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Period Ending April 30, 1956

TO: E. G. Bohlmann

FROM: J. C. Griess, H. C. Savage, J. L. English, R. S. Greeley,
S. R. Buxton, R. M. Warner and R. M. Pierce.

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For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

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I. SUMMARY

The all-titanium loop, Loop G, has been modified to simplify operation. The small 1-1/2 in. diameter pipe which has served as a pressurizer has been replaced with a 3-1/2 in. diameter pressurizer and a by-pass line has been added to the loop. The former change makes the liquid volume of solution in the loop less critical and the latter allows corrosion specimens to be exposed at two different flow rates.

A new stainless steel loop is being constructed to circulate uranyl sulfate solutions containing beryllium sulfate. Because of the toxicity of beryllium, the shield will be of leak-tight construction with a filtered exhaust system.

Further testing with uranyl sulfate - lithium sulfate solutions has been completed. It has been shown that at 200°C a protective coating does not form on stainless steel and corrosion proceeds at a rate dependent on the uranium concentration; however, the rate is substantially lower than is found using a comparable solution without lithium sulfate. Recent tests at higher temperatures have confirmed previous results which demonstrated the beneficial action of including essentially an equimolar concentration of lithium sulfate in uranyl sulfate solutions. However, in the concentration range of 40 to 200 g of uranium per liter, no change in critical velocity was observed on the addition of lithium sulfate to uranyl sulfate solutions at 250°C.

Additional testing at 250 C in a solution containing 0.03 m UO_3 in 0.17 m Li_2CO_3 with oxygen and carbon dioxide overpressure has been completed. The results show that carbon steel and the austenitic stainless steels corrode at a rate of less than one mpy after a protective film has formed. The critical velocity on stainless steel was about 45 fps.

The 4000 gpm loop has been used to make two runs at 250°C with a solution similar to that proposed for use in the HRT. In both runs, the oxygen concentration was maintained at 50 to 100 ppm and average corrosion rates for the high-temperature system were 0.3 to 0.5 mpy. No signs of solution instability were noted.

Four 100A loops have been descaled with a descaling solution developed by the Chemical Technology Division. Only in one case was the loop completely descaled but in the other loops substantial quantities of oxide scale were dissolved. With further development, the solution should be very useful in decontaminating reactor systems.

The susceptibility of type 347 stainless steel to stress corrosion cracking was demonstrated by spraying tap water on bent pipes through which 153°C steam was passed. After approximately 10,000 hr, all pipes showed many transgranular cracks, some of which very nearly penetrated the pipe wall. Presumably the low concentration of chloride ions in the tap water was the cause of the cracking.

Elgilloy, which had shown good corrosion resistance to uranyl sulfate solutions at 300°C, has shown on continued testing a marked tendency toward stress corrosion cracking both in the solution and in the gas phases. Careful analysis of the solution showed that chlorine or chloride was not responsible for the cracking in this particular case.

A number of high-strength titanium alloys have been tested in a variety of uranyl sulfate solutions both in the stressed and annealed condition. No evidence of cracking has been observed and in all cases the attack of the metal has been nearly negligible.

II. INTRODUCTION

The following report presents the data that have been obtained by the out-of-pile solution corrosion group during the past quarter (January 31, 1956 to April 30, 1956). A summary of the results has been included in the Quarterly Progress Report of the Homogeneous Reactor Project for the period ending April 30, 1956.

In several instances, the results do not represent a completion report but merely a progress report, since a number of tests are still continuing. When viewing the results, it should be kept in mind that future testing may change the interpretation of the data.

In the following sections the results obtained in the dynamic and the static testing programs are discussed.

III. 100A LOOP PROGRAM (J. C. Griess, H. C. Savage, R. S. Greeley, R. M. Pierce, R. M. Warner and S. R. Buxton)

A. Loop Engineering

Loop G - Titanium. The all-titanium 100A dynamic corrosion test loop has accumulated approximately 8500 hr of operating time at temperatures and pressures up to 300°C and 1800 psig. The excellent corrosion resistance of titanium to solutions of uranyl sulfate has made this loop extremely valuable in corrosion tests at the higher concentrations of uranyl sulfate (up to 300 g of uranium per liter).

As originally designed and built¹, the titanium pressurizer of Loop G was of 1-1/2 in. O.D. by 1-1/8 in. I.D. pipe. Flexibility of operation of the loop was limited by the relatively low volume of the pressurizer. Very close control of the loop inventory was required to insure that the solution level was above the pressurizer heater section at all times and still allow for expansion of the solution in heating to 300°C.

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1. E. G. Bohlmann, HRP Quar.Prog.Rep., March 31, 1953, ORNL 1554, p. 47.

One pressurizer failure² in this loop was attributed to low pressurizer solution level with resultant overheating of the titanium pipe wall. Thus, sampling of the loop solution was limited and temperature and pressure control was not entirely satisfactory.

With the availability of titanium pipe in larger sizes, along with improved welding techniques, Loop G has been modified to increase the flexibility of operation in the following manner: A new titanium pressurizer has been made from 3-1/2 in. O. D. by 2-3/4 in. I. D. pipe with a volume of 6.0 liters as compared to the 1.7 liter volume of the original 1-1/2 in. O. D. pressurizer. A typical weld in the pressurizer is shown in Fig. 1. Figure 2 is a photograph of the completed pressurizer.

In addition to the larger pressurizer, a new all-titanium by-pass line with provisions for corrosion specimens has been installed in Loop G. Previously only one corrosion specimen holder could be exposed to the circulating solution, and that in the main line. Thus, pin type specimens could be exposed to only one velocity in a given run. Variations in velocity, particularly at the lower velocities (under approximately 40 fps), were obtainable only by varying the circulating pump speed. This was done by operating the pump with a variable frequency motor-generator. With the added by-pass line, pin type corrosion specimens can be exposed to two different velocities in each run.

The modifications to the titanium loop described above have been completed and satisfactory operation at temperatures up to 300°C has been demonstrated.

Loop O - Beryllium Solution Loop: One new 100A dynamic corrosion test loop, designated Loop O, has been designed and is now being fabricated. This is a loop of type 347 stainless steel similar to dynamic corrosion test loops previously described³. This loop is to be used primarily to circulate uranyl sulfate solutions containing beryllium sulfate as an additive. Due to the toxicity of beryllium, the shielding facilities of the loop will be of leak tight construction with a filtered exhaust system. All auxiliary equipment necessary for loop operation such as sampling equipment, pulsafeder addition system, fill and drain lines, will be incorporated inside the shield with provisions for remote operation. Instrumentation and control equipment are provided for operation up to 350°C.

B. General Corrosion Rates for Pin-Type Specimens.

Table I lists the corrosion rates obtained on all the pin-type specimens exposed to uranium containing solutions during the past quarter. The form of the table is the same as it has been in previous reports^{4, 5}.

2. E. G. Bohlmann, HRP Quar.Prog.Rep., April 30, 1954, ORNL-1753, p.60 and Fig. 49.
3. E. G. Bohlmann, HRP Quar.Prog.Rep., March 15, 1952, ORNL-1280, p. 40-44.
4. J. C. Griess, et al., HRP Quar.Prog.Rep., Jan. 31, 1953, ORNL-1778, p. 63; Mar. 31, 1953, ORNL-1554, p. 49; July 31, 1953, ORNL-1605, p. 74, Oct. 31, 1953, ORNL-1650, p. 45; Jan. 31, 1954, ORNL-1678, p. 45; Apr. 30, 1954, ORNL-1753, p.61; July 31, 1954, ORNL-1772, p.60; Oct. 31, 1954, ORNL-1813, p.67; Jan. 31, 1955, ORNL-1853, p. 56; Apr. 30, 1955, ORNL-1895, p.69; July 31, 1955, ORNL-1943, p.72; Oct. 31, 1955, ORNL-2004, p.82.
5. J. C. Griess, et al., Quar.Rep. of the Solution Corrosion Group, January 31, 1956, ORNL CF-56-1-167.

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Fig. 1. Titanium Pressurizer Weld

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Fig.2. Titanium Pressurizer

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The reported corrosion rates are given in terms of mils penetration per year (mpy) and the rates are average rates for that particular run. In general, at low flow, the corrosion rates of stainless steel specimens are high initially and decrease as the exposure time increases, becoming very small after one to two hundred hours. Consequently, in a short-term run, even at low flow rates, high average corrosion rates are observed; if the duration of the run were increased, the average corrosion rates would be less. Hence, for comparative purposes, runs of similar duration should be used. At flow rates in excess of the critical velocity, corrosion rates are constant and the reported rates are independent of exposure time.

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TABLE I. Corrosion Rates of Pin Type Corrosion Specimens in Uranyl Sulfate Solutions.

Run No.	UO ₂ SO ₄ Concen- tration (m)	Temp. °C	Time (hrs)	Additions	Flow Rate (fps ± 10%)	Pin Material	No. of Pins	Corrosion Rate (mpy)		
								Min.	Avg.	Max.
D-61	3.7	330- 350	52	3.7 m Li ₂ SO ₄ 1000-2000 ppm O ₂	8	309 SCb SS	4	22	24	26
						347 SS	8	28	46	77
						Ti RC-55	5	1.2	1.4	1.8
						Titanium (5% Al, 2.5% Sn)	2		5.3	
						Titanium (3% Al, 6% V)	2	8.2	8.5	8.8
						Titanium (3% Al, 5% Cr)	2	4.1	5.6	7.1
						Zircaloy-2	3	0.0	0.28	0.83
						Zirconium (crystal bar)	2		1.2	
						309 SCb SS	4	47	53	59
						347 SS	4	38	45	48
						Ti-RC-55	3	1.8	2.4	2.9
						Zircaloy-2	3	0.0	1.3	2.5
D-62	2.7	200	500	3.0 m Li ₂ SO ₄ 4000-5000 ppm O ₂ ^a	8	304L SS	4	11	13	15
						347 SS	8	12	14	16
						Ti RC-55	3		0.0	
						Titanium (5% Al, 2.5% Sn)	3	0.0	0.020	0.061
						Titanium (6% Al, 4% V)	1		0.0	
						Titanium (4% Al, 4% Mn)	2		0.0	
						Titanium (3% Al, 5% Cr)	2		0.0	
						Zircaloy-2	3		0.0	
						Zirconium (crystal bar)	2		0.0	

				31	304L SS	4	20	33	45	
					347 SS	4	27	30	34	
					Ti RC-55	2		0.0		
					Titanium (4% Al, 4% Mn)	1		0.061		
					Zircaloy 2	2		0.0		
					Zirconium (crystal bar)	1		0.0		
I-35	0.03 ^b	250	1175	0.17 m Li ₂ CO ₃ 1000-2000 ppm O ₂ 400 psi CO ₂ ^c	7	304L SS	3	0.12	0.20	0.26
						304 Sens. SS	2	0.26	0.27	0.27
						309 SCb SS	4	0.17	0.27	0.32
						316 SS	1		0.17	
						318 SS	2	0.16	0.18	0.19
						321 SS	1		0.20	
						347 SS	4	0.20	0.22	0.23
						430 SS	1		0.17	
						Carbon Steel	4	0.80	1.2	1.9
						Carpenter 20	1		0.39	
						Hastelloy C	1		0.33	
						Inconel X	2	2.7	3.0	3.2
						Titanium (5% Al, 2.5% Sn)	1		1.3	
						Worthite	1		0.30	
				20	304L SS	2	0.29	0.30	0.30	
					309 SCb SS	3	0.48	0.52	0.54	
					316 SS	1		0.32		
					347 SS	3	0.19	0.28	0.35	
					Carbon Steel	2	0.94	0.96	0.98	
					Hastelloy C	1		0.32		
					Nickel	1		4.2		
					Titanium (5% Al, 2.5% Sn)	1		0.43		
				26	302B SS	1		0.23		
					304L SS	3	0.22	0.33	0.46	
					309 SCb SS	3	0.56	0.60	0.69	
					316 SS	1		0.42		
					318 SS	1		0.81		
					321 SS	1		0.43		
					347 SS	4	0.38	0.42	0.45	
					347-347 Weld SS	1		0.33		
					410 SS	1		1.6		
					430 SS	1		1.6		
					440 C SS	2	0.52	0.55	0.58	
					Carbon Steel	4	0.98	1.0	1.1	

H-83	1.4	300	223	0.4 m Li ₂ SO ₄ 2000-4000 ppm O ₂	10	26	Miscro 4	1		0.17		
							Ti 75A	1		0.43		
							Titanium (6% Al, 4% Mn)	2	0.43	0.46	0.49	
							Zircaloy-2	1		0.0		
						42	302B SS	1		0.25		
							304L SS	3	0.26	0.52	0.61	
							309 SCb SS	3	0.87	0.98	1.1	
							316 SS	1		0.19		
							321 SS	1		0.74		
							347 SS	4	0.68	0.75	0.88	
							347-347 Weld SS	1		0.62		
							410 SS	1		0.38		
							430 SS	1		0.40		
							440C SS	2	0.61	0.75	0.88	
							Carbon Steel	4	1.0	1.1	1.3	
							Miscro 4	1		0.25		
							Ti 75A	1		0.51		
							Titanium (6% Al, 4% V)	1		0.54		
							Titanium (3% Al, 5% Cr)	1		0.57		
							Zircaloy-2	1		0.0		
							304L SS	3	52	58	63	
							309 SCb SS	1		22		
							316 SS	1		97		
							318 SS	1		28		
							321 SS	1		76		
							347 SS	4	10	41	59	
							Titanium (4% Al, 4% Mn)	1		0.55		
							Titanium RC-55	1		0.0		
							Zircaloy-2	1		0.0		
						70	304L SS	3	920	950	1000	
							309 SCb SS	1		1100		
							318 SS	1		790		
							347 SS	5	550	980	1400	
							Gold	1		3.5		
							Titanium (4% Al, 4% Mn)	1		4.6		
							Titanium RC-55	1		0.0		
							Zircaloy-2	1		0.29		

H-85	0.17 ^d	250	200	0.14 m Li ₂ SO ₄ 1000-2000 ppm O ₂	13	304L SS	3	1.4	2.7	3.9	
						316 SS	2	4.5	4.7	4.8	
						318 SS	2	2.4	4.1	5.8	
						321 SS	1		4.8		
						347 SS	4	1.7	3.6	4.3	
						Titanium RC-55	1		0.15		
						Zirconium (crystal bar)	1		0.0		
						68	304L SS	4	13	110	250
						318 SS	2	100	100	100	
						347 SS	5	71	83	100	
						Titanium (4% Al, 4% Mn)	1		86		
						Titanium RC-55	1		0.61		
						Zirconium (crystal bar)	1		1.5		
H-86	0.17	250	200	0.14 m Li ₂ SO ₄ 1000-2000 ppm O ₂	13	304L SS	3	1.6	6.3	8.8	
						318 SS	2	2.4	11	19	
						321 SS	1		13		
						347 SS (cast)	2	12	12	12	
						347 SS	4	10	12	17	
						Titanium RC-55	1		0.0		
						Zirconium (crystal bar)	1		0.0		
						68	304L SS	4	45	47	48
						316 SS	2	39	43	47	
						347 SS (cast)	2	42	47	52	
						347 SS	4	45	48	51	
						Titanium RC-55	1		0.61		
						Zirconium (crystal bar)	1		0.97		
N-15	0.0	250 for 200 hrs 300 for 275 hrs	475	0.002 m H ₂ SO ₄ 0.0005 m CuSO ₄ 1000-2000 ppm O ₂	18	304L SS	3	0.18	0.20	0.21	
						309SCb SS	3	0.21	0.22	0.25	
						347 SS	6	0.14	0.18	0.21	
						Ti RC-55	1		0.0		
						Zircaloy-2	1		0.0		
						75	304L SS	3	0.21	0.24	0.25
						309 SCb SS	3	0.29	0.32	0.36	
						347 SS	5	0.25	0.28	0.32	
						Ti RC-55	2	0.07	0.10	0.13	
						Zircaloy-2	1		0.0		

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N-16	0.4	300	200	0.4 m Li ₂ SO ₄ 1000-2000 ppm O ₂	18	304L SS	3	1.5	1.5	1.5
						318 SS	1		36	
						321 SS	2	12	13	14
						347 SS	6	5.1	10	14
						Ti RC-55	1		0.76	
						Zircaloy-2	1		0.0	
						75 304L SS	2	100	110	110
						318SS	1		290	
						321 SS	1		1.8	
						347 SS	4	87	95	100
						Ti RC-55	2	0.76	5.0	9.2
						Ti (4% Al, 4% Mn)	2	3.8	4.1	4.3
						Zircaloy-2	1		0.0	
N-17	0.4	250	176	0.4 m Li ₂ SO ₄ 1000-2000 ppm O ₂	15	304L SS	3	7.2	22	50
						318 SS	1		17	
						321 SS	2	46	49	52
						347 SS	6	48	58	70
						Ti RC-55	1		0.17	
						Zirconium (crystal bar)	1		0.2	
						63 304L SS	3	70	110	190
						318 SS	2	66	71	76
						321 SS	2	49	150	250
						347 SS	4	62	120	140
						Ti RC-55	1		0.35	
						Ti (4% Al, 4% Mn)	1		1.6	
						Zircaloy-2	1		0.30	
N-18	0.9	250	200	0.9 m Li ₂ SO ₄ 1000-2000 ppm O ₂	16	304L SS	3	16	59	81
						318 SS	1		96	
						321 SS	2	33	59	84
						347 SS	6	16	74	99
						Ti RC-55	1		0.31	
						Zirconium (crystal bar)	1		0.11	
						65 304L SS	3	110	127	150
						318 SS	2	150	160	160
						347 SS	4	94	130	150
						Ti RC-55	1		0.15	
						Ti (4% Al, 4% Mn)	1		0.92	
						Zircaloy-2	1		0.0	

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N-19	0.9	200	200	0.8 m Li ₂ SO ₄ 1000-2000 ppm O ₂	15	304L SS	3	14	15	16
						321 SS	2	13	14	14
						347 SS	6	13	16	17
						Niobium	1		32	
						Ti RC-55	1		0.0	
						Zircaloy (crystal bar)	1		0.11	
					61	304L SS	3	14	21	25
						318 SS	1		13	
						321 SS	2	13	14	14
						347 SS	4	14	17	18
						Niobium	1		37	
						Ti RC-55	1		0.30	
						Ti (4% Al, 4% Mn)	1		0.0	
						Zircaloy-2	1		0.11	
N-20	0.4	200	200	0.4 m Li ₂ SO ₄ 1000-2000 ppm O ₂	15	304L SS	3	6.5	7.0	7.5
						321 SS	2	6.5	7.1	7.6
						347 SS	6	6.6	7.2	8.0
						Niobium	1		23	
						Ti RC-55	1		0.15	
						Zirconium (crystal bar)	1		0.0	
					61	304L SS	3	8.2	12	19
						318 SS	1		6.9	
						321 SS	2	8.6	14	19
						347 SS	4	7.8	8.8	10
						Niobium	1		30	
						Ti RC-55	1		0.0	
						Ti (4% Al, 4% Mn)	1		0.15	
						Zircaloy-2	1		0.32	
4000-4	--	250	46	H ₂ O + 50 ppm O ₂	20	304 SS	2	0.26	0.30	0.34
						316 SS	2	0.41	0.44	0.47
	0.003	250	120	0.003 m H ₂ SO ₄ 50-100 ppm O ₂		322W hard SS	2	0.34	0.35	0.36
						347 SS	3	0.23	0.25	0.28
	0.009	250	100	0.003 m H ₂ SO ₄ 50-100 ppm O ₂		347 sand cast SS	2		0.26	
						Stellite 1	1		38	
	0.017	250	334	0.005 m CuSO ₄ 0.006 m H ₂ SO ₄ 50-100 ppm O ₂		Stellite 6	1		130	
						Zircaloy-2	1		0.0	

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4000-5	--	250	85	H ₂ O	20	304 SS	2	1.6	1.9	2.1
				50-100 ppm O ₂		304L SS	2	1.7	1.8	1.9
	0.03	250	144	0.008 m H ₂ SO ₄		309 SCb	1		4.5	
				0.007 m CuSO ₄		318 SS	2	13	14	15
				50-100 ppm O ₂		347 SS	3	3.7	4.0	4.5
	0.04	250	167	0.010 m H ₂ SO ₄		Ti RC-55	1		0.07	
				0.006 m CuSO ₄		Zirconium (crystal				
				50-100 ppm O ₂		bar)	1		0.0	
	0.04	250	110	0.015 m H ₂ SO ₄						
				0.006 m CuSO ₄						
				50-100 ppm O ₂						

- Footnotes to Table -

- During the run, the circulating stream contained entrapped oxygen bubbles. This is the reason for the abnormally high oxygen concentration.
- The solution was prepared by dissolving 0.03 moles of UO₃ per liter of 0.17 m Li₂CO₃ solution saturated with CO₂.
- The loop was charged with 400 psi CO₂ at room temperature to give about 700 psi partial pressure of CO₂ at 250°C. This was equivalent to roughly 12 gm CO₂ per liter in solution. After 1000 hr, more CO₂ was added, bringing the partial pressure to 900 psi CO₂.
- Prior to this run, the loop was defilmed and then pretreated with a dilute nitric acid solution to which chromic acid had been added. Some of the chromium was precipitated during the pretreatment. In Run H-85, the uranyl sulfate solution oxidized a large amount of the precipitated chromium to the hexavalent state. This Cr(VI) inhibited corrosion to a certain extent at low flow rates.

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C. Corrosion Testing with Uranyl Sulfate-Lithium Sulfate Solutions.

In the last quarterly report⁶ a run was reported in which a solution containing 3.8 m UO_2SO_4 and 3.8 m Li_2SO_4 was circulated at 350°C. During the past quarter, a similar run, D-61, was carried out in which an attempt was made to circulate a 3.7 m UO_2SO_4 - 3.7 m Li_2SO_4 at 360°C or higher. However, at 360°C or slightly higher, the concentration of salts became so high (~ 5.7 m UO_2SO_4) due to loss of water to the vapor that the solution actually crystallized in the cool rotor region of the pump. The vapor pressure of the solution was in accord with the more recent data which showed rough agreement with Raoult's Law⁷.

Corrosion rates for pin-type specimens are shown in Table I. The rates for stainless steel were higher than observed in the run at 350°C and this was probably due to the several thermal cycles between 300 and 360°C to which the loop was subjected. Apparently during a thermal cycle, the stresses developed in the protective oxide coating caused cracking and some removal of oxide. At the areas where the metal was not protected, corrosion proceeded until a new protective film developed. Thus, the higher corrosion rates observed in Run D-61 were not unexpected. The type 347 stainless steel coupons showed the critical velocity to be about 60 fps.

In a previous report⁸, the corrosion results obtained with several rather concentrated uranyl sulfate-lithium sulfate solutions at 200°C were presented. Additional testing with equimolar uranyl sulfate-lithium sulfate solutions at 200°C has been completed this quarter. The results obtained with pin-type specimens are reported in Table I, run N-20 for 0.4 m uranium, run N-19 for 0.8 m , and run D-62 for 2.7 m . At all concentrations and at all flow rates the specimens were covered with a rather loosely adherent coating and showed no velocity effect. At all concentrations the corrosion rate of the austenitic stainless steels was fairly constant with time and approximately proportional to the uranium concentration. Figure 3 shows the corrosion rate of type 347 stainless steel as a function of uranium concentration. The value at 0.8 m is out of line, possibly because the lithium sulfate concentration was somewhat lower than equimolar.

The aqueous uranyl sulfate-lithium sulfate system at the equimolar level has also been investigated at the 0.17 (H-85 and H-86), 0.4 (N-16 and N-17) and the 0.9 m (N-18) uranium level in the temperature range of 250 to 300°C. The results obtained with pin-type specimens are shown in Table I. Generally, the results are similar to those previously reported.

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6. A previous run at 350°C has been reported. See: J. C. Griess, et al., "HRP Quarterly Progress Report, January 31, 1956", ORNL-2057, p. 85.
  7. Ibid., p. 86.
  8. J. C. Griess, et al., "HRP Quarterly Progress Report, October 31, 1955", ORNL-2004, pp. 84-85 and 90-91.

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Fig. 3. Corrosion Rates of Type 347 Stainless Steel at 200°C in Equimolal UO_2SO_4 - Li_2SO_4 Solutions (15-60 fps)

That is, the presence of lithium sulfate substantially reduced the corrosion of the austenitic stainless steels at all flow rates from that observed in similar runs not containing the lithium sulfate. At flow rates less than the critical velocity weight losses were substantially lower. After a short time, a protective film formed and subsequent corrosion rates were low. The presence of lithium sulfate had little, if any, effect on the critical velocity but the high-velocity corrosion rates were reduced by the lithium sulfate. Table II shows the results obtained and compares them with similar runs not containing lithium sulfate. Run H-85, not included in Table II, was essentially a duplicate of run H-86 but the corrosion was substantially less than in run H-86. The abnormally low corrosion during run H-85 was a result of the relatively high chromium VI concentration in this run. Immediately preceding run H-85, the loop was pretreated with a chromium-containing solution and some of the chromium was deposited on the loop walls. The solution circulated during run H-85 oxidized much of the chromium deposit to the soluble hexavalent state, which partially inhibited corrosion. The chromium content of the solution in Run H-86 was normal.

TABLE II

Corrosion of Type 347 Stainless Steel in
Uranyl Sulfate Solutions With and Without
Equimolar Lithium Sulfate

Uranium Concen- tration g/l	Temp. °C	With Li ₂ SO ₄			Without Li ₂ SO ₄		
		Critical Velocity fps	Wt. Loss at 15 fps mg/cm ² (a)	Corr. Rate at 70 fps mpy	Critical Velocity fps	Wt. Loss at 15 fps mg/cm ² (a)	Corr. Rate at 70 fps mpy
40	250	20-30	1-3	40	20-30	9	240
100	250	10-20	23	70	10-20	33	380
	300	30-40	4	230	(b)	(b)	(b)
200	250	10-20	27	130	10-20	70	660

(a) At this flow rate after the initial weight loss a protective film forms and the corrosion rate decreases to a very low value.

(b) No run made since solution would form two liquid phases.

The last quarterly report⁹ included descriptions of runs in which uranyl sulfate solutions containing 300 g of uranium per liter with both more and less than equimolar concentrations of lithium sulfate were circulated at 300°C. Run H-83 represents an additional run at 250°C with the same concentration of uranyl sulfate and containing 0.4 m Li₂SO₄. Weight losses at low flow rates were relatively low and since the samples were filmed over, the weight losses probably would not have increased significantly with time. However, the critical velocity was below 15 fps and above that flow rate corrosion was severe.

9. J. C. Griess, et al., Quarterly Report of the Solution Corrosion Group, January 31, 1956, ORNL CF-56-1-167, pp. 7-8.

Runs with uranyl sulfate solutions containing 300 g of uranium per liter have now been made with 0.4, 0.7, 1.4 (approximately equimolar) and 2.0 m Li_2SO_4 at 300°C. In all cases the systems were phase stable at 300°C. With 0.4 and 0.7 m Li_2SO_4 the critical velocity was low, 10 to 15 fps; with 1.4 and 2.0 m Li_2SO_4 the critical velocity was 25 to 30 fps in both cases. In excess of the critical velocity, the corrosion rate was constant and high, being lower the higher the lithium sulfate concentration.

Table I lists several titanium and zirconium alloys together with gold and niobium pins exposed in the runs discussed above. In general, only the niobium was attacked. As can be seen in runs N-19 and N-20, the niobium pins corroded at a rate roughly double that of type 347 stainless steel. The niobium pins formed no protective film even at the lowest flow rate. A gold pin in H-83 lost eleven milligrams probably due to abrasion by particles of oxide suspended in the circulating stream. Crystal bar zirconium, Zircaloy-2, and titanium RC-55 showed weight losses of only a few tenths of a milligram per specimen (2.5 cm^2) at all flow rates in nearly all runs. The alloys of titanium with aluminum and tin, aluminum and chromium, aluminum and manganese, and aluminum and vanadium showed low, though perceptible, corrosion rates (1 to 4 mpy).

D. Corrosion Testing in the $\text{Li}_2\text{O-UO}_3 - \text{CO}_2 - \text{H}_2\text{O}$ System.

A solution composed of 0.03 m UO_3 in 0.17 m Li_2CO_3 with partial pressures of 600 psi carbon dioxide and 400 psi oxygen was circulated at 250°C for 1175 hr in run I-35. The solution was not entirely stable, due presumably to a decrease in the carbon dioxide partial pressure. The pressure decrease was unexplained, but when the total pressure had dropped from the initial 1600 psi to 1350 psi, the uranium concentration suddenly dropped from the starting concentration to 0.02 m. The lithium carbonate concentration possibly decreased slightly also. The loop was shut down and more carbon dioxide was added so that the total pressure on reaching 250°C was 1900 psi. The uranium concentration immediately increased to 0.03 m and remained at that level for the duration of the run. Table I lists the pin data for the variety of alloys exposed. In comparison with two shorter runs (200 and 537 hr)¹⁰, it was observed that the carbon steels and the austenitic stainless steels essentially stopped corroding after the first 200-hr run. The carbon steels lost about four times as much weight as the austenitic stainless steels during the initial period of film formation.

Titanium 75A and titanium alloyed with aluminum and chromium, aluminum and vanadium, or aluminum and tin showed low corrosion rates (< 1 mpy). Zircaloy-2 pins lost no measurable weight. The type 347 stainless steel coupons showed a critical velocity of 40 to 50 fps; above the critical velocity the attack was localized at machining marks, as is shown in Fig. 4.

10. J. C. Griess, et al., HRP Quar. Prog. Rep., January 31, 1956, ORNL-2057, p. 85.

Fig. 4. A photograph of a portion of the surface of a type 347 stainless steel coupon exposed to the $\text{UO}_3\text{-Li}_2\text{O-CO}_2\text{-H}_2\text{O}$ system at 250°C at a flow rate of approximately 60 fps. (10X Magnification)

E. Corrosion Results from the 4000 gpm Loop.

The 4000 gpm loop, after installation and check-out by the Engineering Development Section, has been turned over to the Corrosion Section for routine corrosion testing. Three clean-up runs were made without samples, 4000-1, 2, and 3; and two runs with samples and dilute uranyl sulfate solution were completed, 4000-4 and 5. Table I gives the pin data obtained. Table III gives the conditions of each run. Run 4000-4 was planned as a simulation of the start-up procedure for the HRT¹¹ but due to uncertainties in the amount of hold-up in several components, the desired concentrations were not attained. A component failure forced termination of the run at a concentration level of $0.02 \text{ m UO}_2\text{SO}_4$ (see Table III). Hence, run 4000-5 was a continuation with $0.02 \text{ m UO}_2\text{SO}_4$ for 100 hr followed by 200 hr with $0.04 \text{ m UO}_2\text{SO}_4$ containing $0.015 \text{ m H}_2\text{SO}_4$ and 0.005 m CuSO_4 . Again the concentrations were not attained and component failure forced shutdown.

One purpose of these runs was to determine if there were a "scale-up" factor in the extent of corrosion in a large loop; that is, whether the small surface area - volume ratio would affect the amount of weight loss of low velocity samples or the corrosion rate of high velocity samples. No such factor was found. All samples except the Stellite pins in 4000-4 and the type 347 stainless steel coupons above the critical velocity in 4000-5 were covered with a uniform oxide film and had lost no more weight than normally observed in dilute uranyl sulfate at 250°C . The Stellite pins were black and severely corroded as was expected. The critical velocity of type 347 stainless steel coupons was 45 to 50 fps in 4000-4 and 20 to 30 fps in 4000-5 (higher acidity).

Oxygen concentration was maintained between 50 and 100 ppm throughout both runs. No evidence of solution instability due to low oxygen was noticed. Generalized corrosion rates of the loop as determined from nickel concentration were 0.5 and 0.3 mpy in 4000-4 and 4000-5, respectively.

The cobalt concentration increased in solution in run 4000-4 to 50 ppm and then levelled off. In run 4000-5 it increased steadily, reaching 70 ppm at the end of the run. This cobalt came from the Stellite wear rings and represents the dissolution of nearly 200 grams of Stellite. The Stellite surface exposed to hot solution is about 2 ft^2 , so this represents about 5 mils penetration during the above runs, assuming uniform attack.

11. J. C. Griess, et al., HRP Quar. Prog. Rep., October 31, 1955, ORNL-2004, p.80.

TABLE III
CONDITIONS OF 4000 GPM LOOP RUNS

Run No.	Time (hr)	Conditions
4000-1	4.5	3% trisodium phosphate, $\sim 100^{\circ}\text{C}$
	6	3% nitric acid, 115°C
	180	$\text{H}_2\text{O} + \sim 100 \text{ ppm } \text{O}_2$, 250°C
4000-2	56	$0.003 \text{ m } \text{UO}_2\text{SO}_4$ (0.8 gm U/l) + $0.002 \text{ m } \text{H}_2\text{SO}_4$ + $0.005 \text{ m } \text{CuSO}_4$, 240°C , $\sim 100 \text{ ppm } \text{O}_2$
	4.5	3% trisodium phosphate, 135°C .
	3.2	3% nitric acid, 125°C .
4000-3	48	$\text{H}_2\text{O} + \sim 100 \text{ ppm } \text{O}_2$, 250°C then intermittent rinses with 3% trisodium phosphate, 1% nitric acid, and water at room temperature.
4000-4	46	$\text{H}_2\text{O} + \sim 50 \text{ ppm } \text{O}_2$, 250°C
	120	$0.003 \text{ m } \text{UO}_2\text{SO}_4$ (0.8 gm U/l) + $0.003 \text{ m } \text{H}_2\text{SO}_4$ + $\sim 50 \text{ ppm } \text{O}_2$, 250°C
	100	$0.009 \text{ m } \text{UO}_2\text{SO}_4$ (2.2 gm U/l) + $0.003 \text{ m } \text{H}_2\text{SO}_4$ + $\sim 50 \text{ ppm } \text{O}_2$, 250°C
	334	$0.017 \text{ m } \text{UO}_2\text{SO}_4$ (4 gm U/l) + $0.006 \text{ m } \text{H}_2\text{SO}_4$ + $0.005 \text{ m } \text{CuSO}_4$ + $\sim 50 \text{ ppm } \text{O}_2$, 250°C
4000-5	85	$\text{H}_2\text{O} + \sim 50 \text{ ppm } \text{O}_2$, 250°C
	144	$0.03 \text{ m } \text{UO}_2\text{SO}_4$ (7 gm U/l) + $0.008 \text{ m } \text{H}_2\text{SO}_4$, + 460 ppm Cu as CuSO_4 , 50 to 100 ppm O_2 , 250°C
	167	$0.04 \text{ m } \text{UO}_2\text{SO}_4$ (9 gm U/l) + $0.010 \text{ m } \text{H}_2\text{SO}_4$ + 400 ppm Cu as CuSO_4 , 50 to 100 ppm O_2 , 250°C
	110	$0.04 \text{ m } \text{UO}_2\text{SO}_4$ (9 gm U/l) + $0.015 \text{ m } \text{H}_2\text{SO}_4$ + 400 ppm Cu as CuSO_4 , 50 to 100 ppm O_2 , 250°C

F. Stability of Very Dilute Copper Sulfate-Sulfuric Acid Solution.

Since the D₂O blanket of the HRT might need a small amount of an internal recombination catalyst, it was of interest to determine if a very dilute copper sulfate solution would be stable with regard to hydrolytic precipitation. Hence, 30 ppm copper as copper sulfate in 0.002 M sulfuric acid was circulated for 200 hr at 250°C and for 275 hr at 300°C. No loss of copper from solution occurred. Corrosion rates were very low, as can be seen for run N-15 in Table I. Only an insignificant velocity effect was observed over the range 10 to 90 fps.

G. Effect of Grain Size on the Critical Velocity of Stainless Steel.

A small difference in critical velocity has long been noticed between types 304L and 347 stainless steel. Chemical differences are slight; type 304L has 0.03% maximum carbon, whereas type 347 has 0.08% maximum carbon stabilized with about 1% niobium and/or tantalum. However, the grain sizes of the two alloys are usually quite different; type 304L generally has a grain size (ASTM scale) of 2 to 5, while type 347 has a grain size of 7 to 8 or even smaller. Therefore, it was of interest to compare the corrosion resistance of both types 347 and 304L in a variety of different grain sizes at flow rates in the critical velocity region.

The specimens with different grain sizes were prepared by the HRP Metallurgy Section. Table IV lists the heat treatments used to develop the specific grain sizes after the material had been cold reduced. Some specimens were then electropolished and some were buffed with 320 grit paper to get a uniform finish. Duplicate pins of each type and grain size were exposed to 0.17 M uranyl sulfate at 250°C at various flow rates in the critical velocity region for 200 hr.

TABLE IV

Heat Treatments Used in Preparation of Grain Size Specimens

Type 304L Stainless Steel (Cold Reduced 71%)			Type 347 Stainless Steel (Cold Reduced 84%)		
Temp. °C	Time (hr)	Grain Size ASTM	Temp. °C	Time (hr)	Grain Size ASTM
1950	3 min	8 or less	1950	10	7-8
1950	4 min	6	1950	32	6-7
1950	13 min	4	2200	2-1/2	
1950	98 hr	2	then		
			1950	1/2	3-4
			2300	26	
			then		
			1950	1/2	2-3

All specimens were pickled following quench to remove oxide scale.

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The results for type 304L specimens of different grain sizes are shown in Table V. Apparent critical velocities were taken to be the flow rate at which the weight loss increased sharply. Values are approximate but show a definite trend of increasing critical velocity with decreasing grain size (increasing grain size number). Also, a definite trend of decreasing weight loss with decreasing grain size is apparent. This reflects, too, the increase in critical velocity, since a material with a higher critical velocity forms its protective scale sooner and hence shows a lower weight loss. No significant difference between electropolished and buffed surfaces was evident. Correlation between control pins (pins machined from stock with grain size 2 as received from the mill) and grain size 2 pins prepared by recrystallizing the cold worked material was good. Correlation between normal type 347 pins (grain size 7 to 8) with grain size 6 and 8 pins of type 304L was also good.

The type 347 "grain size" specimens were very erratic and showed much lower critical velocities than control pins, even in the same grain size. A small trend in the direction of decreasing weight loss with decreasing grain size was determined by taking the over-all average for each grain size. The results are given in Table VI.

To determine the reason for the discrepancy in critical velocity between the type 347 control pins (machined from steel as received from the mill) and the grain size 8 pins, more type 347 samples were heat treated as indicated in Table IV, but without prior cold work. Photomicrographs indicated little change in grain size as a result of the heat treatments. These samples and control pins from the same stock were exposed to $0.17 \text{ m } \text{UO}_2\text{SO}_4$ at 250°C . Results are shown in Table VII.

As can be seen, the heat treatments alone had a marked effect on corrosion resistance. Evidently, annealing the pins for one hour or more at 1950°F was beneficial, whereas heat treatments at higher temperatures were detrimental. Metallographic examination showed that the higher temperature treatments caused dissolution of niobium carbides followed by reprecipitation of large carbide particles upon cooling to 1950°F . The presence of the large carbide particles in the steel was deleterious to corrosion resistance. The results of the above experiments indicate that at least in the case of the 347 stainless steel, the distribution of carbides is at least as important as the grain size in determining the critical velocity.

It should be noted that the effects of grain size and/or heat treatment are observable only at flow rates near the critical velocity. At low flow rates all specimens develop protective films and weight losses are similar; at sufficiently high flow rates all specimens remain free of film and corrode at about the same rate. The reason why type 304L stainless steel with a small grain size is able to retain its film better than the same alloy with a larger grain size is not known. It is possible that the oxide developed on the steel is actually keyed to the surface at grain boundaries and if this is the case the smaller the grain size, the better the adherence of the oxide.

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TABLE V

AVERAGE WEIGHT LOSSES FOR TYPE 304L
STAINLESS STEEL GRAIN SIZE PINS
IN 0.17 M UO_2SO_4 AT 250°C

Flow Rate (fps)	Surface Treatment	Weight Loss, mg/cm ²					Control*** (GS 7-8)
		Control** (GS 2)	Grain Size 2	Grain Size 4	Grain Size 6	Grain Size 8	
9	Buffed	9.4	9.3	8.8	8.2	7.2	9.6
15	Buffed	46	44	24	14	11	20
16	Electro- polished	60	53	43	16	10	18
17*	Electro- polished	40	32	13	17	12	---
17	Electro- polished	57	52	35	14	11	24
19	Buffed	49	47	40	18	11	18
22	Electro- polished	40	44	24	28	21	18
26*	Buffed	100	110	88	57	35	36
Over-all Average		50	49	35	22	15	21
Apparent Critical Velocity (fps)							
		<15	<15	~15	~19	~22	~24

* 174 hour run. All others were 200 hours.

** Type 304L SS pins from same stock - as machined

*** Type 347 SS pins - as machined

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TABLE VI
 AVERAGE WEIGHT LOSSES FOR TYPE 347
 STAINLESS STEEL GRAIN SIZE PINS
 IN 0.17 M UO_2SO_4 AT 250°C

Flow Rate (fps)	Surface Treatment	Weight Loss, mg/cm ²				Control** (GS 8)
		Grain Size 2	Grain Size 4	Grain Size 6	Grain Size 8	
9	Buffed	19	12	7.4	8.3	9.6
15	Buffed	58	54	38	18	20
16	Electropolished	56	59	55	53	18
17*	Electropolished	34	54	17	37	---
17	Electropolished	56	59	55	53	24
19	Buffed	55	54	49	16	18
22*	Electropolished	40	47	37	47	18
26	Buffed	110	110	100	85	36
Over-all Average		57	54	51	37	21

Apparent Critical Velocity (fps)

~9   <15   <15   ~15   ~24

* 174 hour run. All others were 200 hours.

** Control pins were from a different stock of 347 SS. They were used "as-machined".

TABLE VII

AVERAGE WEIGHT LOSSES FOR TYPE 347
STAINLESS STEEL HEAT TREATED PINS
IN 0.17 $\text{m UO}_2\text{SO}_4$ AT 250°C FOR 200 HR AT 15 FPS

<u>Heat Treatment</u>	<u>Time (hr)</u>		<u>Average Weight Loss (mg/cm²)</u>
1950°F	1		7.5
1950°F	10	(Grain Size 8 "treatment")	7.6
1950°F	32	(Grain Size 6 "treatment")	5.7
2200°F 1950°F	2-1/2) 1/2)	(Grain Size 4 "treatment")	{32
2300°F 1950°F	32) 1/2)	(Grain Size 2 "treatment")	{39
Control Pins (as-machined)			21

All pins were from the same stock.

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H. Loop Descaling Experiments.

When a stainless steel system is exposed to a uranyl sulfate solution at high temperatures, a relatively thick scale of corrosion products forms on the surface of the stainless steel and protects the metal, at least partially, from further attack. The scale has been shown to be composed of chromic and ferric oxides in a very unreactive state. If the solution in the system contains low concentrations of fission products and/or plutonium, some of these elements are trapped in the oxide crystals and are not removed by reagents which would ordinarily dissolve them. Hence, in order to decontaminate the surface of the steel, it is necessary to remove the oxide scale.

Previous attempts¹² at descaling stainless steel have depended on using reagents which did not dissolve the oxide scale but dissolved the stainless steel at the oxide-metal interface, thereby allowing the oxide to slough off. Since the scale was not dissolved, the flakes of oxide had to be physically removed and in a complex piping system the removal was not an easy operation.

Recently, the Chemical Technology Division developed a method of descaling stainless steel by actually dissolving the scale¹³. The method involves reducing the ferric oxide, the major component of the scale, to the ferrous state which is readily soluble in dilute acid solutions. The most promising reducing reagent has been found to be chromous sulfate.

In cooperation with the Chemical Technology Division, four 100A loops (Loops E, H, J and N) have been descaled with chromous sulfate solutions. In each case, a solution containing about 0.3 M CrSO_4 and 0.5 M H_2SO_4 was circulated in the loop at 80 to 85 C using helium pressurization. Corrosion specimens were included in all loops except Loop N. During each run aliquots of the solution were taken to determine the progress of the descaling process. Table IX shows the efficiency observed in each run and the actual amounts of scale dissolved. Also shown are the average penetrations of the loop surface based on nickel analyses. The efficiency was determined from the analytical data since one equivalent of chromous sulfate will reduce one equivalent of ferric oxide to the soluble ferrous state. The remainder of the chromous sulfate was consumed in producing hydrogen by the reduction of hydrogen ions. It is evident that about half of the chromous sulfate was consumed in the latter process.

In descaling E and H loops one charge of the chromous sulfate was circulated. In each case, descaling was extensive but not complete. When the solution was drained from the loop there were some solids in the solution and certain randomly located areas of the loop still retained some scale. Analytical results in each case showed that the chromous sulfate was completely consumed after less than two hours; after the chromous ions had been oxidized, practically no further dissolution of the oxide was accomplished.

12. J. C. Griess, et al., HRP Quar. Prog. Rep., October 31, 1953, ORNL-1658, p. 63.

13. D. E. Ferguson, et al., HRP Quar. Prog. Rep., January 31, 1956, ORNL-2057, p.128.

TABLE IX
RESULTS OF DEFILMING RUNS

<u>Run No.</u>	<u>Amount of Oxide Scale Dissolved (gms Fe_2O_3)</u>	<u>Average Corrosive Penetration of Loop (mils)</u>	<u>Efficiency (%)</u>
E-57	250	0.06	56
H-84	220	0.21	63
J-77	94	0.31	45
N-21	185	0.03	25

Instead of using only one charge of chromous sulfate solution, two different charges were used to descale Loops J and N. In each loop, the first charge was circulated for about three hours, then drained from the loop and the new charge was added and circulated for approximately three hours. The descaling of Loop N was essentially complete, possibly because the loop had not been used extensively and there was less oxide to dissolve than in the other loops. This fact accounts for the low efficiency given in Table IX.

The descaling of Loop J was very incomplete. The reason for the ineffective descaling was shown to be attributable to low concentration of chromous sulfate in both solutions. Either the chromium alum used to prepare the chromous sulfate solution was not completely reduced, or after preparation the chromous sulfate was oxidized, perhaps by exposure to air. In either event, the defilming solutions contained only low concentrations of chromous ions.

Table IX shows the total penetration observed on the loop surfaces. The corrosion specimens exposed in the loops showed very high corrosion rates but since the exposure times were short, total penetrations were slight. On the austenitic stainless steels, corrosion rates as high as 1000 mpy were observed but even this high rate corresponded to total penetrations of only a few tenths of a mil. Titanium and zirconium showed very low corrosion rates except at high velocities where the extent of penetration was comparable to that of the stainless steel. It appeared that in the case of all specimens the corrosion rates were accelerated by the abrasive action of the solid particles of oxide in the circulating stream.

The chromous sulfate descaling technique certainly represents an improvement over any methods previously used in descaling the 100A loops. However, because of the ability of chromous ions to react with hydrogen ions, the efficiency of the chromous sulfate is only about 50% and to descale a large system relatively large amounts of chromous sulfate

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would be necessary. Also, the corrosivity of the solution is high but this is not a serious disadvantage since the runs need be of only short duration. The first mentioned disadvantage may be partially overcome by including an active metal such as aluminum or zinc in a by-pass line of the system and in this manner continually keeping most of the chromium in the divalent state.

One attempt was made to descale a loop using sulphur dioxide in 0.5 M H_2SO_4 as the reducing agent. The results were poor in that only about 35 grams of oxide dissolved in three hours and corrosion of the stainless steel was severe, much more so than was observed in the chromous sulfate solutions. Hence, it was concluded that acidified solutions of sulphur dioxide were not practical for defilming stainless steel.

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

A. Stress-Corrosion Cracking of Type 347 Stainless Steel.

A pipe U-bend spray test that was designed to simulate cooling conditions under which two service failures by cracking were reported for dynamic-corrosion test Loop C was completed after 10,790 hr of operation¹⁴. The construction and operation of the pipe U-bend spray test were reported previously¹⁵. The test apparatus consisted of six U-bends of type 347 stainless steel welded pipe, four of which were fabricated from 1/2-in sch 40 pipe and two bends that were fabricated from 3/8-in sch 40 pipe. The U-bends were attached to common steam and condensate headers. Steam pressure at 60 psig (153°C) was maintained within the pipes which were externally-cooled by a continuous spray of filtered tap water. At approximately 500-hr intervals, the flow of cooling water was stopped and the U-bends were visually inspected for steam leaks. No such leaks, indicative of possible cracking of the pipes, were detected during the 10,790-hr test.

Considerable quantities of scale accumulated on the water-cooled surfaces of the U-bends during operation of the test. The major constituents of the scale in weight per cent were as follows: magnesium 3.7, calcium 33.7, and sulfate 2.15. In addition, a chloride content of 0.076 weight per cent (760 ppm) was detected. Probably the remainder of the scale was carbonate and water.

The U-bends were cleaned of deposited scale by immersion in warm 30 per cent HNO_3 and were then treated by the Zyglo process (Magnaflux Corporation) to disclose the presence or the absence of cracks. Numerous cracks were found on all of the U-bends and the cracks were randomly-distributed over the entire surface of each bend.

14. H. C. Savage and F. J. Walter, HRP Quar. Prog. Rep., April 30, 1954, ORNL-1753, p. 59-61.
15. E. L. Compere and J. L. English, HRP Quar. Prog. Rep., July 31, 1954, ORNL-1772, p. 94.

A metallographic examination was made on several of the cracked areas found on one of the 3/8-in stainless steel U-bends (No.5). Photomicrographs of the cracks appear in Figs. 6, 7 and 8. Figure 5 shows the location of the crack area used for the metallographic examination. Figures 6 and 7 show different sections of the crack area; nearly-complete penetration of the 0.091-in wall thickness of the 3/8-in pipe is shown in Fig. 7. The transgranular nature of the cracks is illustrated by Fig. 8.

Although the possibility remained that the cracks resulted from the original cold-bending operation on the pipes, the presence of 760 ppm of chloride in the water-formed scale on the outside of the pipes gave strong support to a stress-corrosion cracking mechanism due to the combined effects of stress and localized corrosion attack by the chloride ions. Supplementary testing and examination of the original U-bend stainless steel pipe materials are being pursued.

B. Corrosion of Elgiloy by Uranyl Sulfate Solution.

The results of preliminary corrosion studies with Elgiloy, a spring alloy under consideration for use in the HRT liquid-level controller, were reported previously¹⁶. The alloy showed promising corrosion behavior after 445 hr at 300°C in oxygen-pressurized 0.04 M UO_2SO_4 solution containing 0.02 M H_2SO_4 and 0.005 M CuSO_4 . The solution contained less than 2 ppm chloride. The observed rate during this period was 3.5 mpy and was decreasing with time. A vapor-exposed specimen underwent negligible attack for the 445 hr.

In a following 500-hr run with the same solution at 300°C, both solution and vapor-exposed specimens showed a marked susceptibility to stress-corrosion cracking. The origin of the cracks appeared to be areas of highly-localized residual stresses such as the sheared edges of the 30-mil thick specimens and the numbers stamped on each specimen for test identification. Cracking was so severe on the solution-exposed specimen that a wedge-shaped portion had broken completely away from the remainder of the specimen. There was no significant increase in the intensity of generalized corrosion attack on the specimen during the 500-hr run.

Further work with Elgiloy has been delayed pending the arrival of a supply of the alloy from the Elgin Watch Company. To be included in the new studies will be an examination of the susceptibility of the alloy to stress-corrosion cracking as influenced by the heat treatment to which it is subjected.

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16. J. L. English and J. C. Griess, HRP Quar. Prog. Rep., January 31, 1956, ORNL-2057, p. 86.

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Fig. 5. General View of Section of U-Bend Type 347
Stainless Steel Pipe (No. 5) Used for Crack Examination. Ringed Areas Denote Location of Cracks.

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Fig. 6. Cracks Originating from Pitted Area Formed on Cooled Surface of 3/8-in Type 347 Stainless Steel Pipe. Magnification 100X.

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Fig. 7. Crack Formation on 3/8-in Type 347 Stainless Steel Pipe. Crack Initiated on Outer Cooled Surface of Pipe (Left Side of Photo) and Penetrated Almost Completely Through 0.091-In Wall Thickness. Magnification 100X.

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Fig. 8. Enlarged View of Cracks in 3/8-In Type 347 Stainless Steel Pipe Showing Transgranular Characteristics. Magnification 750X.

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C. Corrosion of Titanium Alloys by Uranyl Sulfate Solutions.

Several high-strength alloys of titanium metal have been exposed in uranyl sulfate solutions at temperatures ranging from boiling to 300°C and for periods up to 3550 hr. The alloys in test include titanium Al10-AT (5% Al - 2-1/2% Sn) and titanium Cl30-AM (4% Al - 4% Mn). Both alloys are products of the Rem-Cru Titanium Corporation.

A summary of the laboratory static corrosion tests is included in Table X. In all cases, the observed corrosion behavior of the two alloys was excellent; thin, adherent, brilliantly-colored films characterized the general appearance of the specimens.

A stressed specimen of titanium alloy MST 6Al-4V (Mallory-Sharon) was exposed for 2000 hr at 300°C in oxygen-pressurized 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m CuSO_4 . The specimen, a twin-strip type, was stressed at 100,000 psi. During the period of the test, no cracking was observed and the specimen exhibited negligible corrosion attack.

The observed behavior of the above alloys was no different than the corrosion of commercial-grade titanium metal exposed in similar environments. Generalized attack on the latter material was usually negligible or near-negligible after extended periods of exposure, and there was no indication of stress-cracking of titanium 75A specimens, stressed at 40,000 psi, after 5000 hr at 250°C in oxygen-pressurized 0.17 m UO_2SO_4 solution containing 0.04 m H_2SO_4 and 0.03 m CuSO_4 .

D. Corrosion of Dissimilar-Metal Couples by Boiling Nitric Acid and Uranyl Sulfate Solutions.

Dissimilar-metal couples of type 347 stainless steel with Zircaloy-2 and titanium 75A were exposed for 2020 hr in boiling 5 wt.% HNO_3 solution followed by exposure for 2870 hr in boiling 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m CuSO_4 . A description of the tests and preliminary tests results have been reported^{17, 18}. No evidence of galvanic corrosion attack was observed on any of the test materials under all conditions of test which included solution sparging with oxygen and with helium gases. Defilmed corrosion rates for type 347 stainless steel were less than 0.1 mpy; the Zircaloy-2 and titanium 75A specimens exhibited negligible weight changes.

Similar tests in which a high area ratio of gold-to-stainless steel was maintained (1 cm^2 of gold per 0.06 cm^2 of stainless steel) resulted in no measurable galvanic corrosion attack on the type 347 stainless steel after 2870 hr in boiling 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m CuSO_4 .

17. J. L. English, HRP Quar. Prog. Rep., July 31, 1955, ORNL-1943, pp. 138-139.
18. J. L. English and J. C. Griess, HRP Quar. Prog. Rep., Jan 31, 1956, ORNL-2057, p. 87.

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TABLE X

CORROSION OF TITANIUM ALLOYS BY URANYL SULFATE SOLUTIONS

Medium	Titanium Alloy	Temp. (°C)	Total Time (hr)	Corrosion Rate (mpy)	Specimen Appearance
0.04 m UO_2SO_4 0.006 m H_2SO_4 0.005 m CuSO_4 Air aeration	Al10-AT	Boiling	3160	Negligible	Brilliant interference colors
Same as above 150 psi O_2	Al10-AT	300	2000	Negligible	Lustrous golden-brown thin adherent film
Same as above 150 psi O_2	Al10-AT	300	2000	0.07, 0.08	Lustrous dark-blue and tan thin adherent film
1.33 m UO_2SO_4 Air aeration	Al10-AT	Boiling	3550	0.01, 0.02	Lustrous golden-yellow thin film
1.33 m UO_2SO_4 150 psi O_2	Al10-AT	250	2000	Gain, 0.2	Lustrous purple-tan thin film
0.04 m UO_2SO_4 0.006 m H_2SO_4 0.005 m CuSO_4 Air aeration	C130-AM	Boiling	3550	Negligible	Brilliant interference colors
Same as above 150 psi O_2	C130-AM	250	2000	Negligible	Dark lustrous purple film
Same as above 150 psi O_2	C130-AM	300	2000	0.02	Vivid dark-blue thin film
1.33 m UO_2SO_4 Air aeration	C130-AM	Boiling	3550	0.02	Lustrous golden-tan thin film
1.33 m UO_2SO_4 150 psi O_2	C130-AM	250	2000	Gain	Lustrous mottled purple-blue thin film

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