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CF-56-7-52

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POST OFFICE BOX P
OAK RIDGE, TENNESSEE

METALLURGY AND CERAMICS

DATE: July 31, 1956

SUBJECT: HRP Dynamic Solution Corrosion Studies: Quarter Ending July 31, 1956

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0071228.030

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I. SUMMARY

A mockup of the expansion joint and Zircaloy-stainless steel transition joint as used in the HRT reactor vessel has been installed in a test loop for evaluation of corrosion and joint integrity.

Aluminum oxide bearings are under test in the model 100A Westinghouse pumps for evaluation and comparison with Graphitar-Stellite 98M2. Preliminary results are encouraging.

Long-term tests with solutions containing 0.04 m UO_2SO_4 , 0.005 m CuSO_4 and 0.015 m H_2SO_4 have been completed at 200, 250 and 300°C. The results show low corrosion rates for stainless steel below about 40 fps except at 200°C where corrosion rates were high at flow rates as low as 34 fps. However, the solutions were not completely stable at 250 and 300°C; both uranium and copper were slowly lost from solution.

A run made in the 4000-gpm loop at 250°C with a solution composed of 0.04 m UO_2SO_4 , 0.005 m CuSO_4 and 0.02 m H_2SO_4 has shown that the system was stable with even very low oxygen concentrations. The system was operated for 225 hr with 25 ppm oxygen and for 100 hr with approximately 3 ppm with no evidence of accelerated corrosion or uranium precipitation.

A series of runs in which uranyl sulfate solutions containing the same concentrations of uranium, copper and sulfuric acid as have been circulated in "in-pile" loops has been completed in the 100A loops. To date the results have not shown agreement with results obtained in "in-pile" loops operated out-of-pile. It seems probable that differences in pressurization (steam vs. gas), pretreatment, and loop history are causes.

The addition of chromium (VI) ions to uranyl sulfate solutions has been investigated further. It has been shown that even very low concentrations increase the high velocity, film-free corrosion rate of stainless steel in a very pronounced way. At low velocities, however, the amount of metal that dissolved during the period of film formation was less the higher the chromium (VI) concentration.

Further corrosion testing with uranyl fluoride systems has shown that stainless steel is attacked to a lesser extent in uranyl fluoride than in uranyl sulfate solutions. The reverse is true with titanium, particularly in crevices where the attack rate can be high in fluoride systems. Both titanium and stainless steel show adequate corrosion resistance in the gas phase above fluoride solutions, but zirconium is completely destroyed in both the gas and liquid phases.

Quartz-tube investigations have shown that solutions containing equimolar concentrations of beryllium sulfate and uranyl sulfate are stable over quite wide temperature and concentration ranges. It has also been shown that beryllium sulfate solutions are capable of dissolving appreciable quantities of uranium trioxide and remaining stable at high temperatures. To date no corrosion tests have been completed with beryllium-containing solutions.

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A laboratory-scale corrosion study has shown the susceptibility of stainless steel to stress-corrosion cracking in boiling simulated HRT fuel solutions ($0.04 \text{ M } \text{UO}_2\text{SO}_4$, $0.005 \text{ M } \text{CuSO}_4$ and $0.02 \text{ M } \text{H}_2\text{SO}_4$) containing chloride ions. During a 500-hr test period stressed specimens showed cracking at chloride concentrations of 25 and 50 ppm; no cracks were apparent at the 5, 10 and 100 ppm levels. At the two lower chloride concentrations no acceleration of corrosion was noted. At all other concentrations generalized corrosion was appreciable, being the highest at the 100 ppm level. Very preliminary tests with the simulated HRT solution containing 100 ppm bromide or iodide have shown no cracking of the specimens, although generalized attack was increased by the presence of the bromide.

One phase of a test program to examine the corrosion-fatigue behavior of type 347 stainless steel bellows in uranyl sulfate solutions at elevated temperatures has been completed. The results indicate that the life of the bellows is not greatly shortened when a uranyl sulfate solution is used as the corrodant instead of distilled water.

The corrosion of aluminum oxide in 0.04 to $0.17 \text{ M } \text{UO}_2\text{SO}_4$ containing copper sulfate and sulfuric acid at 150°C has been studied in toroid runs. Corrosion rates between 1 and 3 mpy were observed.

II. INTRODUCTION

The data to be presented in the following sections represent the detailed results obtained during the past quarter (April 30, 1956 to July 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.

The general form of the report is essentially the same as in past reports with the exception of the manner in which the actual corrosion rates of the pin-type specimens exposed in the LOOA loops are reported. Formerly one large table was used to show all test conditions and all average corrosion rates. Average corrosion rates are frequently misleading because under some conditions corrosion rates are not constant but decrease to a very low rate after an initial period of rapid corrosion. Hence, it was felt that inclusion of the results in the appropriate subsections would allow a better description of the results than was possible in the large table and thus eliminate misinterpretation of the data.

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

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

A. Loop Engineering.

Loop F - Mockup of HRT Core Vessel Expansion Joint and Zircaloy-Stainless Steel Gasket. - A mockup of the expansion joint¹ and Zircaloy-stainless steel transition joint² as used in the HRT reactor

* On loan from TVA

vessel has been installed in 100A dynamic corrosion loop F. The mockup test assembly is shown in Fig. 1.

The purpose of the mockup of the joint and gasket assembly is to study the corrosion behavior of the component parts by uranyl sulfate solution, as well as the integrity of the bellows and Zircaloy-stainless steel joint, under reactor conditions of temperature and pressure. It is planned to simulate reactor startup and shutdown by thermally cycling the entire unit between 300°C and 100°C and mechanically deflecting the bellows to simulate expansion and contraction as expected under service conditions.

As presently installed in loop F, the inside of the bellows expansion joint is filled with distilled water and connected through a condenser to the vapor space of the loop pressurizer. A side stream of fuel from the main pump loop circulates through the test assembly on the outside of the bellows and joint. A pressure differential of approximately 50 psia is maintained across the joint by loop pressure differential. This pressure differential is recorded and interlocked with the system to prevent overpressure. A schematic diagram of the bellows joint as installed in loop F is shown in Fig. 2.

Periodic helium leak checks of the joint will be made. In addition, it is hoped that any leakage of fuel solution through the test unit can be detected and monitored by sampling the water inside the bellows for contamination by fuel solution. The fuel solution side of the bellows is at a higher pressure (~ 50 psia) than the water side.

Standard corrosion specimen arrays are installed in the main loop circuit. Other corrosion samples in the form of coupons and stressed specimens have been installed in various locations in the bellows joint. These specimens of Zircaloy-2, titanium and stainless steel will be used as an aid in correlating the corrosion of the test components in localized fuel environments.

Loop O - Beryllium Solution Loop. - A new loop designed to handle solutions of uranyl sulfate containing beryllium salts as additives has been completed. This loop is described in detail in another report³.

Aluminum Oxide Pump Bearings. - As previously reported⁴, the use of pure sintered aluminum oxide as bearing and journal material has improved the bearing life and reliability of bearings as used in the 5 gpm pumps in in-pile loops. Based on this experience, bearings and journals of pure sintered aluminum oxide were installed in a Westinghouse Model 100A pump on an experimental basis. Figure 3 is a photograph of the aluminum oxide bearings and journals after approximately 1500 hr of operation. This included 200 hr operation circulating water at 190°C and 1300 hr circulating 0.04 M UO_2SO_4 solution containing 0.015 M H_2SO_4 and 0.005 M CuSO_4 at 300°C. No visual or measurable wear was observed. This pump has now been installed in slurry loop BS for an evaluation of the aluminum oxide as a bearing and journal material in model 100A pumps circulating thorium oxide slurries.

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Fig 1 Bellows and Zircaloy - Stainless Steel Transition Joint Test Assembly

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Fig. 2. Loop F with Bellows Test Assembly

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A black and white photograph of a circular metal flange. The flange has a central circular opening. Around the inner edge of this opening is a raised ring. The outer edge of the flange features ten evenly spaced circular bolt holes. The metal surface shows some texture and wear. The flange is centered against a light, slightly mottled background.

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Additional 100A pumps will be equipped with the aluminum oxide bearings and journals in order to evaluate this material further.

- B. Long Term Runs with Proposed HRT Solution. Three long-term runs with proposed HRT solution, 0.04 M UO_2SO_4 containing 0.015 M H_2SO_4 and 0.005 M CuSO_4 , were terminated⁵. Conditions of the runs are listed in Table I. They were made to observe the long-term stability of the solution containing 0.15 M (38 mole %) H_2SO_4 and to expose a wide variety of alloys to this more acid solution at 200, 250 and 300°C.

Despite the increased acid concentration, loss of 15 to 20% of the copper and 5 to 10% of the uranium occurred in loop K at 300°C and in loop M at 250°C, probably by hydrolytic precipitation. The solution was completely stable at 200°C. Rate of loss of copper was slower than in the less acid runs reported previously⁶ but did not level off with time. The uranium was lost at a very slow rate. The pH of the solutions did not appear to decrease appreciably, remaining about 1.6 to 1.7 throughout the runs. However, more acid, perhaps 0.02 M (50 mole %), will be needed to ensure solution stability for long operating periods.

TABLE I

CONDITIONS AND OBSERVATIONS OF RUNS WITH PROPOSED HRT SOLUTION
IN K, L, AND M LOOPS

Run No.	UO_2SO_4 (M)	Additions (M)	Oxygen (ppm)	Temp (°C)	Time (hr)	Remarks
K-16	0.04	0.015 H_2SO_4 0.005 CuSO_4	500	300	3231	Loss of Cu and some slight loss of U occurred.
L-34	0.04	0.015 H_2SO_4 0.005 CuSO_4	500	200	4093	No detectable loss of Cu or U
M-28	0.04	0.015 H_2SO_4 0.005 CuSO_4	500	250	4151	Loss of Cu and some slight loss of U occurred.

The corrosion rates of the pin-type specimens exposed in these tests are summarized in Table II. In these runs a number of new pins of different alloys were exposed and also several pins were carried over from runs L-32 and 33, M-26 and 27, and K-14 and 15.⁷ The pins carried over in loop L have now been exposed to uranyl sulfate solution for a total of 12,031 hr, those carried over in loop M for 12,586 hr, and those carried over in loop K for 12,691 hr. The pins carried over all had uniform protective oxide films. Surprisingly enough, these pins all maintained their films, even those stainless steel pins exposed at flow rates above the critical velocity for new pins at this acid concentration (e. g., at 34 and 42 fps in L-34). In fact, they gained weight during the present runs by deposition of additional corrosion products from the solution. Hence, it is possible that pretreatment of a stainless steel system at low acid concentration could build up a film that would be protective for long periods of time at higher acid concentrations. In practice, however, it would be difficult to

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utilize such a procedure since a localized film breakdown would be very difficult to determine in an operating reactor and the corrosion rates in the area of film breakdown would be very high.

TABLE II

CORROSION RATES IN LONG TERM RUNS WITH 0.04 M UO_2SO_4 , 0.015 M H_2SO_4 , 0.005 M CuSO_4

Materials	Flow Rate, fps	Corrosion Rates, mpy		
		L-34 (200°C)	M-28 (250°C)	K-16 (300°C)
Ave. Stainless Steels (new pins) ^c	8	1.8	----	----
	13	----	0.36	0.24
	20	3.3	0.66	0.20
	26	----	0.50	0.27
	34	13	0.68	0.37
	42	17	----	----
Ave. Stainless Steels ^c (filmed-over pins from previous runs)	8-42	0	0	0
Ave. Zirconium Alloys ^d	8	0	0	0 ^a
Ave. Titanium Alloys ^e	8	0	----	----
Ave. Titanium Alloys	13	----	0	0
Ave. "Pure" Titanium	20	0	0	0
Titanium, 3% Al, 5% Cr	20	0	0.18 ^b	0.26 ^b
Titanium, 5% Al, 2-1/2% Sn	20	0	0	0.14 ^b
Ave. "Pure" Titanium	26	----	0	0
Titanium, 3% Al, 5% Cr	26	----	----	0.39 ^b
Titanium, 75A	34	0	0	0
Titanium, 100A	34	----	0	0.03
Titanium, 150A	34	----	0	0.14
Titanium, 3% Al, 5% Cr	34	----	0.52 ^b	0.45 ^b
Titanium, 5% Al, 2-1/2% Sn	34	----	0.04 ^b	0.23 ^b
Titanium, 6% Al, 4% V	34	----	0.01	0.40

- a. Except one Zirconium-2-1/2% Sn pin corroded at 1.3 mpy.
 b. Corrosion rate based on scrubbed weight; so, somewhat low.
 c. Includes types 304, 304 cast, 304L, 309 SCB, 316, 347, 347 cast, 430 and 446.
 d. Includes crystal bar zirconium, zirconium-2-1/2% Sn, and Zircaloy-2.
 e. Includes 75A, 100A, 150A, 3% Al + 5% Cr, 5% Al + 2-1/2% Sn, 6% Al + 4% V, and RC-55.

The new stainless steel pins gave average corrosion rates that decreased with increasing temperature. At 200°C the rates were appreciable at 8 to 20 fps during the first part of the run, but after a protective film formed the pins slowly gained weight by deposition of corrosion products on their surfaces; however, the pins at 34 and 42 fps were above the critical velocity and continued corroding

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steadily. At 250 and 300°C at all velocities tested, corrosion rates were low and pins were filmed over. The differences between the various types of stainless steels listed in footnote "c" of Table II were small and well within the spread of data for any one type of alloy. Carpenter-20 and Incoloy pins were also exposed. These showed average corrosion rates higher by factors of 2 to 5.

The zirconium pins, most of which were carried over from the two previous runs, gained weight by deposition of corrosion products from solution with the exception of one zirconium-2-1/2% tin pin at 300°C, which corroded at 1.3 mpy. The titanium pins, most of which were carried over from previous runs, were generally quite corrosion resistant, but at 250 and particularly at 300°C some slight but definite corrosion rates were observed in the case of the alloys. The titanium-aluminum alloy pins were the most susceptible to attack (the "pure" titanium listed represents commercially pure metal such as types RC-55 and 75A).

The type 347 stainless steel coupons exposed in each run were new and their weight losses are shown in Fig. 4. As noted with the new stainless steel pins, the extent of corrosion decreased with increasing temperature. Also, the critical velocity increased from 20 to 30 fps at 200°C to 25 to 35 fps at 250°C to 30 to 40 fps at 300°C. Agreement with previous short-term runs was good.

The generalized corrosion rates for the over-all loop as determined from increase in nickel concentration were as follows: 0.30 mpy at 200°C; 0.07 mpy at 250°C; and 0.08 mpy at 300°C.

In summary, the results of the runs to date show that 0.04 M UO_2SO_4 solutions containing 0.005 M CuSO_4 and 0.015 M H_2SO_4 are not stable over long periods of time in stainless steel systems at 250 and 300°C; both uranium and copper are slowly lost from solution, presumably by hydrolysis. Furthermore, the results suggest that a pretreatment of the system may be of value in extending the critical velocity for appreciable periods of time. This fact is demonstrated by the pin-type specimens in run L-34 at flow rates of 34 and 42 fps where previously filmed over pins showed no attack but newly machined pins did not develop a protective film and continued to corrode actively throughout the run.

- C. Corrosion Results with Very Low Oxygen Concentrations. - Run 4000-6 was made in the 4000-gpm pump loop in order to determine whether there would be increased corrosion at minimum oxygen concentrations in 0.04 M UO_2SO_4 containing 0.02 M H_2SO_4 and 0.005 M CuSO_4 at 250°C. For 250 hr the oxygen concentration was maintained at less than 25 ppm by adjusting the oxygen feed and the let-down rates in the 4000-gpm loop. For over 100 hr the oxygen concentration was about 3 ppm. No evidence of solution instability was observed and corrosion rates were similar to those obtained in other runs with much higher oxygen concentrations (about 1000 ppm).

Two "crevice" coupons were exposed. The "crevice" coupons were standard size type 347 stainless steel coupons except that they were of half thickness and the two halves were pressed together in the holder to give the crevice. No accelerated attack in the crevice occurred.

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Fig. 4. Weight Losses of Type 347 SS Coupons in 0.04 m UO_2SO_4 + 0.015 m H_2SO_4 + 0.005 m CuSO_4 .

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Hence, low oxygen concentrations per se do not cause increased attack in dilute uranyl sulfate solutions, although if complete oxygen depletion occurs, as is possible in certain crevice regions, accelerated attack can occur.

After these runs the 4000-gpm pump was disassembled for examination.

- D. Circulation of Simulated In-Pile Solutions in 100A Loops. - A number of runs in "in-pile" loops have shown that the "in-line" corrosion specimens (those not exposed to the pile neutron flux near the lattice) do not show the same corrosion rates as are observed in 100A loops operated under the same conditions. In recent in-pile loops, the solution has been composed of 0.17 M UO_2SO_4 , 0.04 M H_2SO_4 and 0.03 M CuSO_4 and the temperature of the main stream has been 250°C. With the loops operated in-pile, a critical velocity has never been found, whereas in the 100A loops, a critical velocity is always found at relatively low flow rates under these conditions.

Four possible reasons for the discrepancy in observed results are: geometry of the specimens and specimen holder; steam pressurization; pretreatment of the loop and corrosion samples; and loop history. The results of experiments designed to determine which, if any, of the above are responsible for the differences observed are described below. Also, the results of experiments at higher temperatures and one run with magnesium sulfate added are reported. The conditions used in all these runs are summarized in Table III.

Geometry. In the 100A loops ten coupon-type specimens, each 0.20 in. x 1.4 in. x 1.4 in. are exposed in a double-tapered titanium holder. In this case, the bulk velocity increases along the length of the holder so that the last coupon in the holder is exposed to the highest flow rate. In the case of the "in-pile" type specimens, twelve coupons - each 0.06 in. x 0.5 in. x 0.5 in., are exposed in a venturi type titanium holder. With this type holder the coupons near the middle of the holder are exposed to the highest flow.

In all of the runs listed in Table III, both types of holders were exposed and in all cases, the agreement was very good between the two types of holders. There was no indication that either the size or the geometry of the holder influenced the results in any way. In all cases the observed corrosion rates were much higher than observed under similar conditions in "in-pile" loops and in all cases a critical velocity was observed.

Steam Overpressure: It has been postulated that steam overpressure in the in-pile loops caused by maintaining the pressurizer temperature 30°C above loop temperature could prevent cavitation or gas bubble formation in the coupon holders and thus prevent destruction of the protective film on coupons. One previous 100A loop run⁶ indicated a possible effect also. Hence, runs E-51 and E-62 were made as nearly isothermal as the system allowed while runs E-56 and E-61 were made with the pressurizer temperature as high above the loop temperature as possible to provide steam pressurization. However, the difference in pressurizer temperatures between E-51 and 62 and E-56 and 61 was only 10 to 15°C so that the

TABLE III

CONDITIONS OF SIMULATED "IN-PILE" RUNS IN 100A LOOPS

Run No.	UO ₂ SO ₄ (m)	Additives (m)	Oxygen (ppm)	Time (hr)	Loop Temp.	Remarks
E-51	0.17	0.04 H ₂ SO ₄ 0.03 CuSO ₄	1000-2000	200	250	Isothermal run, gas pressurized.
E-53	0.17	0.04 H ₂ SO ₄ 0.03 CuSO ₄ 0.04 MgSO ₄	"	"	"	Pressurizer temperature 265°C.
E-56	0.17	0.04 H ₂ SO ₄ 0.03 CuSO ₄	"	"	"	Pressurizer temperature 265°C. Plugging of sample holders occurred.
E-58	0.17	" "	"	"	"	Pressurizer temperature 265°C. Loop and specimens pretreated with water and oxygen at 250°C for 24 hr prior to run. Loop descaled prior to pretreatment.
E-61	0.17	" "	"	"	"	Pressurizer temperature 265°C.
E-62	0.17	" "	"	"	"	Isothermal run, gas pressurized.
E-63	0.17	" "	"	"	280	Isothermal run, gas pressurized.
E-64	0.17	" "	"	"	250	Isothermal run, gas pressurized. Loop and specimens pretreated with 3% trisodium phosphate at 100°C for 4 hr, 5% nitric acid at 100°C for 12 hr and water with oxygen at 250°C for 24 hr.
A-102	0.17	" "	"	"	300	Isothermal run, gas pressurized.

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difference in steam pressures was only 100 to 150 psi.

Differences in the corrosion results caused by the slightly greater steam pressure in E-56 and 61 were not at all clearcut. Coupon weight losses overlapped and the agreement between supposedly identical runs was not good. Flow measurements were made at the end of E-56 so that a correction for the partial plugging that occurred could be made in the flow rates, but the accuracy of the data for that run is in doubt. Figure 5 illustrates the results obtained for weight losses of the coupons as a function of flow rate. Slightly lower low velocity weight losses and a slightly higher critical velocity are possibly indicated for the steam pressurized runs, E-56 and 61. However, in neither case did the results correspond with in-pile loop results.

The results of these experiments are not clear cut due primarily to experimental difficulties. There is an indication, however, that steam overpressure may increase the critical velocity slightly but further work will be necessary to verify this point.

Loop and Corrosion Sample Pretreatment: Every in-pile loop with corrosion specimens enclosed is pretreated before being run with Uranyl sulfate solution, usually in the following manner: 4 hr with trisodium phosphate at 100°C, 12 hr with 5% nitric acid at 100°C, and 24 hr with oxygenated water at 250°C. On the other hand, in the LOOA loops a pretreatment is usually not employed before each run.

Two runs, E-58 and E-64, were made to see what effect pretreatment would have on the results obtained in a LOOA loop. The pretreatment of the loop and corrosion specimens prior to E-58 consisted of only 24 hr on oxygenated water at 250°C. Then the uranyl sulfate solution was run with about 100 psi steam overpressure. The results of E-58 and E-64 are shown in Fig. 6 with E-61 included for comparison. As can be seen, a large decrease in the corrosion at all velocities occurred in E-58 and the critical velocity was increased significantly from that in a run with no pretreatment. This seemed to indicate that pretreatment was substantially effective in reducing corrosion.

However, run E-64, made isothermally, gave the opposite effect. The full pretreatment as listed above was given the loop and corrosion specimens prior to running on uranyl sulfate solution. A substantial increase in weight loss at each flow rate was observed and the critical velocity decreased slightly from the isothermal runs E-51 and 62 made without pretreatment.

Further testing must be carried out to determine the effectiveness of pretreatments in the above system. Previous studies have shown that pretreatments cannot be used to extend the critical velocity of a system.

Loop History: Each in-pile loop test is necessarily carried out in a new loop. To investigate how the prior condition of the loop might affect corrosion of coupons, Loop E was descaled⁹ prior to run E-58. A pretreatment was then made similar to that used for in-pile tests as listed above. Inadvertently the coupons were left out of the loop

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Fig. 5. Weight Losses of Type 347 Stainless Steel Coupons in $0.17 \text{ M } \text{UO}_2\text{SO}_4 + 0.04 \text{ M } \text{H}_2\text{SO}_4 + 0.03 \text{ M } \text{CuSO}_4$ at 250°C .

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Fig. 6. Weight Losses of Type 347 Stainless Steel Coupons in $0.17 \text{ m } \text{UO}_2\text{SO}_4 + 0.04 \text{ m } \text{H}_2\text{SO}_4 + 0.03 \text{ m } \text{CuSO}_4$ at 250°C .

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during this pretreatment. Therefore, the coupons were installed and an additional pretreatment was made consisting of 24 hr on oxygenated water at 250°C. The results as shown in Fig. 6 are discussed above. Very likely, the difference in corrosion behavior between E-58 and E-64 was due more to the nearly film-free condition of the loop walls in E-58 than to differences in steam pressure or pretreatment.

Corrosion rates of the coupons in E-58 were still not as low as for in-pile loop coupons. However, the descaling of loop E was not complete⁹ and the pretreatment made prior to installing the samples undoubtedly put a small amount of scale back on the loop surfaces. It seems clear that the condition of the loop, whether scaled-over or new and scale-free, can markedly affect corrosion of new stainless steel specimens installed in the loop. This decrease of corrosion of specimens in a new loop has been observed previously in LOOA loops¹⁰.

While the results obtained to date do not allow any definite conclusions to be drawn, it seems that steam pressurization (compared to gas pressurization), pretreatment and loop history are all possible reasons for the difference in results obtained in LOOA loops and in "in-pile" loops. Further testing should more clearly define the relative importance of each.

Higher Temperatures: In anticipation of the use of higher temperatures in in-pile testing, runs E-63 and A-102 were made at 280 and 300°C, respectively, under essentially isothermal conditions. Results are plotted in Fig. 7 with E-62 included for comparison with a run at 250°C. As observed with other uranyl sulfate solutions, low velocity weight losses decreased and the critical velocity increased with increasing temperature. Usually high velocity weight losses increase with temperature; the low value for high velocity weight losses in A-102 was due to the fact that nearly all of the last coupon was filmed over.

Magnesium Sulfate Addition: Run E-53 was made with 0.17 M $MgSO_4$ added to the 0.17 M UO_2SO_4 solution containing 0.04 M H_2SO_4 and 0.03 M $CuSO_4$ to see if such a solution might be suitable for in-pile testing. Figure 8 shows the decrease in corrosion that occurred from the similar run without $MgSO_4$, E-61. The added sulfate salt evidently was a fairly effective inhibitor at high flow rates and the solution was stable for the 200-hr test period. In 0.17 M UO_2SO_4 without the added copper sulfate, magnesium sulfate has been shown to be a more effective inhibitor¹¹ in the absence of sulfuric acid than in its presence. Possibly the effect of the magnesium sulfate is to lower the hydrogen ion concentration by bisulfate formation at 250°C; the addition of sulfuric acid would nullify this effect.

E. Effect of Chromium (VI) on the Corrosion of Stainless Steel:

Previous studies¹² have shown that chromium (VI) in uranyl sulfate solutions markedly affects the corrosion rate of stainless steel. Investigation of this effect in stainless steel loops is unsatisfactory because the concentration of hexavalent chromium increases during a run at 250 or 300°C by oxidation of chromium from the steel or oxide film. Hence, the all-titanium loop was used for a series of runs so the

Fig. 7. Weight Losses of Type 347 Stainless Steel Coupons in 0.17 m UO₂SO₄ + 0.04 m H₂SO₄ + 0.03 m CuSO₄ (Isothermal Operation)

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Fig. 8. Weight Losses of Type 347 Stainless Steel Coupons in 0.17m UO_2SO_4 + 0.04m H_2SO_4 + 0.03m CuSO_4 at 250°C (Steam Pressurization)

dichromate concentration could be maintained at various desired levels without interference from the loop itself. Table IV lists the conditions of the runs made.

TABLE IV
CONDITIONS OF RUNS MADE IN LOOP G

Run No.	UO ₂ SO ₄ (conc) (m)	Additive Conc. (m)	Oxygen Conc. (m)	Temp (°C)	Time (hr)	Dichromate Conc. (ppm Cr ⁺⁶)	Remarks
G-39	2.4	2.1 Li ₂ SO ₄	100-500	300	200	17	Cr ⁺⁶ built up during run.
G-40	2.2	2.2 " "	100-300	250	200	10	" " " " "
G-41	2.1	2.1 " "	1000-2000	250	100	16	" " " " "
G-42	2.1	2.1 " "	1000-2000	300	100	17	" " " " "
G-43	0.17		1000-2000	250	19	1	
G-44	0.17		1000-2000	250	100	1	
G-45	0.17		1000-2000	250	100	11	Added as K ₂ Cr ₂ O ₇ .
G-46	0.17		1000-2000	250	100	11	20 ppm Cr ⁺⁶ added as K ₂ Cr ₂ O ₇ .
G-47	0.17		1000-2000	250	100	42	Added as K ₂ Cr ₂ O ₇ .
G-48	0.17		1000-2000	250	100	100	" " "
G-49	0.17		1000-2000	250	100	190	" " "
G-50	0.17		1000-2000	250	100	484	" " "

Runs G-39 through G-42 were made to see if very low dichromate concentration would affect the corrosion of stainless steel pins in 2 m UO₂SO₄ containing equimolar lithium sulfate at 250 and 300°C. The results are tabulated in Table V and are compared with similar runs in a stainless steel loop where the chromium (VI) concentration increased to high levels (> 200 ppm) during the run. In the runs in Loop G no dichromate ions were added to the solution, but some entered during the run from corrosion of the 2 to 4 stainless steel pins exposed in each run.

At low velocity, 10 to 25 fps, average corrosion rates were much higher in the runs with low chromium (VI) concentration than in the runs with higher chromium (VI) concentration. However, at 10 to 12 fps, the pins exposed in loop G were filmed over and thus the average corrosion rates

would have decreased if the runs were prolonged. That is, the initial weight losses of the pins exposed to low chromium (VI) concentration during film formation were much higher than for those exposed to high chromium (VI) concentration, but the ultimate corrosion rates would probably be the same for both sets of pins - essentially zero - since protective films were formed in both cases. On the other hand, the pins exposed at 25 fps in Loop G were not completely filmed over and were corroding steadily, whereas pins at 25 fps in Loop D were filmed over. This indicates the critical velocity is lower at lower chromium (VI) concentration.

TABLE V

CORROSION OF TYPE 347 STAINLESS STEEL PINS IN 2 m UO_2SO_4 + 2 m Li_2SO_4 .

Run No.	Loop Mat'l	Temp ($^{\circ}\text{C}$)	Time (hr)	Final Cr Conc. (ppm)	Average Corrosion Rate		
					10 - 12 fps (mpy)	25 fps (mpy)	68 - 70 fps (mpy)
G-40	Ti	250	200	10	--	110	---
G-41	Ti	250	100	16	90	---	150
G-53	SS	250	200	300	39	40	200
G-39	Ti	300	200	17	--	150	---
G-42	Ti	300	100	17	90	---	260
D-50	SS	300	200	1200	9	10	330

At high velocity, 68 to 70 fps, corrosion rates were lower at the lower chromium (VI) concentration. This result has been observed before¹² and is discussed below.

Runs G-43 through G-50 constituted a series of runs using 0.17 m UO_2SO_4 at 250 $^{\circ}\text{C}$ with definite additions of potassium dichromate to define further the action of chromium (VI). Figure 9 illustrates the results, with corrosion rate at high (68 to 70 fps) and low (10 to 12 fps) velocities plotted against chromium (VI) concentration. The results are in agreement with those discussed above in the more concentrated solutions. At low velocity average corrosion rates decreased with increasing chromium (VI) concentration. However, all pins were filmed over; so, actually, the results indicated that the initial weight loss during film formation decreased with increasing chromium (VI) concentration. In other words, the pins became filmed over faster the higher the chromium (VI) concentration. At the high flow rate the pins remained free of film and were apparently corroding at a constant rate with time.

One possible explanation for the fact that relatively high concentrations of chromium (VI) behave as a corrosion inhibitor at low flow rates and actually increase the critical velocity substantially¹³ may be partially related to the observation that chromium (VI) increases the corrosion rate of stainless steel at very high flow rates where a stable film does not form. At the beginning of the corrosion process

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Fig. 9. Corrosion Rates of Type 347 Stainless Steel Pins as a Function of Chromium (VI) Concentration in 0.17 m UO_2SO_4 at 250°C. (100 hour Runs)

[illegible]

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all specimens, regardless of velocity, are essentially film-free. It has been postulated¹⁴ that a bulk, protective film is formed from the corrosion products at sufficiently low flow rates in the following manner: the iron, chromium, and nickel of the stainless steel dissolve initially to form ferrous, chromic and nickelous ions; the ferrous and nickelous ions are soluble. If the system contains an oxidizing agent such as chromium (VI) or oxygen or both, the ferrous ions are rapidly oxidized and hydrolyzed with the chromic ions to form the protective oxide film. The process of film formation is in competition with diffusion and turbulence in that the latter both tend to remove the corrosion products before they have a chance to form a protective film on the surface of the stainless steel. If the ions originating at the surface of the steel were formed very slowly and if the oxidation and hydrolysis steps were also slow, the corrosion products would probably be able to diffuse away from the surface and not form a protective film. On the other hand, if the corrosion product ions enter the solution at a very fast rate and are oxidized and hydrolyzed rapidly, a protective film would be expected to form, even if some of the ions were removed from the surface of the stainless steel by diffusion. The critical velocity is that flow rate (or turbulence) at which the diffusion layer is reduced to such an extent that the corrosion products diffuse away from the surface so fast that the ions do not have a chance to be oxidized, hydrolyzed and crystallized on the surface of the steel. When other conditions, such as acidity and temperature, are constant, anything that would increase either the rate of formation of corrosion product ions, the rate of oxidation of the ferrous ions to the ferric state, or the rate of hydrolysis, would be expected to increase the critical velocity by virtue of the fact that the formation of the protective film would be faster and a thinner diffusion layer would suffice to prevent the escape of film-forming ions into the main circulating stream.

If the postulated corrosion process is correct, the addition of chromium (VI) ions which actually accelerate the corrosion of stainless steel in the film-free condition and possibly increase the rate of oxidation of ferrous to ferric ions, would be expected to increase the rate of film-formation and thereby increase the critical velocity of the system. Similarly, increasing the temperature would be expected to lead to more rapid film formation since the rate of all processes postulated as necessary to form a film would be increased. The results presented above and those reported previously have shown that either the addition of chromium (VI)¹³ or an increase in temperature¹⁵ or both increases the critical velocity and decreases the amount of metal that dissolves during the period when a film is forming; likewise, both increase the rate of attack of unprotected stainless steel in uranyl sulfate solutions.

F. Corrosion in Uranyl Fluoride Solutions.

Several runs have been made previously with 0.02 to 1.3 μ UO_2F_2 at 250°C¹⁶. These runs showed that stainless steel was corroded to a lesser extent in uranyl fluoride solutions than in corresponding concentrations of uranyl sulfate. The present study was made to confirm the previous results and to investigate the effects of increasing the temperature and of adding lithium or sodium fluoride on the corrosion of stainless steel and titanium by uranyl fluoride solutions. No zirconium specimens were

exposed in the solution since zirconium and its alloys are rapidly dissolved by uranyl fluoride solutions at high temperature.

Table VI lists the conditions of the runs in the present study. In each run, Zircaloy-2, titanium (MST Grade III), and stainless steel specimens were exposed in the vapor phase above the solution. In every case the Zircaloy-2 specimens were missing at the end of the run and were presumed to have been totally dissolved. The titanium specimens were unattacked, whereas type 347 stainless steel specimens were only very slightly attacked (about 1 mpy). Similar results have been obtained above uranyl sulfate solutions except that zirconium was unattacked.

TABLE VI

THE OPERATING CONDITIONS FOR URANYL FLUORIDE RUNS.

Run No.	UO ₂ F ₂ Conc'n (m)	Additive Conc'n (m)	Oxygen Conc'n (ppm)	Time (hr)	Temp (°C)
H-87	1.3	---	1000-2000	150	250
H-88	1.3	---	1000-2000	50	300
H-89	1.3	1.3 NaF	1000-2000	125	250
H-90	0.17	0.1 LiF	1000-2000	235	250
A-97	0.17	---	1000-2000	200	250

The corrosion of type 347 stainless steel as a function of flow rate in 1.3 m UO₂F₂ at 250°C for 150 hr is shown in Fig. 10 (run H-87). For comparison, run H-36 data, obtained under similar conditions with uranyl sulfate, are also plotted in Fig. 10 and show that under comparable conditions uranyl sulfate is approximately twice as corrosive as uranyl fluoride. Run H-89 was also made at 250°C and in addition to 1.3 m UO₂F₂, contained 1.3 m NaF. From Fig. 10 it can be seen that the addition of an equimolar concentration of sodium fluoride reduced the corrosiveness of the uranyl fluoride by a substantial factor.

The only run in which 1.3 m UO₂F₂ was circulated at 300°C was run H-88 and the corrosion of the stainless steel coupons is also shown in Fig. 10. The weight loss of specimens exposed at low flow rates is much lower than that of comparable specimens at 250°C but high-velocity corrosion rates were about three times greater at 300°C than at 250°C.

Titanium, titanium alloyed with aluminum-chromium and aluminum-manganese, niobium, and gold pins were exposed in these runs. In straight uranyl fluoride the commercially pure titanium pins showed relatively low corrosion rates, 0 to 6 mpy. However, the titanium 75A pin and coupon holders were severely attacked underneath the stainless steel clamping bands, due either to a galvanic or a crevice attack. The titanium alloy pins were attacked also, showing corrosion rates greater than 20 mpy which increased with temperature and velocity. One titanium-aluminum-manganese pin in H-87 at 70 fps was almost totally dissolved. Niobium pins were severely attacked in H-88 (none were included in H-87). They formed no film even at 13 fps and corroded at 3500 to 4300 mpy. One gold pin in H-87 showed a negligible corrosion rate.

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Fig. 10. Weight Losses of Type 347 Stainless Steel Coupons in Concentrated Uranium Solution.

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Fig. 11. Weight Losses of Type 347 Stainless Steel Coupons in 0.17m UO_2F_2 for 200 Hours at 250°C.

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With 1.3 m UO_2F_2 and 1.3 m NaF at 300°C (run H-89), commercially pure titanium pins corroded at very high rates, about 300 mpy at 7 fps. The titanium alloy pins showed similar corrosion rates. However, a large amount of the corrosion on these pins occurred in the crevices underneath the teflon insulator sleeves. These results indicate that an abundant supply of oxygen is necessary to minimize corrosion of titanium in uranyl fluoride solutions. In the crevices oxygen reaches the surface of the titanium metal only by diffusion and possibly the supply of oxygen at the surface of the titanium was not sufficient to prevent reduction and hydrolytic precipitation of uranium (IV) which would be accompanied by the formation of hydrofluoric acid.

Two runs, A-97 and H-90, were made with 0.17 m UO_2F_2 , at 250°C , as shown in Table VI. Figure 11 illustrates the results obtained with stainless steel coupons and compares them with a previous run, D-22, in 0.17 m UO_2F_2 and with runs in 0.17 m UO_2SO_4 . Again stainless steel corrosion in uranyl fluoride was substantially less than in uranyl sulfate. Run A-97 supposedly was identical to D-22 but the coupon weight losses were very different. Pin weight losses were in better agreement, however, suggesting that the coupon flow rates in A-97 were in error.

Run H-90 containing 0.17 m UO_2F_2 and 0.1 m LiF at 250°C again showed the beneficial effect of the added fluoride salt on stainless steel corrosion. Corrosion rates were very low (1 to 4 mpy) below flow rates of 45 fps. Titanium corrosion rates, on the other hand, were still higher than in uranyl sulfate, ranging from about 1 mpy for commercially pure titanium pins to 3 mpy for alloy pins at 13 fps.

This series of runs with uranyl fluoride solutions has been concluded and the results were in agreement with previous runs. Corrosion of stainless steel was significantly less in uranyl fluoride than in uranyl sulfate but the effects of uranium concentration, time, temperature and velocity were similar in both solutions; soluble fluoride salt addition decreased corrosion in uranyl fluoride solutions as did sulfate salt addition in uranyl sulfate solutions. Titanium corrosion was greater in uranyl fluoride than in uranyl sulfate and could be disastrous in crevices, particularly in solutions with added fluoride salts. Furthermore, zirconium is completely incompatible with uranyl fluoride solutions, a fact which precludes the use of uranyl fluoride in two-region reactors.

G. Phase Stability of Lithium Sulfate and Beryllium Sulfate Solutions Containing Uranium.

It was reported previously¹⁷ that lithium sulfate added to concentrated uranyl sulfate solutions raised the temperature of appearance of a second liquid phase and also inhibited to an appreciable extent the corrosion of stainless steel. A more extensive investigation of the second liquid phase temperatures for uranyl sulfate-lithium sulfate solutions has been carried out by the fused silica tube method. Solutions of uranyl sulfate at several concentrations containing various amounts of lithium sulfate were heated in 1 mm ID fused silica tubes and observed through a 10 power microscope. The temperature of appearance of a second liquid phase was

read on a potentiometer using a thermocouple close to the tube. The results are shown in Fig. 12. The temperatures indicated are correct to $\pm 1^\circ\text{C}$, but the concentrations have not been corrected for loss of water to the vapor phase (significant at temperatures above 300°C) and so are approximate only. Also, several uranyl sulfate concentrations have not been investigated at all of the lithium sulfate concentrations. Hence Figure 12 gives only a rough indication of the system.

Lithium sulfate in amounts equimolal to the uranyl sulfate raised the second liquid phase temperature 60 to 70°C over that for uranyl sulfate. Amounts of lithium sulfate less than equimolal raised the second liquid phase temperature a proportionately smaller amount. As noted in a previous report¹⁸, equimolal lithium sulfate gave optimum corrosion inhibition. It should be noted that the second liquid phase data for straight uranyl sulfate do not agree with previous work, falling between the data given by Secoy¹⁹ and that given by Jones²⁰. Evidently purity of uranyl sulfate is very important. That used in this study was production quality.

Lithium sulfate added to dilute uranyl sulfate solutions ($< 0.2 \text{ m}$) in amounts which would give an appreciable increase in second liquid phase temperature or appreciable corrosion inhibition, gives a precipitate containing lithium, uranium, and sulfate at temperatures below 300°C . Sodium and magnesium sulfates behave similarly. Beryllium sulfate, on the other hand, had not been investigated and the possibility existed that it might be soluble enough to give inhibition of corrosion in dilute as well as concentrated solutions. Therefore, solutions of uranyl sulfate containing equimolal beryllium sulfate were observed in fused silica tubes. In $0.04 \text{ m } \text{UO}_2\text{SO}_4$ - $0.04 \text{ m } \text{BeSO}_4$ solutions crystals were observed to form near 300°C . Since the formation of crystals may be a slow reaction and since the solutions attack the silica tube to give insoluble products, more precise temperatures of precipitate appearance could not be determined. The addition of $0.02 \text{ m } \text{H}_2\text{SO}_4$ to the $0.04 \text{ m } \text{UO}_2\text{SO}_4$ - $0.04 \text{ m } \text{BeSO}_4$ ($0.005 \text{ m } \text{CuSO}_4$ was also present), however, raised the temperature of immediate formation of a precipitate to above 320°C .

Equimolal beryllium sulfate in uranyl sulfate solutions of higher concentrations gave second liquid phases as indicated in Fig. 12. One hundred mole percent beryllium sulfate was about as effective as 25 mole percent lithium sulfate in raising the second liquid phase temperature.

Beryllium sulfate solutions are known to dissolve appreciable quantities of beryllium oxide and thus it was of interest to investigate the solubility of uranium trioxide in beryllium sulfate solutions. It was found that uranium trioxide is appreciably soluble in beryllium sulfate solutions also. Table VII gives the solubility at room temperature ($28 \pm 1^\circ\text{C}$). The pH of the solutions is interesting in that a uranyl sulfate solution having the same uranium concentration would have a considerably lower pH and hence would presumably be more corrosive. Loop O, presently under construction, will be used to study corrosion in such solutions. Also, interesting are the ratios of uranium to beryllium sulfate indicated by the data shown in Table VII; within experimental error the ratio is constant at one mole of uranium to three moles of beryllium sulfate over

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Fig. 12. Second Liquid Phase Temperatures for UO_2SO_4 Solutions Containing Li_2SO_4 or BeSO_4 .

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Fig. 13. Second Liquid Phase Temperature with Beryllium Sulfate Solutions Containing UO₃

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a concentration range of 0.01 m to 2.4 m BeSO_4 . However, more recent analyses of other solutions of uranium trioxide in beryllium sulfate have not shown a constant ratio.

TABLE VII

SOLUBILITY OF UO_3 IN BeSO_4 SOLUTIONS AT ROOM TEMPERATURE

BeSO_4 Conc. (M)	Uranium Conc. (g U/l)	pH
0.01	0.8	4.5
0.1	7.9	3.5
1.0	82.2	3.2
2.4	178	2.7

Solutions of beryllium sulfate with and without additions of uranium trioxide were heated in 1 mm ID fused silica tubes in order to observe their high-temperature stability. Table VIII gives a tabulation of the results. Figure 13 illustrates the temperature of appearance of a second liquid phase versus molality of beryllium sulfate for the solutions with and without uranium trioxide additions. Interestingly enough, beryllium sulfate solutions form two liquid phases similar to those obtained with uranyl sulfate solutions. Addition of uranium trioxide lowers the temperature of appearance of this second liquid phase.

Table VIII mentions the observation of the appearance of colorless crystals in many of the solutions. It was thought at first that they were a beryllium-containing precipitate, but the very small amount observed, regardless of solution concentration, and the random temperatures of appearance suggested that they were an impurity present on the surface of the 1 mm ID tubes. Several of these solutions were heated in carefully cleaned 4 mm ID tubes and no crystals were observed. In any case, long runs in Loop 0 will be necessary to establish firmly their high temperature stability.

The results discussed above must be considered preliminary. However, certain conclusions are valid. Beryllium sulfate will dissolve significant amounts of uranium trioxide to give solutions of relatively high pH. These solutions give promise of being stable at temperatures near 300°C. Beryllium sulfate added in equimolar amounts to uranyl sulfate solutions raises the two-liquid-phase temperature, but to a much smaller degree than does lithium sulfate. In dilute uranyl sulfate solutions beryllium sulfate gives promise of being more soluble than lithium sulfate.

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TABLE VIII

PHASE CHANGES WITH BERYLLIUM SULFATE SOLUTIONS

Solution	pH	Phase Change	Temp (°C)	Remarks
0.01 M BeSO ₄	3.44	Crystals appeared.	150	Small amount white crystals.
		Crystals disappeared.	310	
		Liquid disappeared.	373	Supercritical
0.01 M BeSO ₄ +0.8 g U/l as UO ₃	4.5	Meniscus disappeared.	370	Supercritical with no change.
0.1 M BeSO ₄	2.74	Crystals appeared.	50	Amount of small white crystals increased up to 250°C and then decreased up to 341°C. Amount was always barely visible.
		Second liquid phase.	341	
0.1 M BeSO ₄ + 1 g U/l as UO ₃	----	Second liquid phase.	336	
0.1 M BeSO ₄ + 7.9 g U/l as UO ₃	3.2	Second liquid phase.	312	
0.5 M BeSO ₄	2.14	Crystals appeared.	250	Barely visible white crystals.
		Second liquid phase.	332	
0.5 M BeSO ₄ +0.92 M H ₂ SO ₄	----	None.		No change up to 391°C.
1.0 M BeSO ₄	1.80	Crystals appeared.	140	Barely visible white crystals.
		Second liquid phase.	335	
1.0 M BeSO ₄ + 1 g U/l as UO ₃	1.83	Second liquid phase.	332	

TABLE VIII
(cont'd)

Solution	pH	Phase Change	Temp	Remarks
Saturated BeSO_4^*	0.97	Crystals appeared.	270	Inserted tube at 270°C. Within 2 minutes could see some small white crystals.
		Second liquid phase.	349	
Saturated BeSO_4^* + 1 g U/l as UO_3	1.05	Second liquid phase.	349	
1 M BeSO_4 + 10 g U/l as UO_3	2.20	Crystals appeared.	110	Barely visible colorless crystals; amt increased up to 200°C and decreased to 250°C. Uranium went with heavy phase
		Crystals disappeared.	250	
		Second liquid phase.	325	
Saturated BeSO_4^* + 10 g U/l as UO_3	1.22	Crystals appeared.	215	Barely visible colorless crystals.
		Second liquid phase.	344	
1 M BeSO_4 + 40 g U/l as UO_3	2.82	Crystals appeared.	200	Barely visible colorless crystals.
		Second liquid phase.	302	
1 M BeSO_4 + 82 g U/l as UO_3	3.2	Second liquid phase.	278	
Saturated BeSO_4^* + 40 g U/l as UO_3	1.73	Crystals appeared.	125	Slightly yellow crystals.
		Crystals disappeared.	250	
		Second liquid phase.	333	
Saturated BeSO_4^* + 178 g U/l as UO_3	2.73	Second liquid phase.	293	

* Nearly saturated at room temperature - about 2.4 M.

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TABLE VIII
(cont'd)

<u>Solution</u>	<u>pH</u>	<u>Phase Change</u>	<u>Temp</u>	<u>Remarks</u>
0.18 M BeSO ₄ + 0.19 M UO ₂ SO ₄		Crystals appeared. Crystals disappeared. Second liquid phase.	150 250 308	Small amount colorless crystals.
0.43 M BeSO ₄ + 0.44 M UO ₂ SO ₄		Crystals appeared. Second liquid phase.	300 306	Small amount colorless crystals.
1.4 M BeSO ₄ + 1.3 M UO ₂ SO ₄		Crystals appeared. Second liquid phase.	270 334	Inserted tube at 270°C. Barely visible colorless crystals.

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The solubility of lithium sulfate in water is currently being determined as a function of temperature. Two liquid phases are not observed, the lithium sulfate crystallizing out instead; the room temperature solubility of uranium trioxide in the solutions is less than 0.12 g of uranium per liter.

It should be pointed out that no corrosion results have been obtained in uranyl sulfate solutions containing beryllium sulfate and it is entirely possible that beryllium-containing solutions may actually be more corrosive than similar solutions not containing beryllium salts. Loop O, which should be completed shortly, will be used to determine the corrosivity and stability of some of the above discussed solutions.

IV. LABORATORY SERVICE CORROSION STUDIES. (J. L. English and J. C. Griess)

A. Stress Corrosion of Type 347 Stainless Steel.

During the past quarter, a laboratory-scale corrosion study was initiated to examine the susceptibility of type 347 stainless steel to stress-corrosion cracking in boiling and aerated uranyl sulfate solutions containing chloride, bromide, and iodide additions. The stress specimens used for the study were a three-point loading simple beam, constant-strain type that were stressed to values of 15,000 and 30,000 psi (37.5 and 75 % of the annealed yield strength of the alloy, respectively). A photograph of such an assembly is shown in Fig. 14. Duplicate unstressed control specimens were exposed in the same environment as the stress specimens. Prior to test, the control and the stress specimens of the stress assemblies were annealed for 1/2 hr at 1065°C (1950°F) followed by quenching in water. The heat-treated specimens were pickled and mechanically abraded on No. 80 and No. 120 grit papers. The test medium was 0.04 M UO_2SO_4 containing 0.02 M H_2SO_4 and 0.005 M CuSO_4 . The chloride concentration levels included in the study were 0, 5, 10, 25, 50, and 100 ppm; the chloride was added as potassium chloride. In addition, corrosion tests were run in a uranyl sulfate solution containing initial concentrations of 100 ppm of bromide and iodide ions, respectively. Additions of the latter two anions were also made in the form of the potassium salts. The tests were operated under reflux conditions at the boiling temperature of the solution, 100 to 101°C, with filtered air bubbled into the solution.

The specimens were removed from the test solutions after total elapsed times of 50, 100, 200, and 500 hr for weighing and for examination for indications of stress-corrosion cracking. The 500-hr results are included in Table IX. The reported corrosion rates were determined from the as-removed and scrubbed weight losses. The corrosion rates for the stress specimens were based on the entire surface area of the individual stress assemblies, approximately 140 cm². In the stress assemblies only the stressed member was polished whereas the rest of the assembly was not. Visually the unpolished areas appeared corroded to a lesser extent than the polished areas and this may account for the lower corrosion rates of the stress assemblies than for the unstressed control specimens.

Photo No. 1549-4

Fig. 14. Side View of Stress Assembly Used for Stress-Corrosion Studies with Type 347 Stainless Steel in Boiling and Aerated Uranyl Sulfate Solution. Magnification 1.2X.

TABLE IX

STRESS-CORROSION CRACKING OF TYPE 347 STAINLESS STEEL AFTER 500 HR IN BOILING
AND AERATED 0.04 M UO_2SO_4 - 0.02 M H_2SO_4 - 0.005 M CuSO_4 SOLUTION
CONTAINING CHLORIDE, BROMIDE, AND IODIDE ADDITIONS

Test No.	Additive Type	Additive Conc. (ppm)	Stress Level (psi)	Observed Corrosion Rate (mpy)	Specimen Condition
P-9	None	0	Unstressed	0.1, 0.1	Metallic luster; light generalized attack
			15,000	0.1	Similar to above; <u>no cracking</u>
			30,000	0.1	Similar to above; <u>no cracking</u>
P-10	Cl^-	5	Unstressed	0.1, 0.1	Metallic luster; light generalized attack
			15,000	0.1	Similar to above; <u>no cracking</u>
			30,000	0.1	Similar to above; <u>no cracking</u>
P-11	Cl^-	10	Unstressed	0.1, 0.1	Metallic luster; light generalized attack
			15,000	0.2	Similar to above; <u>no cracking</u>
			30,000	0.1	Similar to above; <u>no cracking</u>
P-12	Cl^-	25	Unstressed	8.1, 8.1	Metallic; random pitting; <u>cracks</u> developed near edges between 100 and 200 hr
			15,000	1.4	Metallic; some pitting; <u>no apparent cracking</u>
			30,000	4.2	Metallic; pitting; <u>2 cracks</u> developed between 100 and 200 hr; <u>3 additional cracks</u> formed between 200 and 500 hr
P-13	Cl^-	50	Unstressed	19.2, 10.1	Metallic; heavy pitting; <u>no cracking</u>
			15,000	4.5	Metallic; pitting; <u>1 crack</u> developed between 100 and 200 hr; <u>5 additional cracks</u> formed between 200 and 500 hr
			30,000	4.0	Metallic; pitting; <u>4 cracks</u> developed between 100 and 200 hr; <u>additional cracks</u> formed between 200 and 500 hr.
P-14	Cl^-	100	Unstressed	9.9, 12.5	Metallic; random pitting; generalized attack
			15,000	8.1	Similar to above; <u>no cracking</u>
			30,000	10.2	Similar to above; <u>no cracking</u>
P-15	Br^-	100	Unstressed	7.0, 3.2	Metallic with black stains; generalized attack
			15,000	1.1	Metallic; some pitting; <u>no cracking</u>
			30,000	5.6	Similar to above; <u>no cracking</u>
P-16	I^-	100	Unstressed	0.1, 0.1	Metallic; light generalized attack
			15,000	0.1	Similar to above; <u>no cracking</u>
			30,000	0.1	Similar to above; <u>no cracking</u>

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With a single exception, cracking occurred on all stress specimens exposed in boiling uranyl sulfate solution containing 25 and 50 ppm of chloride ion, respectively. The cracks were first observed after the cumulative exposure period between 100 and 200 hr. The intensity and the frequency of the cracks increased with increased exposure time up to 500 hr. Several cracks, attributed to stresses produced by the polishing of the specimens prior to test, were observed on the control specimens exposed in the solution containing 25 ppm of chloride. No cracking occurred after 500 hr on stress specimens exposed in solutions containing 0, 5, 10, and 100 ppm of chloride, nor in solutions containing either 100 ppm bromide or iodide. However, in the case of the iodide-containing solution the iodide content of the solution decreased substantially, presumably by loss to the air, and at the end of the tests, its concentration was only a few ppm. The location of the cracked areas on the specimens that exhibited cracking was confined to the area on and around the region of the maximum applied stress which was directly above the centrally-located fulcrum in the stress assembly. The origin of the cracks appeared to be on the edge surface of the stress specimens from which point the propagation of the cracks continued across the width of the specimens, normal to the direction of the applied stress. Low-power microscopic examination disclosed the cracks to be of a branched-type, a characteristic generally associated with stress-corrosion cracking in austenitic stainless steels. Figures 15 and 16 show photographs which illustrate the distribution of cracks on the stress specimens exposed in 25 and 50 ppm chloride-containing uranyl sulfate solution, respectively. Figure 17 shows the condition of the stress specimens exposed for 500 hr in the uranyl sulfate solution containing 100 ppm of chloride; no cracking was observed on these specimens.

The observed generalized corrosion rates for the stress assemblies and the control specimens exposed in boiling uranyl sulfate solution containing 5 and 10 ppm of dissolved chloride and in the solution containing, initially at least, 100 ppm of dissolved iodide ion showed no acceleration over the 500-hr exposure due to the presence of the additives. The rates were similar to those obtained with specimens exposed for a similar period in the additive-free control solution and were not in excess of 0.2 mpy. The corrosion attack was of a light generalized nature and there was no apparent change in the physical appearance of the specimens from the original condition. No pitting attack was observed.

The generalized corrosion rates for specimens exposed in the 25, 50, and 100 ppm chloride-containing uranyl sulfate solution were accelerated appreciably as a result of the additions. The most severe attack on stress assemblies, 8 to 10 mpy, occurred in the solution containing 100 ppm of chloride. As noted previously, no cracking was observed on the stress specimens after 500 hr. The corrosion rates for control specimens exposed in the above solutions were noticeably higher than the rates exhibited by the stress assemblies, reaching a maximum value of 19 mpy in the solution containing 50 ppm of chloride. The corrosion attack was primarily of a generalized type accompanied by random but severe pitting. The more severe pitting occurred on control and stress

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Photo No. 1624

Test P-12

Unclassified

Fig. 15. Distribution of Stress-Corrosion Cracks on Type 347 Stainless Steel After 500 Hours 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 ppm of Dissolved Chloride. Magnification 1.4X

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Photo No. 1625

Test P-13

Unclassified

Fig. 16. Distribution of Stress-Corrosion Cracks on Type 347 Stainless Steel After 500 Hours 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 50 ppm of Dissolved Chloride. Magnification 1.4 X

Photo No. 1626

Test P-14

Unclassified

Fig. 17. Appearance of Type 347 Stainless Steel Stress Specimens After 500 Hours 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 100 ppm of Dissolved Chloride. No Cracking Was Observed. Magnification 1.4X.

assemblies exposed in 25 and 50 ppm chloride-containing solutions; the incidence and severity of pitting attack was considerably less on the specimens exposed in the 100 ppm chloride solution.

A graph showing the effect of dissolved chloride ion concentrations on the corrosion of the duplicate unstressed type 347 stainless steel control specimens is included in Fig. 18. The observed weight losses and corrosion rates are plotted as a function of the chloride concentration for an exposure period of 500 hr. The portion of the curve exhibiting the greatest acceleration in rate of corrosion attack due to chloride ion was in the concentration range between 15 and 50 ppm; there was no further increase in the rate of corrosion attack in solutions containing 50 and 100 ppm of dissolved chloride.

A significant corrosion attack was found on the control specimens exposed in the uranyl sulfate solution with 100 ppm of bromide ion as an additive. The observed generalized corrosion rates were 3.2 and 7.0 mpy for duplicate specimens after 500 hr. The attack was generalized with no indications of pitting. The corrosion rates of the stress assemblies were 1.1 mpy at 15,000 psi and 5.6 mpy at 30,000 psi of applied stress. Some random pitting attack was noted on the specimen stressed at 15,000 psi; no cracking was found on either of the stress specimens after 500 hr of exposure.

The present series of tests will be continued. In addition, the program will be expanded to include dissolved chloride concentrations up to 500 ppm in order to examine the susceptibility of stressed type 347 stainless steel to cracking under conditions which promote severe generalized corrosion attack.

B. Corrosion-Fatigue Testing of Type 347 Stainless Steel.

One phase of a test program to examine the corrosion-fatigue behavior of type 347 stainless steel bellows in uranyl sulfate solution at elevated temperature was completed. The results to be described were obtained with five HRE-type low-pressure bellows fabricated by the Fulton-Sylphon Co. (Fulton-Sylphon Drawing Number SS 94639-28-2R). The bellows were 3-ply construction with a 0.0085-in. thickness for each ply; the outer diameter of the fabricated bellows was 1-1/8 in. The type 347 stainless steel used to form the bellows was not necessarily representative of HRP-approved material; that is, the material was not purchased specifically in accordance with presently-existent HRP specifications for the alloy. The rating of the bellows (number of cycles to failure) as designated by the Fulton-Sylphon Co. was 70,000 cycles at room temperature for a pressure differential of 1090 psi across the wall of the bellows or 70,000 cycles at 538°C (1000°F) for a pressure differential of 500 psi.

The corrosion-fatigue test apparatus consisted of an electrically heated stainless steel autoclave through the bottom of which passed the shaft of a Foxboro pneumatic operator. The individual bellows was mounted in the autoclave in such a manner that the total vertical movement, effected by the pneumatic operator, was 1/8 in. per cycle (1/16 in. in compression and 1/16 in. in expansion.) The bellows was operated on a 10 cycle/min basis until rupture occurred.

Fig. 18. The Effect of Chloride Ion Concentration on the Corrosion of Unstressed Type 347 Stainless Steel After 500 hr in Boiling and Aerated 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 Solution.

The test environment (on the outside surface of the bellows) was 0.04 M UO_2SO_4 solution with 0.02 M H_2SO_4 and 0.005 M CuSO_4 . A volume of 600 ml of solution was used for each test. The system was pressurized with 650 psi of oxygen at room temperature in order to obtain a pressure differential of 2100 to 2300 psi across the wall thickness of the bellows, 0.0255 in., at the operating temperature of approximately 285°C. The environmental conditions were selected for the purpose of procuring corrosion-fatigue information on the stainless steel bellows under conditions comparable to their usage in HRT operation.

The fatigue test was operated until failure of the bellows occurred by rupture. The number of cycles to failure was recorded by an electric timer. Control specimens of type 347 stainless steel were mounted in the autoclave along with the bellows to determine the extent of corrosion attack during the period of time required for rupture of the bellows. A summary of the number of cycles to failure and the observed corrosion rates for the control specimens for the five fatigue tests are included in Table X. Before the start of the uranyl sulfate fatigue tests, a control test was operated in distilled water at 285°C.

If one were to exclude the single value of 24,600 cycles to failure in the uranyl sulfate solution, the reproducibility of the fatigue-test results on the stainless steel bellows under the described conditions was considerably improved; the mean value of the number of cycles to failure for the three tests was 43,700 $\pm$ 2,250. This value was approximately 9000 cycles less than the 52,800 cycles to failure obtained on the single distilled water control test; no significance is attached at present to the observed difference between the uranyl sulfate and the distilled water results.

The observed corrosion rates for control specimens exposed in the uranyl sulfate solution for the above three fatigue tests ranged from 0.9 to 2.0 mpy for periods between 69.1 and 76.6 hr; the corrosion rate on specimens exposed for 41.0 hr in the test which operated for 24,600 cycles before failure occurred was 0.8 $\pm$ 0.4 mpy.

TABLE X

CORROSION-FATIGUE TESTS WITH TYPE 347 STAINLESS STEEL HRE LOW-PRESSURE BELLOWS
AT 285°C AND 2200 psi IN 0.04 M UO_2SO_4 -0.02 M H_2SO_4 -0.005 M CuSO_4 SOLUTION

Test No.	Operating Time (hr)	Number of Cycles to Failure	Observed Corrosion Rate for Control Specimens (mpy)
J42-1*	88.0	52,800	(No control specimens included)
J42-2	72.8	43,680	1.8, 1.9, 2.0
J42-3	69.1	41,460	1.7, 2.0, 2.0
J42-4	41.0	24,600	1.2, 0.7, 0.5
J42-5	76.6	45,960	0.9, 1.0, 1.1

* Control test operated with distilled water at 285°C and 2200 psi.

The type of failure generally observed on the ruptured bellows is illustrated in Fig. 19, which shows an internal view of the longitudinal section of the bellows (test J-42-2). An enlarged photograph of a cross-section through the area of rupture is included in Fig. 20. The original site of the metal fracture was not disclosed in the photographs nor in photomicrographs made of the ruptured area. Pitting attack and presumably corrosion-fatigue cracks on the center ply of the 3-ply bellows are shown in Figs. 21 and 22. Cracks may be seen originating from the base of several of the sharp, deep pits in the two photomicrographs.

Further corrosion-fatigue testing is in progress and a more complete discussion of the data will be given in the future.

V. TOROID STUDIES WITH ALUMINUM OXIDE. (G. E. Moore)

Due to the interest in aluminum oxide bearings for pumps, two toroid runs have been completed which investigated the attack of aluminum oxide by uranyl sulfate solutions at approximately 150°C and 25 fps relative velocity. Titanium toroids were used. The composition of the solutions used were (1) 0.04 M UO_2SO_4 , 0.005 M $CuSO_4$, and 0.025 M H_2SO_4 , (2) 0.17 M UO_2SO_4 , 0.03 M $CuSO_4$, and 0.04 M H_2SO_4 , and (3) distilled water. The first solution approximated that proposed for the HRT, and the second, that frequently used in in-pile testing.

The aluminum oxide specimens were fabricated from an unused but damaged aluminum oxide bearing manufactured by the Kearfott Mineral Company. Specimens of type 347 stainless steel, titanium 75A and Zircaloy-2 were also exposed with the aluminum oxide specimens in these runs.

The corrosion results are shown in Table XI. The aluminum oxide specimens showed attack rates less than 3 mpy with no detectable dimensional changes after the exposure. The two runs were of 165 and 1348-hr duration with one aluminum oxide specimen exposed to the total 1513-hr of circulation for each concentration of uranyl sulfate. The corrosion rates for titanium, stainless steel and Zircaloy-2 are in fair agreement with previously reported data²² for the lower uranium concentration.

In the 1348-hr run both solutions of uranyl sulfate contained a small amount of precipitate after circulation (2 to 3% of the total salt concentration) which consisted chiefly of uranium and iron by spectrographic analysis. The appearance of a small amount of precipitate of approximately the same composition has been observed in all toroid runs with uranyl sulfate and hence was probably not related to the fact that the system contained aluminum oxide.

TABLE XI

THE CORROSION RATE OF SEVERAL MATERIALS IN TOROIDS.
RELATIVE VELOCITY: 25 fps TEMPERATURE: 150°C.

Material	Time (hr)	0.04 m UO_2SO_4	0.17 m UO_2SO_4	Distilled Water
		0.005 m CuSO_4 0.025 m H_2SO_4	0.03 m CuSO_4 0.04 m H_2SO_4	
Al_2O_3	165	2.7	2.3	1.5
347 SS		1.5	3.4	0.5
Titanium		1.1	0.5	0.6
Zircaloy-2		3.3	0.4	0.7
<hr/>				
Al_2O_3 (exposed)*	1348	0.8	2.9	---
Al_2O_3 (new)		1.2	2.4	---
347 SS		1.4	2.3	---
Zircaloy-2		0.0	0.0	---

*The incremental average attack rate over the 1348-hr exposure. For the entire exposure period of 1513 hr, the average attack rates were: 1.0 mpy for 0.04 m UO_2SO_4 and 2.8 mpy for 0.17 m UO_2SO_4 .

Fig. 19. Internal View of Type 347 Stainless Steel Bellows Showing Area of Rupture After 43,680 Cycles in $0.04 \text{ m } \text{UO}_2\text{SO}_4$ - $0.02 \text{ m } \text{H}_2\text{SO}_4$ - $0.005 \text{ m } \text{CuSO}_4$ Solution at 285 C and 2200 psi Pressure.

Fig. 20. Enlarged Cross-Sectional View of Type 347 Stainless Steel Bellows Showing area of Rupture After 43,680 cycles in $0.04 \text{ m } \text{UO}_2\text{SO}_4$ - $0.02 \text{ m } \text{H}_2\text{SO}_4$ - $0.005 \text{ m } \text{CuSO}_4$ Solution at 285 C and 2200 psi Total Pressure. Magnification 5X.

Fig. 21. Pitting and Corrosion-Fatigue Cracks on Middle Ply in Ruptured Area of 3-Ply Type 347 Stainless Steel Bellows After 43,680 Cycles in $0.04 \text{ m UO}_2\text{SO}_4$ - $0.02 \text{ m H}_2\text{SO}_4$ - 0.005 m CuSO_4 Solution at 285°C and 2200 psi Total Pressure. Magnification 250X. Etched in Aqua Regia.

Fig. 22. Corrosion-Fatigue Cracks on Middle Ply in Ruptured Area of 3-Ply Type 347 Stainless Steel Bellows After 43,680 Cycles in $0.04 \text{ m UO}_2\text{SO}_4$ - $0.02 \text{ m H}_2\text{SO}_4$ - 0.005 m CuSO_4 Solution at 285°C and 2200 psi Total Pressure. Magnification 750X. Etched in Aqua Regia.

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