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I. SUMMARY

A fifth test has been made on the HRT core - pressure-vessel flange and transition mockup. No leakage occurred in 951 hr for a total of 5069 hr of successful operation.

Metallographic examination has shown the occurrence of stress-corrosion cracks on the outside of a straight section of type 347 stainless steel pipe exposed to a tap- and demineralized-water spray for 20,000 hr. The section of pipe was part of a 100A loop and temperature of the solution circulated in the loop varied from 200 to 300°C. The cracks did not penetrate more than about 1/4 of the wall thickness. In the same loop, ferrite in a type 347 stainless steel weld was found to have been selectively attacked by the various uranyl sulfate solutions circulated during the 20,000 hr lifetime of the loop.

A hydride phase was found metallographically in a titanium-75A sample holder exposed to 1.3 m uranyl fluoride at 250°C and in a titanium insert exposed to oxygen-free uranyl sulfate for several thousand hours at 200 to 300°C.

It was shown that sulfate ions inhibit corrosion of stainless steel in 0.17 m uranyl sulfate solution at 250°C; the degree of inhibition was proportional to the concentration of the added sulfate ion concentration up to 0.17 m. Other compounds shown to be without value as inhibitors under the above conditions were: $\text{Ce}(\text{SO}_4)_2$, $\text{H}_7\text{P}(\text{MoO}_4)_{12}$, As_2O_5 , NaBiO_3 , H_3SbO_4 , $(\text{RuNO})_2(\text{SO}_4)_3$, NaNO_3 , and AgSO_4 .

Uranyl nitrate and uranyl perchlorate solutions were circulated at 250°C in a stainless steel loop. Corrosion of stainless steel was less in 0.17 m $\text{UO}_2(\text{NO}_3)_2$ than in 0.17 m UO_2SO_4 , but in 0.17 m $\text{UO}_2(\text{ClO}_4)_2$ corrosion of stainless steel was extremely severe.

The initial run in the new all-titanium loop, loop H, gave low corrosion rates on pretreated stainless steel coupons. The second run in the same loop gave higher corrosion rates for similarly pretreated coupons, but this effect may have been due to small differences in pretreatment rather than to an effect of the loop itself.

A solution of 0.001 *m* CuSO₄ containing 0.003 *m* H₂SO₄ was shown to be satisfactory for the blanket region of the HRT both from a stability and a corrosion standpoint.

Films formed on stressed type 347 stainless steel by exposure in boiling and aerated chloride-free uranyl sulfate solutions were found to provide at least some protection to the alloy from stress-corrosion cracking when exposed in a similar solution containing chloride ions. On the other hand, films or scales formed by heating the stainless steel in air at 1250°F did not protect the steel from stress-corrosion cracking in boiling chloride-containing uranyl sulfate solutions.

Stressed type 347 stainless steel was not subject to cracking after 2500 hr in boiling and aerated water containing 100 ppm chloride at pH values of 2.8 and 10.3. However, under similar conditions and with an oxygen overpressure of 150 psi, cracking was produced during the initial 300 hr of test.

The presence of magnesium metal (out of contact with the specimen) or stannous chloride in boiling 42% MgCl₂ solution was of no consequence in reducing the susceptibility of type 347 stainless steel to cracking; however, magnesium metal in contact with the stainless steel completely eliminated the susceptibility of the latter to cracking during a 100-hr test.

Chloride-containing marking inks caused cracking of stressed stainless steel when specimens which had been marked were exposed to oxygen-containing steam at 300°C.

A number of alloys of zirconium were tested in simulated HRT fuel solution at 300°C. The best corrosion resistance was shown by a 20Nb-80Zr cast alloy. A pre-oxidized 33Nb-67Zr also showed excellent corrosion resistance.

A number of miscellaneous tests were conducted with materials of possible interest to the HRP. Elgiloy, a spring alloy considered for use in the liquid-level control for the HRT pressurizer, was found - in the aged condition - to be subject to cracking in chloride-free HRT core solution at 300°C. The corrosion rate of AlSiMag 652 (a sintered alumina) was 8 mpy

after 1000 hr at 150°C in oxygenated 0.17 m UO_2SO_4 containing 0.04 m H_2SO_4 and 0.03 m CuSO_4 . A ceramic electrical insulator material, Ceramicite C-100, was completely unsatisfactory in high-temperature uranyl sulfate solutions. Similarly, Frogalloys C and M were subject to excessive corrosion attack in boiling simulated HRT core solution. Nitrided titanium showed excellent corrosion resistance to oxygenated 0.04 m UO_2SO_4 containing 0.02 m H_2SO_4 and 0.005 m CuSO_4 at 300°C.

II. INTRODUCTION

The data presented in the following sections represent the detailed results obtained during the past quarter (July 31, 1957 to October 31, 1957) by the out-of-reactor solution corrosion group of the Homogeneous Reactor Project. A summary of the data has been reported in the Homogeneous Reactor Project Quarterly Progress Report for the period ending October 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, S. E. Bolt, W. C. Ulrich, H. C. Savage, and J. C. Griess)

A. Fifth Test of the HRT Core - Pressure-Vessel Flange and Transition Joint Mockup.

A fifth test of the mockup of the Zircaloy-2 - stainless steel transition and expansion joint as used in the HRT reactor vessel has been made in 100A dynamic loop F. The first four tests were mentioned previously¹⁻⁴ and detailed reports of the first three tests were published elsewhere.^{5,6}

The test lasted 951 hr, 23 hr in water and 928 hr on fuel solution (0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , 0.005 m CuSO_4). The system was started and checked out on water at 300°C and a concentrated solution was then added to bring the concentration to that of the fuel solution. Only one thermal cycle was made during the entire run (not counting startup and shutdown) and that was made to allow repair of the jack that deflects the bellows. Otherwise, the run was made isothermally at 300°C and 1550 psig. Six mechanical deflections of the bellows were made each day for a total of 226 deflections.

Prior to disassembly, the 10-in.-IPS, 1500-lb test vessel oval-ring joint was helium leak tested. 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.

During the run water samples withdrawn periodically from the interior of the bellows were analyzed for uranium to indicate whether fuel solution was entering through the bellows or across the transition joint. (The interior of the bellows was maintained at about 35 psi below the pressure on the exterior of the bellows). No uranium was detected. After disassembly of the flanged joint, the bellows and transition joint were also helium leak tested and no leakage was detected. Therefore, throughout the five tests, the bellows and transition joint have remained sound and leak-tight for 5069 hr total operating time, which includes 4545 hr of exposure to fuel solution, 168 thermal cycles, and 374 mechanical deflections.

The pitted areas on the bellows⁷ were examined again by moving the reinforcing rings to reveal the crevice area between the rings and the bellows. A microscope-dial gauge indicator assembly was used as before to measure the pit depths. An increase of 0.003 in., on the average, was observed in the depths of the pits with the deepest pits measuring 0.022 to 0.024 in. Also the pitted areas were again partially covered with a loose, red oxide. It was apparent that the pitting attack, which had ceased in the previous test during which no mechanical deflections were made,⁸ had started again. Therefore, the pitting attack must in some way be caused by the mechanical deflections.

X-ray diffraction analysis of the loose oxide collected from the crevice between the reinforcing rings indicated the presence of only ferric oxide. The absence of reduced uranium in the oxide is in contrast to all of the previous tests in which 10 to 40% UO_2 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 stainless steel pins at 12 fps and coupons at 7 to 50 fps gained or lost insignificant amounts of weight. The commercially pure titanium

(RC-55 and RC-70) and the crystal bar zirconium and Zircaloy-2 pins at 68 fps also showed insignificant weight changes. As in the previous tests, the high-strength titanium alloys exposed at 68 fps continued to corrode at low rates, 0.4 to 3 mpy. It appeared that weight losses of stainless steel specimens were slightly greater in the previous run with thermal cycles than in this run without thermal cycles.

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 value was about the same as in the previous test with thermal cycles. The hexavalent chromium concentration increased at a rate about double that of the nickel concentration during the first 200 hr of the test. Such behavior is usually observed in runs at 300°C. However, the oxygen concentration in solution decreased from about 1000 ppm to about 100 ppm during this part of the run. When the oxygen concentration dropped below about 500 ppm, the rate of increase of chromium VI concentration dropped to zero. The addition of oxygen to bring the oxygen concentration back up to 1000 ppm then caused the rate of increase of chromium VI concentration to return to its former value. This dependence of the chromium VI concentration on the oxygen concentration shows that in order to get an increase in chromium VI in solution in out-of-reactor tests for inhibition of corrosion of stainless steel, the oxygen concentration should be greater than 500 ppm.

B. Metallographic Results from Previous Tests.

Metallographic results from several previous tests have recently become available. In general these corroborate other data previously reported.

1. Examination of Loop H: Stress-Corrosion Cracks in the Line Cooler.

Loop H was dismantled and sectioned for investigation after having been in use for 19,700 hr. Solutions circulated included 0.04 to 1.3 m UO_2SO_4 , 0.2 to 1.3 m UO_2F_2 , 0.05 m H_2SO_4 , and 0.1 m HF at 200 to 300°C. Chloride ions were added only in three runs: in H-104, 0.17 m UO_2SO_4 containing 50 ppm of Cl was circulated for 768 hr at 250°C; in H-105 the same solution was circulated for 441 hr at 200°C; and in the last run, H-107, 0.02 m UO_2SO_4 containing 0.05 m CuCl_2 was circulated for 22 hr. The failure by stress-corrosion cracking of the 3/8-in. type 347 stainless

steel by-pass line was discussed in a previous report.⁹ Visual inspection of the 1-1/2-in.-OD Schedule 80 type 347 stainless steel main-line piping and the 4-in.-OD Schedule 80 type 347 stainless steel pressurizer after sectioning revealed that much less attack had occurred in the main loop than in the by-pass that failed. Several welds were attacked 0.02 to 0.03-in. deeper than the base metal, and the piping downstream from the high-velocity sample holder was badly pitted.

The line cooler was examined metallographically. This section of main line piping had been exposed to a demineralized water spray with frequent periods of tap water spray on the outside for cooling purposes. The inside of the pipe was corroded fairly uniformly and had no cracks. However, stress-corrosion cracks about 0.025 to 0.050-in. deep were discovered starting from the outside of the bottom half of the pipe. The top half of the pipe had no cracks. Evidently the cracks propagated from the outside due to chloride in the tap-water spray until the surface stresses in the metal were relieved, and then the rate of cracking slowed or stopped. This behavior is in contrast to a previous failure¹⁰ where the pipe exposed to the water spray had been cold-formed into a bend and where the stresses induced throughout the wall of the pipe caused the cracks to penetrate the entire wall. The significance of the cracks in the cooler from loop H is that stress-corrosion cracking did occur even on a straight run of austenitic stainless steel pipe in contact with water containing small amounts of chloride (the tap water runs between 5 and 8 ppm of chloride), although the cracks did not propagate through the entire wall thickness during the 19,700-hr life of the loop.

One weld from loop H, which had been corroded to a depth of 0.02 to 0.03-in. deeper than the base metal, was examined metallographically. A photomicrograph of the attacked area is shown in Fig. 1. It was observed that the ferrite in the weld metal had been selectively attacked. The weld between a type 347 stainless steel 1-1/2-in. tee and a length of type 347 stainless steel 1-1/2-in. pipe was made as usual by the heliarc method using type 347 stainless steel weld rod. Previous observations on the corrosion of welds in uranyl sulfate solution have been that the ferrite content in a type 347 stainless steel weld was not the controlling

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Fig. 1 Photomicrograph of Type 347 Weld from Loop H Showing Selective Attack of Ferrite. 250X

factor.¹¹ Therefore the reason for the selective attack is not known.

2. Hydrogen Embrittlement of a Titanium Sample Holder.--A commercially pure titanium (75A) corrosion sample holder which had become severely pitted beneath a stainless steel clamping band during a 151-hr exposure to $1.3\text{ m UO}_2\text{F}_2$ at 250°C was found to have been severely embrittled in the pitted area. The sample holder snapped at the pitted area when clamped in a vise for repair. Figure 2 is a photograph of the snapped holder and Fig. 3 is an enlargement of a photograph of the pitted area. Figure 4 is a photomicrograph of the metal directly under the pitted area. The dark material is the hydride phase which caused the embrittlement. Figure 5 is a photomicrograph of the metal away from the pitted area and illustrates the absence of hydride in the uncorroded section. Other photomicrographs of the pitted area showed that the hydride extended throughout the thickness of the holder (about $3/8$ in.) and was not concentrated in a surface layer next to the pits. Analysis of a piece of metal cut from the pitted area for hydrogen by the equilibrium-pressure method¹² confirmed the presence of a significantly larger amount of hydrogen in that area than in the metal away from the pitted area or in the original stock from which the holder was made. This indicates that massive titanium can become hydrogen embrittled within a few hundred hours under certain corrosive conditions.

Although the attack occurred underneath a stainless steel clamping band in metallic contact with the titanium holder, the corrosion did not appear to be galvanic in nature but rather a form of crevice corrosion. Titanium pins insulated with Teflon and exposed in the same run also corroded severely in the crevice region. In the crevice, where oxygen was absent, hydrogen would be a product of the corrosion reaction.

3. Hydrogen Pickup by a Titanium Insert.--In a previous report a description was given of a titanium 75A insert which was used to protect a stainless steel loop in a turbulent area during exposure for 9900 hr to 0.04 to $1.3\text{ m UO}_2\text{SO}_4$ at 175 to 300°C .¹³ Oxygen exhaustion had occurred in the crevice between the titanium and the stainless steel pipe wall. Vacuum fusion analysis of the titanium indicated the hydrogen concentration in the metal had increased from 40 to 120 ppm. Figure 6 is a photomicrograph of the original material and Fig. 7 is a photomicrograph of the insert after

Fig. 2 Titanium 75A Corrosion Sample Holder. The Broken Pieces Do Not Match Since a Piece Was Cut Off For Examination.

Fig. 3 Enlargement of Pitted Section Shown in Fig. 2. 5X

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Fig. 4 Photomicrograph of Metal Below Pitted Area Shown in Fig. 3. The Dark Material is the Hydride Phase. 250 X

Fig. 5 Photomicrograph of Titanium 75A Corrosion Sample Holder Array from Pitted Area. 500X.

Fig. 6 Photomicrograph of As-Received Titanium 75A. 250 X.

Fig. 7 Photomicrograph of Titanium 75A Insert After Pickup of Hydrogen. The Dark Stringer-Like Material at the Grain Boundaries is Hydride. 250X.

exposure. A significant amount of hydride is visible in Fig. 7 as the dark, stringer-like material. The hydrogen pickup by the titanium insert did not impair the usefulness of the insert in this instance, but the observation does indicate that titanium can absorb hydrogen under certain conditions in uranyl sulfate solutions.

4. Stress-Corrosion Specimens Exposed in HRT Solution.--In a previous report it was mentioned that no cracks or significantly greater corrosion due to stress was observed by microscopic examination of stress specimens exposed in HRT solution ($0.04\text{ }m\text{ }UO_2SO_4$ containing 0.010 to $0.025\text{ }m\text{ }H_2SO_4$ and $0.005\text{ }m\text{ }CuSO_4$).¹⁴ Types 309 SCb, 347, 17-4 PH, and AM-350 stainless steel and titanium alloys 110AT and 130AM were stressed to 75% of their 250°C yield strength and exposed for 12,543 hr at 200°C . Another set of specimens was exposed 13,385 hr at 250°C . Metallographic sections of the area of maximum applied stress were taken from each specimen and the microscopic results were confirmed. No cracks were found in any of the metallographic sections taken.

C. Effect of Additives to $0.17\text{ }m\text{ }UO_2SO_4$ on the Corrosion of Stainless Steel.

A large number of chemical compounds have been tested previously in the 100A loop program as additives to uranyl sulfate to inhibit the corrosion of stainless steel. Among those tested have been $Cr_2(SO_4)_3$, $NiSO_4$, $FeSO_4$, $MnSO_4$, Na_2WO_4 , H_2MoO_4 , Na_2SiO_3 , $(UO_2)_3(PO_4)_2$, $(NH_4)_2TeO_4$, and $K_2Cr_2O_7$.¹⁵ Of these, only $K_2Cr_2O_7$ has shown significant inhibiting properties. More recently the alkali and alkaline earth metal sulfates have been shown to inhibit corrosion of stainless steel.¹⁶ During the last quarter further investigation of additives has been carried out.

1. The Effect of Lithium Sulfate and Magnesium Sulfate in the Absence of Chromium (VI).--The inhibition of corrosion of stainless steel in $0.17\text{ }m\text{ }UO_2SO_4$ by sulfate salts could possibly be due to the hexavalent chromium that builds up in solution in runs in stainless steel loops at 250°C . Therefore, runs were made with 0.035 , 0.07 , 0.10 , and $0.15\text{ }m\text{ }Li_2SO_4$ and $0.15\text{ }m\text{ }MgSO_4$, successively, in $0.17\text{ }m\text{ }UO_2SO_4$ at 250°C in an all-titanium loop to avoid interference from chromium (VI). Each run lasted 100 hr. Two type 347 stainless steel pins were exposed at a flow rate below the critical velocity, 13 fps, and two above, 68 fps.

The results are illustrated in Fig. 8. The chromium (VI) concentration at the end of all runs was less than 5 ppm. It can be seen that corrosion rates of type 347 stainless steel pins at both high and low velocities were progressively decreased as increasing amounts of lithium sulfate were added. Magnesium sulfate in place of lithium sulfate gave approximately the same inhibition as did the lithium sulfate. Therefore, it was concluded that the added sulfate ion was responsible for the inhibition.

The pH of the solutions decreased during the runs, indicating that a possible slow hydrolysis was taking place. Since previous tests with lithium and magnesium sulfates added to dilute (less than 0.2 m) uranyl sulfate solutions have given precipitates containing uranium at 300°C¹⁷ the use of these salts as inhibitors in dilute solutions is questionable.

2. The Effect of Various Other Additives.--In order to find an inhibitor other than chromium VI, which is unstable in radiation fields, or the alkali and alkaline earth metal sulfates, which give precipitates in dilute solution, a variety of compounds were tested. Table I lists the compounds tested and the stability of the resulting solutions. All of the tests were conducted for 200 hr at 250°C with 0.17 m UO_2SO_4 containing the compound to be tested and about 1000 ppm of oxygen. None of the compounds was found to be an effective inhibitor.

- a. 0.0008 m $\text{Ce}(\text{SO}_4)_2$. 0.001 m $\text{Ce}(\text{SO}_4)_2$ was added to the solution but only 110 ppm cerium remained soluble at 250°C. In comparison with a run in which no ceric sulfate was added there was a slight decrease in weight losses of type 347 stainless steel coupons only at velocities above about 30 fps. The difference was not considered large enough to warrant further investigation of ceric ion as an inhibitor.
- b. 0.001 m $\text{H}_7\text{P}(\text{MoO}_4)_{12}$. Phosphomolybdic acid was prepared by adding concentrated HCl to Na_2MoO_4 - Na_2HPO_4 solution and extracting the acid with ether.¹⁸ Chemical and X-ray diffraction analysis showed that the product was actually a mixture of the ten and twelve heteropolyacids. Also, upon addition of the dried compound to the uranyl sulfate solution, a yellow-white precipitate formed, possibly uranyl phosphate, indicating that decomposition of the compound was occurring. Despite these difficulties the run was made. The results were not significantly

Fig. 8 Effect of Added Lithium and Magnesium Sulfate in 0.17m UO₂SO₄ on Corrosion of Type 347 Stainless Steel Pins at 250°C (100 hr. runs)

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Table I. Possible Inhibitors Added to 0.17 m UO_2SO_4 at 250°C.
All Runs Were for 200 Hr and Contained 1000 ppm O_2 .

Additive	Concentration		Remarks
	m	ppm	
$\text{Ce}(\text{SO}_4)_2$	0.0008	110 Ce	Stable solution.
$\text{H}_7\text{P}(\text{MoO}_4)_2$	0.001	1200 Mo	Phosphomolybdic acid decomposed and uranyl phosphate precipitated. 100 ppm Mo remained in solution.
As_2O_5	0.0005	70 As	Arsenic lost from solution.
NaBiO_3	0.0005	100 Bi	Bi_2O_3 precipitated.
H_3SbO_4	0.001	120 Sb	Less than 1 ppm antimony soluble at 250°C.
$(\text{RuNO})_2(\text{SO}_4)_3$	0.001	100 Ru	Ru metal and RuO_2 precipitated.
NaNO_3	0.01	--	Stable solution.
NaNO_3	0.1	--	Stable solution.
Ag_2SO_4	0.005	1000 Ag	Stable solution.

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different from runs without the phosphomolybdic acid, so no further investigation of the heteropolyacids is planned.

c. 0.0005 m As₂O₅.--Arsenic pentoxide dissolved in the 0.17 m UO₂SO₄ to give 70 ppm arsenic in solution initially. During the run arsenic was lost from solution, the final concentration being 25 ppm. Corrosion of stainless steel appeared to be slightly greater in this solution than in a similar run without arsenic.

d. 0.0005 m NaBiO₃.--Sodium bismuthate did not dissolve at room temperature in 0.17 m UO₂SO₄; so, the slurry was added to the loop. Only 4 ppm of bismuth was soluble at 250°C; the rest precipitated as Bi₂O₃ as shown by X-ray diffraction analysis of the scale on the pins at the end of the run. Corrosion results were no different from similar runs in which no sodium bismuthate was added.

e. 0.001 m H₃SbO₄.--Antimonic acid was prepared by boiling antimony metal briefly with concentrated nitric acid, diluting with water, filtering off the white precipitate of H₃SbO₄, and washing with water. The crumbly precipitate dissolved in 0.17 m UO₂SO₄ only to the extent of 8 ppm antimony and hence, the dilute slurry was added to the loop. Less than one ppm antimony was soluble at 250°C and corrosion results were not significantly different from a run in which no antimonic acid was added.

f. 0.001 m (RuNO)₂(SO₄)₃.--The nitroso complex of ruthenium was prepared by bubbling NO₂ through a solution of ruthenium trichloride. The chloride and nitrate ions were removed by fuming with sulfuric acid and the solution was then added to 0.17 m uranyl sulfate to give 100 ppm of ruthenium. In the loop at 250°C the solution was not stable. The ruthenium concentration dropped to 5 ppm or less within 24 hr in each of the three runs made. X-ray diffraction analysis of the scale on the pins at the end of the runs showed the presence of both ruthenium metal and RuO₂. However, in two of the runs weight losses of type 347 stainless steel coupons up to the critical velocity of 30 to 35 fps were 5 to 10 times lower than in runs without the initial addition of ruthenium nitroso sulfate. In both of these runs the chromium (VI) concentration increased much more rapidly than in runs without ruthenium, reaching a final concentration of 820 ppm in 200 hr. It may be that

ruthenium in some way catalyzed the oxidation of chromium to the hexavalent state. Apparently the corrosion inhibition observed was due to the high chromium (VI) concentration. Therefore, ruthenium nitroso sulfate is not considered to be an effective inhibitor.

g. 0.01 and 0.1 m NaNO_3 .--Since nitrate ion is a fairly strong oxidizing agent, it might be expected to have an effect on the corrosion of stainless steel in uranyl sulfate. For this reason two runs were made in which sodium nitrate was added to 0.17 m UO_2SO_4 at 250°C. The results are illustrated in Fig. 9 and show that at a sodium nitrate level of either 0.01 or 0.1 m the critical velocity was decreased. Both solutions were stable for the 200 hr runs.

h. 0.005 m Ag_2SO_4 .--The silver ion has been mentioned as a possible catalyst for the recombination of hydrogen and oxygen. Since silver could possibly have an effect on corrosion, a run was made with uranyl sulfate containing silver sulfate. A quartz-tube test indicated that about 0.005 m Ag_2SO_4 was the limit of solubility in 0.17 m UO_2SO_4 at 260 to 270°C, so that was the concentration used. Subsequent analysis of the solution showed that the solution was stable for 200 hr at 250°C. The corrosion of stainless steel, however, was no different in the presence of 0.005 m Ag_2SO_4 than in its absence.

D. Tests with 0.17 m Uranyl Nitrate and 0.17 m Uranyl Perchlorate.

Uranyl nitrate has been mentioned as a possible fuel for homogeneous reactors operating at elevated temperatures, but its corrosiveness and chemical stability had not been determined in a dynamic system. Uranyl nitrate was also of interest since it has a strongly oxidizing anion in contrast to uranyl sulfate. Uranyl perchlorate was of interest since the perchlorate ion is strongly oxidizing at high temperatures and complexing with the uranyl ion should be small. Runs were made at 250°C using 0.17 m $\text{UO}_2(\text{NO}_3)_2$ with and without oxygen and using 0.17 m $\text{UO}_2(\text{ClO}_4)_2$ with oxygen.

During the 200-hr run, the 0.17 m $\text{UO}_2(\text{NO}_3)_2$ solution with about 1000 ppm of oxygen corroded stainless steel specimens a factor of 2 to 5 less than in a similar run in uranyl sulfate. A critical velocity of 25 to 35 fps was observed. One reason for the lower corrosion in the uranyl nitrate may be that the chromium (VI) concentration increased rapidly, reaching

Fig. 9. Weight Losses of Type 347 Coupons in 0.17m UO₂SO₄
+ NaNO₃ at 250°C, 200 hr.

860 ppm within 26 hr. Apparently nitrate ions catalyze the oxidation of chromium to the hexavalent state in the presence of oxygen since in uranyl sulfate solutions chromium (VI) concentrations lower by a factor of about ten are usually observed. Stainless steel strips hung in the vapor space of the loop showed small weight losses and it is believed little thermal decomposition of nitrate occurred.

In the absence of oxygen, corrosion of stainless steel was much greater in $0.17 \text{ m } \text{UO}_2(\text{NO}_3)_2$ than that described above, corrosion rates of 40 to 300 mpy being observed. However, these rates were much lower than would be observed in $0.17 \text{ m } \text{UO}_2\text{SO}_4$ in the absence of oxygen. The critical velocity was 10 to 15 fps. In this run the chromium (VI) concentration was less than 1 ppm throughout the test. Evidently, nitrate ion is not a strong enough oxidant to oxidize chromium to the hexavalent state in the absence of oxygen. Vapor phase attack of stainless steel strips was about twice as severe as in the oxygenated run.

Corrosion of stainless steel in $0.17 \text{ m } \text{UO}_2(\text{ClO}_4)_2$ was very severe at 250°C . The run lasted only 13 hr when a type 321 stainless steel rupture disk failed. Corrosion rates of 2500 to 3700 mpy were observed on type 347 stainless steel coupons at 8 to 80 fps. The chloride concentration of the solution increased rapidly due very likely to reduction of perchlorate by the steel. The chloride concentration at the end of the run was 1800 ppm. Evidently oxygen is not a strong enough oxidant at 250°C to prevent the reduction of the perchlorate ion.

E. Initial Runs in an All-Titanium Loop.

It was found recently¹⁹ that loop history, in particular whether a loop was new or used, could affect the corrosion results obtained in stainless steel loops. In order to investigate further the effect of loop history on corrosion of stainless steel, the initial runs in loop H, a new all-titanium loop,²⁰ were made to determine whether new titanium surfaces would have as great an effect on corrosion of stainless steel coupons as new stainless steel surfaces. In the first run, type 347 stainless steel coupons in the titanium loop were exposed to the "standard" pretreatment of 4 hr with 3% trisodium phosphate at 100°C , 12 hr with 5% nitric acid at

100°C, and 24 hr with oxygenated water at 250°C. The loop was then charged with 0.17 m UO_2SO_4 containing 0.04 m H_2SO_4 and 0.03 m CuSO_4 and the solution was circulated at 250°C for 200 hr. Corrosion rates on the stainless steel specimens were very low - 0.3 to 0.6 mpy - and no velocity effect was observed on the coupons even at the maximum flow rate of 43 fps.

The second run was identical to the first, including the several pretreatments. In this case, however, a sharp velocity effect was observed and the type 347 stainless steel coupons at 32 to 43 fps corroded at 40 to 50 mpy. The corrosion was a pitting type of attack similar to that observed previously²¹ and indicated the breakdown of the pretreatment film. Therefore, even in the case of a titanium system, the initial run is for some reason anomalous in giving low corrosion and no velocity effect. However, it would appear much more likely that the effect was due to small differences in pretreatment in the first and second runs than to an effect of the loop itself.

In the third run the pretreatments were omitted and the type 347 stainless steel coupons were exposed directly to 0.17 m UO_2SO_4 containing 0.04 m H_2SO_4 and 0.03 m CuSO_4 for 200 hr at 250°C. Corrosion rates were high - 100 to 500 mpy - and a sharp velocity effect was observed. Therefore, the "standard" pretreatment used in the first and second runs was of value in decreasing corrosion. However, as the second run showed, pretreatment cannot be depended upon to increase the critical velocity.

F. Chemical Stability and Corrosiveness of Dilute Copper Sulfate - Sulfuric Acid Solution for the HRT Blanket.

There exists the likelihood that a small amount of copper sulfate will have to be added to the D_2O blanket of the HRT in order to recombine radiolytic gases. It has been calculated that about 0.001 m copper (60 ppm) would be sufficient. A previous run²² showed that a 0.0005 m copper sulfate solution containing 0.002 m H_2SO_4 was stable at 300°C. Therefore, 0.002 m H_2SO_4 was added to the solution containing 0.001 m CuSO_4 in the first run and 0.003 H_2SO_4 in the second run in order to determine the acid concentration necessary to prevent hydrolytic precipitation of 60 ppm of copper. Both runs were made at 300°C.

About 15 ppm of copper were lost from solution within 32 hr in the first run, although the solution was stable for 168 hr with 45 ppm of copper. A slight decrease in the pH of the solution indicated that hydrolytic precipitation of copper probably occurred. The solution in the second run was entirely stable for 343 hr. In both runs corrosion of stainless steel specimens was less than 2 mpy up to 70 fps. Therefore, it appears that a 0.001 *m* CuSO₄ solution containing 0.003 *m* H₂SO₄ would be satisfactory from stability and corrosion standpoints.

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 Pre-Formed Films in Uranyl Sulfate Solution.--During the past quarter, a number of corrosion tests were started to determine the effect of pre-formed films on minimizing or eliminating the susceptibility of type 347 stainless steel to stress-corrosion cracking in chloride-containing boiling and aerated uranyl sulfate solution. Previous experience with stressed type 347 stainless steel showed that the films that formed during 7600 hr of exposure in boiling chloride-free 0.04 *m* UO₂SO₄-0.004 *m* H₂SO₄-0.005 *m* CuSO₄ solution successfully prevented initiation of stress-corrosion cracking for approximately 3000 hr (the length of the test) after 60 ppm chloride were added to the solution.²³ Stress specimens with no pre-formed film cracked severely during the initial 500 hr with chloride present. Furthermore, recent laboratory studies demonstrated that with 50 ppm of chloride present in a boiling and aerated simulated HRT core solution (0.04 *m* UO₂SO₄-0.02 *m* H₂SO₄-0.005 *m* CuSO₄), cracking of stress specimens generally occurred during the first 50 hr of exposure. Thus, there existed some experimental evidence which suggested that initial formation of a film in a chloride-free environment could be of considerable protection against a stress-corrosion cracking of type 347 stainless steel in environments in which chloride ions may accidentally be present.

In the present study, pre-formed films on type 347 stainless steel specimens were produced by two techniques: (1) exposure for 500 hr in boiling and aerated 0.04 *m* UO₂SO₄-0.02 *m* H₂SO₄-0.005 *m* CuSO₄ solution, and (2) heating

for 1 hr in an air atmosphere at 677°C (1250°F). U-bend specimens which were cold-formed from annealed 0.019-in.-thick type 347 stainless steel strip were used. The specimens were elastically stressed by drawing the ends of the U together with a type 347 stainless steel tie-bolt. Films in the boiling chloride-free uranyl sulfate solution were formed on pickled and on electro-polished specimens; the air-formed films were produced on pickled specimens only.

Duplicate sets of pickled and of electropolished specimens were stressed before and after the 500-hr exposure in the boiling, chloride-free environment. Flat, unstressed specimens were cold-formed into a U-bend and elastically stressed after pre-treatment and before exposure in the chloride-containing solution in order to determine whether possible film rupture resulting from the bending operation would lead to early stress-corrosion cracking during exposure. Other specimens were cold-formed into a U-bend and elastically stressed before the start of the 500-hr pretreatment in chloride-free solution. The film formed in air at 677°C was made on specimens that were cold-formed and elastically stressed prior to heating.

All specimens were subjected to the boiling and aerated HRT core solution containing 50 ppm chloride as potassium chloride. Specimens that were stressed before the start of the 500-hr exposure in chloride-free solution have shown no tendency toward cracking after 400 hr of exposure to the chloride-containing solution thus far. Similarly, the specimens that were stressed after the 500-hr pretreatment have not cracked after 500 hr in the chloride-containing solution. The corrosion rates on all specimens were essentially negligible as compared with rates ranging between 0.3 and 0.5 mpy for untreated specimens exposed to similar conditions. As mentioned earlier, the latter specimens, free of pre-formed films, generally cracked in periods of 50 hr and less in the chloride-containing environment.

The second type of pre-formed film was produced by heating stressed specimens for 1 hr in air at 677°C . The specimens were then placed in the boiling chloride-containing uranyl sulfate solution. During the exposure interval from 150 to 205 hr, both specimens developed cracks

in areas of near-maximum stress. It was concluded that an air-formed film at 677°C was of no value for inhibiting chloride-induced stress-corrosion cracking of type 347 stainless steel in boiling uranyl sulfate solution. Additional studies with pre-formed films on stress specimens will be conducted during the forthcoming quarter.

2. Behavior in Chloride-Containing Water at Elevated Temperatures.--It has been found that at temperatures between 150 and 300°C , completely immersed U-bend specimens of type 347 stainless steel develop cracks in 100 to 700 hr in dilute chloride solutions over a wide range of pH and oxygen concentrations.²⁴ During the past quarter, it was also observed that similar specimens developed cracks in less time at lower temperatures. Test results for temperatures from 100 to 250°C are shown in Table II. Each test represents two specimens, both of which were completely submerged in the liquid. Specimens were examined at 100-hr intervals and the time to cracking shown in the table was the time at which cracks were first observed under 15X magnification. Data from the 300°C tests showed that about half of the specimens cracked in less than 300 hr under the same conditions of these tests. All specimens tested at 300°C were completely filmed over by the end of the first 100 hr with thin adherent films that continued to thicken with additional exposure time.

At 250°C , three out of four specimens cracked during the first 100 hr, and the fourth specimen cracked at the end of 300 hr. These specimens were filmed over almost completely after the first 100 hr.

At 200°C , all four specimens developed many small cracks during the first 100 hr. Figure 10 shows two such specimens. It is to be noted that only small areas at or near cracks are filmed over. Figure 11 shows clearly the transgranular nature of the cracks and the close spacing of the cracks along the edge of the specimen.

At 150°C all four specimens developed many small cracks during the first 100-hr exposure, as was the case at 200°C . At this temperature, however, no visible film formed on the specimens.

Sixteen specimens have survived 3,000 hr of test at 100°C in solutions containing 20 to 500 ppm of chloride. The tests were conducted at

Table II. Effect of Temperature on Stress-Corrosion Cracking Behavior of Type 347 Stainless Steel in Chloride-Containing Distilled Water. Each Test Contained Duplicate Specimens.

Test No.	Temp. (°C)	Chloride (ppm)	Initial pH	RT Oxygen Pressure	Results
V-92	250	100	2.8	atmospheric	Both cracked at 100 hr.*
V-93	250	100	2.8	"	One cracked at 100 hr, the other at 300 hr.
V-94	200	100	2.8	"	Both cracked at 100 hr.
V-95	200	100	2.8	"	Both cracked at 100 hr.
X-36	150	100	2.8	"	Both cracked at 100 hr.
X-37	150	100	2.8	"	Both cracked at 100 hr.
X-76	100	100	10.5	150 psi	No cracks at 300 hr.
X-77	100	50	10.5	150 psi	No cracks at 300 hr.
X-78	100	100	2.8	150 psi	Both cracked at 400 hr.
X-79	100	50	2.8	150 psi	One cracked at 100 hr, the other not cracked at 300 hr.

* Specimens examined at 100-hr intervals.

Fig. 10 Stress-Corrosion Cracking in Type 347 Stainless Steel After 100 Hr in Distilled Water with 100 ppm Chloride at pH 2.8 and 200°C. Magnification 3X.

Fig. 11 Photomicrograph of Some Cracks Shown in Fig. 1.

atmospheric boiling with air bubbled into the solution during the test. Since in the above tests the dissolved oxygen concentration was very low, a group of four tests was started in autoclaves at 100°C in which an atmosphere of 150 psi of oxygen was provided to determine if additional oxygen would produce cracks at this low temperature. After 200 hr of testing all eight specimens were bright and shiny with no cracks visible at 15X magnification. At 300 hr thin straw- and blue-colored films had formed and one specimen exhibited a single small crack. After 400 hr, two more specimens had cracked. The remaining five specimens are continuing in test. The three cracked specimens have been submitted for metallographic examination to determine the nature of the crack.

3. Behavior in Boiling 42% Magnesium Chloride Solution.--It was shown previously that neither the deposition of platinum black on type 347 stainless steel U-bends nor the addition of either platinum chloride or mercuric chloride to boiling 42% $MgCl_2$ had any effect on the tendency of the steel toward stress-corrosion cracking.²⁵ Data recently reported by K. W. Len and J. N. Helle²⁶ indicated that the addition of stannous chloride or metallic magnesium - not in electrical contact with the stainless steel - to the solution would prevent cracking of the stainless steel. Some tests were thus conducted to duplicate their work.

The addition of metallic magnesium to the solution apparently had no effect on the time required for the appearance of cracks. However, when the magnesium metal was coupled to the stainless steel, complete immunity to cracking was observed. This latter observation is not surprising in view of the fact that complete cathodic protection is obtained at current densities as low as 50 microamps/cm².²⁷

The results obtained with stannous chloride additions were not clear-cut, and as a result further experimentation is planned. The addition of 50 and 250 ppm of tin as stannous chloride seemed to increase the time for the appearance of cracks but cracks did appear. The results of tests conducted in boiling 42% $MgCl$ during the past quarter are listed in Table III.

Table III. Results of Tests with Type 347 Stainless Steel
in Boiling 42% MgCl_2 Solutions.

Test No.	Additive	Results
U-87		Both specimens cracked 2 hr after application of stress.
W-36		Three specimens showed small cracks after 1 hr, a fourth was completely cracked. The first three failed completely at 20, 25, and 50 hr.
W-33	Mg metal bar in solution	Both specimens showed small cracks at 1 hr. Both extensively cracked at 2 hr.
X-43	Mg-to-347-SS couple	No cracks seen after 100 hr.
W-31	Platinum black plated on specimens.	One specimen cracked after 1 hr, three others after 2 hr.
W-34	50 ppm Pt as PtCl_4	One completely failed at 1 hr, the other showed small crack. Failure occurred after 2 hr.
X-40	50 ppm Pt as PtCl_4 Beam type with 10,000 psi stress.	Small cracks at 1 hr. Fulcrum and base plate developed cracks between 20 and 25 hr. Stud failed at 35 hr. Shallow crack across specimen at 35 hr.
W-35	50 ppm Hg as HgCl_2	One small crack, one failure at 2 hr. Second failure at 3 hr.
X-41	50 ppm Hg as HgCl_2 Beam type with 10,000 psi stress.	Small crack detected after 3 hr. Propagated across specimen after 20 hr.
X-44	250 ppm Sn as SnCl_2	Small crack at 10 hr. Both specimens failed at 20 hr.
X-42	50 ppm Sn as SnCl_2 Beam type with 10,000 psi stress.	Small crack at 10-15 hr. Crack in fulcrum at 25 hr. Stud failed at 30 hr. Crack in specimen most of the way across at 35 hr.

NOTE: Tests involving beam-type specimens have one specimen only.

4. Marking Inks in Stress-Corrosion Cracking.--Chemical analysis of several commonly used marking inks showed them to contain from 3,000 to 19,000 ppm of chloride. Thus, it was of interest to know if stainless steels marked with inks of this type would be susceptible to stress-corrosion cracking in saturated, oxygen-containing steam and in oxygenated high-temperature water.

Eight U-bend specimens were marked with different inks and exposed to saturated and oxygenated steam at 300°C. All specimens developed cracks during exposures ranging from 100 to 300 hr. At present eight similarly marked specimens are being tested in oxygenated distilled water at 300°C. To date 300 hr of testing have been completed and thus far only one crack has developed. The chloride concentrations in solution have varied from 2 to 9 ppm.

Three samples of low-chloride inks have recently been received. These will be tested in the manner described above.

B. Corrosion of Zirconium Alloys by Uranyl Sulfate Solution.

The corrosion test program for the evaluation of zirconium-base alloys was completed during the past quarter. The program, a conjoint effort with the HRP Metallurgy Group, was undertaken for two reasons: (1) to determine the general corrosion behavior of a number of zirconium-base alloys in high-temperature uranyl sulfate solution; and (2) to provide suitable specimens for film structure studies by the HRP Metallurgy Group. Corrosion data for other zirconium alloys tested in the program have been reported.²⁸⁻³⁰

The present tests were concerned with the behavior of rolled and oxidized zirconium-base alloys; a number of tests were also run with non-oxidized as-cast alloys. The oxidizing treatment consisted of heating the specimens for 3 to 5 min at a temperature of 1000°C. The treatment produced films that were found to be highly resistant to acid pickling solutions.

All specimens were exposed for 1000 hr at 300°C in oxygenated 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m CuSO_4 . The results are listed

in Table IV. No attempt was made to defilm the specimens upon completion of the tests.

Of the three as-cast alloys, the 20Nb-80Zr composition exhibited a corrosion rate that was comparable with that for Zircaloy-2 under similar conditions of exposure, < 0.1 mpy. The other two as-cast alloys, 1Fe-15Nb-84Zr and 2Y-2Sn-8Nb-88Zr, exhibited weight gains ranging from 1.8 to 4.9 mg/cm^2 and films that were appreciably bulkier than the highly lustrous, dark blue-black thin film formed on the 20Nb-80Zr alloy.

The pre-oxidized casting alloy of 33Nb-67Zr composition possessed excellent corrosion resistance; no measurable attack occurred during the 1000 hr in high-temperature uranyl sulfate solution. Several of the cast and rolled pre-oxidized alloys exhibited promising corrosion behavior with observed corrosion rates of 0.7 mpy and less for the 1000-hr exposure. These alloys were the 7Mo-20Nb-73Zr, 2Sn-2Mo-15Nb-81Zr, and 1Ni-20Nb-79Zr compositions. The remaining pre-oxidized alloys were corroded at rates ranging between 1.8 to 27.8 mpy. The highest corrosion rate, 27.8 mpy, was for the 10Mo-90Zr alloy.

C. Miscellaneous Tests.

A number of materials -- on the basis of their physical and mechanical properties -- have shown indications of being useful for various applications related to the HRP. A resume of the results of corrosion tests on some of the materials follows:

1. Elgiloy.--Because of the need for a satisfactory spring material for present and contemplated HRT usage, such as in the liquid-level controller for the HRT pressurizer, it was considered pertinent to perform some additional experiments with Elgiloy. Elgiloy, a cobalt-base spring alloy, was developed by Battelle Memorial Institute for the Elgin National Watch Company. Previous work showed the alloy to have good corrosion resistance to high-temperature uranyl sulfate solution but that it was highly susceptible to cracking, even in the absence of an applied static stress and chloride ions.³¹ There were indications that cracking was eliminated when the alloy was aged for 5 hr at 482°C (900°F), air cooled, pickled, and electropolished.

Table IV. Corrosion of Pre-Oxidized^a Zirconium-Base Alloys
During 1000 Hr at 300°C in 0.04 *m* UO₂SO₄-0.02 *m*
H₂SO₄-0.005 *m* CuSO₄ Solution.

Lab No.	Material Identity	Alloy Composition (wt%)	Specimen Number	Corrosion Rate (mpy)
W-83	Zr-18	10Mo-90Zr	1	27.8
T-95	Zr-22	20Nb-80Zr ^b	1	0
			2	< 0.1
W-81	Zr-42	33Nb-67Zr ^c	1	Negligible
T-82	Zr-20	1Fe-15Nb-84Zr ^d	1	(+1.8 mg/cm ²)
			2	(+1.9 mg/cm ²)
W-80	Zr-17	5Mo-15Nb-80Zr	1	4.8
W-78	Zr-12	5Mo-10Nb-85Zr	1	4.8
X-3	Zr-47	7Mo-20Nb-73Zr	1	0.3
W-79	Zr-14	5Mo-5Ta-10Nb-80Zr	1	2.9
W-85	Zr-28	1Pd-15Nb-84Zr	1	1.8
W-84	Zr-27	2Pd-15Nb-83Zr	1	12.5
X-6	Zr-80	2Sn-2Mo-15Nb-81Zr	1	(+0.4 mg/cm ²)
X-6	Zr-80	2Sn-2Mo-15Nb-81Zr ^e	1	0.4
W-82	Zr-67	3Sn-15Nb-82Zr	1	2.7
X-4	Zr-48	1Ni-20Nb-79Zr	1	1.0
			2	0.3
X-5	Zr-68	3V-15Nb-82Zr	1	8.8
T-97	Zr-77	2Y-2Sn-8Nb-88Zr ^f	1	(+4.5 mg/cm ²)
			2	(+1.9 mg/cm ²)

a. Pre-oxidizing treatment: 3 to 5 min in air at 1100°C.

b. Alloy prepared from Bureau of Mines sponge zirconium; all other alloys prepared from high-purity crystal bar zirconium. Specimens cast and mechanically abraded; no oxidizing treatment.

c. Cast specimen; oxidized.

d. Cast specimens homogenized for 3 hr at 1000°C; no oxidizing treatment.

e. Specimens chemically polished before oxidizing.

f. Cast specimens; no oxidizing treatment.

Accordingly, tests were run to examine the susceptibility of the alloy in the above condition to cracking in chloride-free uranyl sulfate solution. Specimens were prepared from 1/32-in-thick strip that was cold-rolled to 75 to 85% reduction in area. The hardness of the strip was 53 Rockwell C. Test specimens for each alloy condition examined consisted of a single unstressed control coupon and duplicate twin-strip stress assemblies. The alloy conditions examined were: (1) pickled; (2) pickled and electropolished; (3) aged 5 hr at 482°C, air cooled, and pickled; and (4) aged 5 hr at 482°C, air cooled, pickled, and electropolished. The test environment was HRT core solution (0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , 0.005 m $CuSO_4$) at 300°C pressurized with approximately 150 psi oxygen.

All specimens, stressed and unstressed, were subject to cracking during the initial 100 hr of test. After 200 hr, specimens were covered with a myriad of fine cracks. In a number of cases, extreme splitting along edge surfaces was observed. The defilmed corrosion rates shown in Table V were in good agreement with the relatively low rates reported previously for the alloy. From the data, slight but not significant reduction in corrosion rates was in evidence for unstressed specimens that were electropolished. Although the general corrosion behavior of the alloy was acceptable, its susceptibility to cracking precludes its use for any reactor application involving contact by high-temperature uranyl sulfate solution.

TABLE V. Corrosion of Elgiloy by Oxygenated 0.04 m UO_2SO_4 Containing 0.02 m H_2SO_4 and 0.005 m $CuSO_4$ at 300°C. Each Exposure Was 200 Hr.

Specimen Type	Treatment	Corrosion Rate (mpy)	
		As-Received*	Aged 5 hr at 482°C
Unstressed	Pickled	4.2	4.0
Stressed	Pickled	4.4	4.6
Unstressed	Pickled and electropolished	2.9	2.7
Stressed	Pickled and electropolished	3.9	4.1

* Cold worked to 75-85% reduction in area.

2. AlSiMag 652.--An AlSiMag 652 (sintered alumina) pump bearing of the type used in the in-pile and out-of-pile 100A corrosion test loops was subjected to test in uranyl sulfate solution in order to determine whether it was sufficiently corrosion resistant for the intended application. The test solution was 0.17 m UO_2SO_4 containing 0.04 m H_2SO_4 and 0.03 m CuSO_4 ; the solution was pressurized with 150 psi oxygen at 150°C.

After 50 hr, the weight loss on the specimen corresponded to a corrosion rate of 29 mpy. The rate of attack decreased with time and upon completion of the test, 1000 hr, the average corrosion rate was 8 mpy. The test solution was submitted for aluminum analyses at various intervals and the corrosion rate determined from the aluminum content of the uranyl sulfate solution was in good agreement with the observed rate based on weight loss of the specimen. For example, the 1000-hr corrosion rate based on weight loss was 8 mpy whereas that determined from the dissolved aluminum content was 11 mpy. The present results with AlSiMag 652 were consistent with results from other tests on the same (or similar) ceramic materials exposed to high-temperature uranyl sulfate solution containing copper sulfate and sulfuric acid.

3. Ceramicite C-100.--A ceramic electrical insulation material with several interesting physical properties was tested in high-temperature uranyl sulfate solution. The material, Ceramicite C-100, is produced by the Consolidated Electrodynamics Corporation in Pasadena, California. Its properties reportedly consist of superior electrical resistivity and high-pressure integrity at temperatures up to 438°C (820°F) and the ability to form a molecular bond with the 400-series stainless steels.

In one experiment, five Ceramicite beads were bonded to a platinum wire by gradual heating from 482 to 621°C (900 to 1150°F). The assembly was placed in an autoclave containing HRT core solution and heated to 300°C. The oxygen overpressure at temperature was approximately 150 psi. After 50 hr, weight measurements indicated that the beads were dissolving at 970 mpy; visually, they appeared to have deteriorated badly. It was subsequently learned that the melting point of the Ceramicite was 649°C (1200°F) and it was decided to repeat the test since the beads were bonded at 621°C.

In the second test, two beads were bonded to type 347 stainless steel wire at the bonding temperature of 649°C. The test environment was the same as in the initial test. After 50 hr, the corrosion rate was determined to be 926 mpy, a value in good agreement with the result of the first test. The obvious conclusion was, therefore, that Ceramicite C-100 is not an acceptable material for any application involving contact by high-temperature uranyl sulfate solution.

4. Nitrided Titanium and Frogalloy.--Preliminary tests were performed on two types of materials of interest to the HRP pulsafeder pump development program. One of the materials was nitrided titanium with a surface hardness of 43 Rockwell C. The test specimen was prepared by Horizons, Incorporated at Cleveland, Ohio. After 1000 hr at 300°C in oxygen-pressurized HRT core solution, the specimen exhibited excellent corrosion behavior. Other than a slight weight gain and darkening of the original golden color, there was no evidence of any corrosion attack.

The second material of interest was Frogalloy which is produced by the McKay Company in York, Pennsylvania. The alloy, extremely prone to hardening by cold work, was developed specifically for use in cross-overs in the railroad industry. Two compositions were tested: (1) Frogalloy C with a nominal composition of 0.4 to 0.6 C, 4 Mn min., 18 to 21 Cr, 9 to 10.5 Ni, 0.5 Mo, and balance, Fe, and (2) Frogalloy M with a nominal composition of 0.5 to 0.6 C, 4 Mn min., 18 to 21 Cr, 9 to 10.5 Ni, and balance, Fe. The specimens were received in the form of check-valve ball seats. Exposures were made in boiling and aerated 5% HNO₃ solution and in boiling and aerated HRT core solution. After 500 hr in the nitric acid environment, Frogalloy C was corroded at a rate of 49 mpy and the rate for Frogalloy M was 43 mpy. After 100 hr in the HRT core solution, the corrosion rates were 500 and 580 mpy, respectively, for Frogalloys M and C. Both alloys became covered with copper during the course of the test. In both environments, deep pitting was encountered.

In conclusion, the data indicate that nitrided titanium would be usable in HRT environments but that the two Frogalloy compositions would be completely unusable in even boiling HRT core solutions.

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3. J. C. Griess, H. C. Savage, et al., Quarterly Report of the Solution Corrosion Group for the Period Ending April 30, 1957, ORNL CF-57-4-55, pp 5-9.
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15. See HRP Dynamic Corrosion Studies Reports as follows:

Cr₂(SO₄)₃
NiSO₄

FeSO₄
MnSO₄

Na₂WO₄

Run B-38

" A-63

" F-12

" F-13

" B-36

" A-63

" B-39,40

" B-41

" D-26

ORNL CF-54-5-20.

" " 54-3-102

" " 53-1-169

" " 53-1-166

" " 54-2-162

" " 54-3-102

" " 54-5-71

" " 54-5-80

" " 54-5-55

15. (Cont'd)

H_2MoO_4	Run D-16,18	ORNL CF-53-12-83
SiO_2	" B-32	" " 53-12-175
Na_2SiO_3	" B-33	" " 53-12-173
	" B-34	" " 53-12-174
	" J-10 thru J-13	" " 53-1-190
	" J-14	" " 53-1-191
$(UO_2)_3(PO_4)_2$	" D-19	" " 53-12-130
$(NH_4)TcO_4$	" D-21	" " 54-1-129
$K_2Cr_2O_7$	" D-30,31	" " 54-8-65
	" D-36,37	" " 54-12-111

16. See, for instance, J. C. Griess, R. S. Greeley, and P. R. Shire, HRP Dynamic Corrosion Studies, Summary of Runs A-76, A-77, and A-78, ORNL CF-55-4-28.
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