_4$ - $0.02 \text{ M } \text{H}_2\text{SO}_4$ - $0.005 \text{ M } \text{CuSO}_4$ solution containing 25 and 50 ppm of chloride ion, respectively¹⁵.

- B. Corrosion of Several Materials in 4 and 10.8 M Sulfuric Acid. At the request of the Chemical Technology Division a number of corrosion tests have been carried out to find a suitable material for construction of a tank in which solids collected in the HRT hydroclone can be dissolved and stored after dilution. The tests to date have been made in boiling (157°C) $10.8 \text{ M } \text{H}_2\text{SO}_4$, in boiling (109°C) $4 \text{ M } \text{H}_2\text{SO}_4$ or in $4 \text{ M } \text{H}_2\text{SO}_4$ at 39°C . Tests have also been carried out in the above acid solutions to which had been added synthetic corrosion and fission products. The results are reported in the following sections.

Duplicate samples of each material were used, and the average corrosion rate of the two specimens is reported in the tables. The over-all corrosion rate was determined by calculating the penetration from the average weight loss of the duplicate specimen during the entire period of test. The final corrosion rate was the incremental rate during the last exposure period, usually between 50 to 100 hr except in cases where the total exposure time was very short. All the samples with the exception of Graphitar-14 and aluminum oxide were prepared for tests by polishing with 80 and 120 grit papers. The samples were then immersed in acetone and in an alcohol solution, dried and weighed. Graphitar-14 and aluminum oxide were immersed in a solution composed of half water and half alcohol, then dried and weighed.

Table II shows the results obtained with several materials in boiling 4 M H_2SO_4 (109°C) through which helium was passed.

TABLE II

THE CORROSION OF SEVERAL MATERIALS IN 4 M H_2SO_4
TEMPERATURE - 109°C ATMOSPHERE - HELIUM

Material	Exposure Time, hr	Corrosion Rate, mpy	
		Over-all	Final
Aluminum Oxide	547	10.	9.7
Carpenter 20-Cb	524	32.0	38
Graphitar-14	530	Wt. Gain	Wt. Gain
Hastelloy-B	437	3.2	3.8
Illium-R	437	15	17.4
Lead	436	1	1
Tantalum	442	0	0
Zircaloy-2	437	0	0
Zirconium	437	0	0
316 Stainless Steel	4.5	2000	2000
347 Stainless Steel	4.5	2500	2500
Stellite 6	2.5	1100	1100
Stellite 98M2	40	150	140

Tantalum, Zircaloy-2 and zirconium showed no appreciable weight change during the test period whereas Carpenter 20-Cb, Hastelloy B and Illium R showed corrosion rates that increased slightly with time. In addition, Carpenter 20-Cb showed cracks in areas of local stress after approximately 250 hr; with continued exposure, the cracks became larger and more numerous. Lead showed erratic weight changes and developed a red-brown film. Aluminum oxide showed a slight weight gain during the first 200 hr of test and then corroded at about 15 mpy for approximately 250 hr and at the end of the test was corroding at 9.7 mpy. Graphitar-14 showed a weight gain, probably because the acid solution could not be completely removed from its pores. Stellites 98M2 and 6 and types 347 and 316 stainless steel corroded rapidly and were tested for only short periods.

To determine the effect of ruthenium on the corrosion of Carpenter 20-Cb, Hastelloy-B and zirconium, one specimen of each alloy was exposed in boiling 4 M H_2SO_4 containing about 25 to 50 ppm ruthenium sulfate. The average corrosion rates for 44-hr runs were: Carpenter 20-Cb, 170 mpy; Hastelloy-B, 41 mpy; and zirconium, 1.0 mpy. In all cases the rates appeared to be decreasing with time, but with Hastelloy-B and Carpenter 20-Cb the rates were much greater than in the absence of the trace of ruthenium.

Table III shows the results obtained in boiling 4 M H_2SO_4 to which had been added the following salts: $\text{Zr}(\text{SO}_4)_2$, 56 g/l; $\text{Fe}_2(\text{SO}_4)_3$, 75 g/l; $\text{Cr}_2(\text{SO}_4)_3$, 24 g/l; $\text{Ru}(\text{SO}_4)_2$, 0.4 g/l; UO_2SO_4 , 28 g/l; and CuSO_4 , 1.5 g/l; oxygen was also bubbled through the solution throughout the test.

TABLE III

THE CORROSION OF SEVERAL MATERIALS IN 4 M H_2SO_4 CONTAINING SIMULATED
CORROSION AND FISSION PRODUCTS.

TEMPERATURE - 111°C

ATMOSPHERE - OXYGEN

Material	Exposure Time, hr	Corrosion Rate, mpy	
		Over-all	Final
Aluminum Oxide	457	4.1	8.2
Carpenter 20-Cb	513	1.5	1.4
Hastelloy-B	24	5300	5300
Illium R	513	29	58
Lead	514	3.4	0
316 SS	510	5.3	3.0
347 SS	510	5.0	3.0
Stellite 98M2	112	240	240
Stellite-6	504	21	27
Tantalum	514	0.1	0
Zircaloy-2	510	0.3	0
Zirconium	509	0.3	0.2
Graphitar-14	457	Wt.Gain	Wt.Gain

Carpenter 20 Cb maintained its original appearance with no sign of cracks around locally stressed areas and showed a uniform corrosion rate. Stellite-6 and Illium-R manifested corrosion rates which increased with time, while types 316 and 347 stainless steels had low corrosion rates which showed little variation with time. Localized attack was also apparent on the Stellite-6 samples. The stainless steel samples developed a red-brown film. Tantalum, Zircaloy-2 and zirconium showed very slight corrosion after the first 30 hr; for the remainder of the run these metals corroded at a negligible rate. Aluminum oxide specimens gained weight the first 100 hr, and then corroded at approximately 8 mpy. A slight black discoloration of the samples was noted. Graphitar-14 remained unchanged in appearance and showed a slight weight gain.

A comparison of Table II with Table III shows the effect of the added salts and oxygen. Future tests will be made to determine the individual effects of certain of the added salts and oxygen. Aluminum oxide, Carpenter 20-Cb, types 316 and 347 stainless steels and Stellite 6 showed lower corrosion rates than in the absence of the added salts and oxygen. In the case of the stainless steels and Stellite 6 the decrease in the corrosion rates was very marked, while the decrease in the Carpenter 20-Cb and aluminum oxide over-all rates was from 32 to 1.5 and from 10 to 4 mpy, respectively. Also, no cracks appeared around locally stressed areas in the Carpenter 20-Cb samples.

Hastelloy-B increased its corrosion rate from 3 mpy in the solution without additives to 5300 mpy in the solution with added salts. Illium-R, lead and Stellite 98M2 showed increased corrosion rates by a factor of about 2 to 3 when placed in the acid-plus-salts solution. Zirconium, Zircaloy-2, tantalum and Graphitar-14 were attacked only slightly in both solutions.

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Table IV shows the corrosion rates of several materials in 4 M H_2SO_4 solution at 39°C through which helium was passed.

TABLE IV

THE CORROSION RATE OF VARIOUS MATERIALS IN 4 M H_2SO_4
TEMPERATURE - 39°C ATMOSPHERE - HELIUM

Material	Exposure Time, hr	Corrosion Rate, mpy	
		Over-all	Final
Aluminum Oxide	413	Wt.Gain	Wt.Gain
Carpenter 20-Cb	439	0.4	0.1
Hastelloy-B	439	0.2	0.2
Illium-R	439	0.14	0.1
Lead	439	0.1	Wt.Gain
316SS	437	7.9	0
Stellite-6	435	11.6	0.5
Tantalum	439	0	0
Zircaloy-2	439	0	0
Zirconium	439	0	0

All the above materials having a measurable corrosion rate showed a uniform attack except Stellite-6. For the first 300 hr Stellite-6 showed localized attack in areas in contact with the glass sample-holder. After that period, attack practically ceased. All other materials had excellent corrosion resistance.

The data obtained in 10.8 M H_2SO_4 are given in Tables V, VI, and VII. Table V indicates the corrosion rate of various metals in boiling 10.8 M H_2SO_4 (157°C) solution. No gas was passed through the solution.

TABLE V

THE CORROSION RATE OF SEVERAL METALS IN 10.8 M H_2SO_4 AT 157°C.

Material	Exposure Time, hr	Corrosion Rate, mpy	
		Over-all	Final
Carpenter 20-Cb	4.5	39,000	39,000
Hastelloy-B	463	70	160
Illium-R	65	1000	930
Lead	439	30	20
Tantalum	436	0.1	0.1
Zircaloy-2	463	11	19
Zirconium	436	6.1	8

The Hastelloy-B corrosion rate increased with time. After about 100 hr in solution the edges of the samples showed localized corrosion. Lead manifested a decreasing corrosion rate and a uniform attack. Tantalum corroded at a nearly negligible rate. A tantalum specimen analyzed by vacuum fusion analysis for hydrogen had 4.6 ppm, while a control sample

had 1.7 ppm. Zircaloy-2 and zirconium were attacked uniformly but the corrosion rates increased with time. A zirconium sample analyzed for hydrogen had 63 ppm of hydrogen while an analysis of a control sample showed 68 ppm.

Table VI presents data obtained from immersing various materials in 10.8 M H₂SO₄ solution at 157°C. Oxygen was bubbled through the solution during the test.

TABLE VI
THE CORROSION RATE OF SEVERAL MATERIALS IN 10.8 M H₂SO₄.
TEMPERATURE - 157°C

Material	Exposure Time, hr	ATMOSPHERE - OXYGEN	
		Corrosion Rate, mpy Over-all	Final
Carpenter 20-Cb	22	22,000	22,000
Hastelloy-B	256	23	44
Illium-R	25	1100	1100
Lead	256	110	130
Tantalum	255	0.2	0.1
Zircaloy-2	255	5.4	5.4
Zirconium	256	7.5	11

Hastelloy-B, after approximately 160 hr of exposure, showed local corrosion attack on the edges which increased with time. At the end of the test the entire surface of the samples showed extensive deterioration. The corrosion rate of lead increased with time although the attack was uniform. As in all other tests the corrosion rate of tantalum was very low. A specimen analyzed by vacuum fusion analysis for hydrogen revealed 3.4 ppm of hydrogen. A control sample analyzed by the same method had 1.7 ppm hydrogen. Zircaloy-2 corroded at a lower rate than zirconium and both metals had a dark gray film on their surfaces. A zirconium sample analyzed for hydrogen had 57 ppm hydrogen. A control sample had 68 ppm hydrogen.

A comparison of Tables V and VI shows that the addition of oxygen to the system decreased the corrosion rate of Carpenter 20-Cb, Hastelloy-B, and Zircaloy-2 but increased the corrosion rates of Illium-R, lead, and zirconium although the solubility of oxygen in the 10.8 M H₂SO₄ solution would be very low.

Table VII presents the corrosion rates of the various metals in 10.8 M H₂SO₄ containing simulated corrosion and fission salts added in the following amounts: Zr(SO₄)₂, 152 g/l; Fe₂(SO₄)₃, 208 g/l; Cr₂(SO₄)₃, 65 g/l; Ru(SO₄)₂, 1.2 g/l; UO₂SO₄, 50 g/l; and CuSO₄, 4 g/l.

TABLE VII

THE CORROSION RATE OF SEVERAL METALS IN 10.8 M H_2SO_4 CONTAINING SIMULATED
CORROSION AND FISSION PRODUCTS
TEMPERATURE - 159 to 161°C ATMOSPHERE - OXYGEN

Material	Exposure Time, hr	Corrosion Rate, mpy	
		Over-all	Final
Hastelloy-B	98	320	130
Lead	117	40	10
Tantalum	98	0.6	0.3
Zircaloy-2	98	200	100
Zirconium	98	700	640

The results indicate a high corrosion rate for all metals except lead and tantalum, both of which are still under test. To date tantalum has shown a slight weight loss but remains unchanged in appearance. Lead specimens have developed a light gray film and seem to be corroding at a decreasing rate.

In comparison with Tables V and VI the addition of the salts accelerated the corrosion rate of Hastelloy-B, Zircaloy-2 and zirconium. The corrosion rate of lead remains approximately the same as in the system without oxygen (Table V), but corrodes slower than in the system through which oxygen was bubbled (Table VI). Tantalum showed excellent resistance to corrosion by all of the various solutions investigated.

Some tests are still in progress but certain conclusions can be drawn at this time. Of the metals and alloys tested, only tantalum seems suitable for use in the dissolver tank. Zirconium and Zircaloy-2 demonstrate fair corrosion resistance to 10.8 M H_2SO_4 at its boiling point but the addition of simulated corrosion products caused a very substantial increase in the corrosion rate of both materials.

In boiling 4 M H_2SO_4 , Carpenter 20-Cb corroded at about 30 to 40 mpy and indicated a strong tendency toward stress-corrosion cracking. The combined addition of corrosion products and ruthenium sulfate to this solution brought about a substantial reduction in the corrosion rate of the alloy, and for the 513-hr test no cracks were observed. However, in view of the cracking observed in the absence of the corrosion products and ruthenium, it would be extremely hazardous to rely on this material until more extensive testing has been completed. The corrosion products in the 4 M H_2SO_4 produced a very marked inhibition of the corrosion of types 316 and 347 stainless steel as well as Carpenter 20-Cb. On the other hand, corrosion products produced a very marked acceleration of the corrosion of Hastelloy-B.

The corrosion resistance of lead in 4.0 M H_2SO_4 was good under all conditions tested although corrosion rates were probably somewhat higher than listed in the tables because it was difficult to remove all of the scale from the surface of the lead.

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