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TO: E. G. Bohlmann

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I. SUMMARY

The corrosion rate of carbon steel in boiler water containing various concentrations of oxygen was determined. Average corrosion rates of 4, 12 and 22 mpy were observed during 200 hr tests with oxygen concentrations of < 0.1, 2 and 10 ppm respectively. Pitting about 1 mil in depth occurred on carbon steel specimens in the presence of 2 and 10 ppm oxygen.

The corrosion resistance of a number of alloys was determined in 0.17 *m* UO_2SO_4 at temperatures of 200, 250 and 295°C. Types 430, 431, 446, AM-350, Croloy 16-1 stainless steels, Incoloy; Carpenter alloys 10, 20, and 20Cb; CD4MCu; Hastelloy R-235; Multimet; and Timken 16-25-6 showed low corrosion rates comparable to those of the austenitic stainless steels. Nionel, types 414 and Croloy 1515 N stainless steel, and the Hastelloys B, C, X, and 25 showed lower corrosion resistance than the austenitic stainless steel.

Additional loop runs with UO_3-Li_2CO_3-CO_2 solution have confirmed previous data with regard to its non-aggressive nature to carbon steel. However, tests completed in the temperature range of 250 to 280°C have demonstrated the low solubility of uranium at the higher temperatures. For example, at temperatures between 265 and 280°C less than 1 g. of uranium per liter remained in the solution.

It was demonstrated that protective films formed in 0.04 *m* UO_2SO_4--0.04 *m* $BeSO_4$-0.005 *m* $CuSO_4$ solutions at 200 to 250°C and that the solution was stable. The same solution was not completely stable at 300°C. Copper and uranium were not lost from solution but beryllium was. However, on lowering the loop temperature to 200°C, the beryllium redissolved.

Dynamic loop tests showed that increasing the copper to 0.03 *m* or decreasing the uranium concentration to 0.02 *m* in simulated HRT fuel solution (0.04 *m* UO_2SO_4, 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$) had no significant effect on the solution stability or corrosiveness of the solution.

The effect of varying the oxygen concentration between 250 and 2800 ppm in 0.17 *m* UO_2SO_4 at 250°C on the corrosion rate of type 347 stainless

steel was found to be negligible in the absence of added chromium (VI). In the presence of 200 ppm chromium (VI), the corrosion rate at 13 fps was unaffected but at 68 fps the corrosion rate increased from about 250 to 350 mpy when the oxygen concentration was increased from 250 to 2800 ppm.

The corrosion rate of type 347 stainless steel in dilute sulfuric acid solutions was determined at 250°C. The data shows that the log of the corrosion rate at high flow rates is linearly related to the pH of the solution at 250°C.

In the course of trying to force a piece of Teflon from a titanium loop with 175 psig oxygen, a fire developed and a portion of the titanium nipple in which the Teflon was lodged was consumed in a flash of flame.

A 17-4 PH stainless steel specimen stressed to 75 percent of its room temperature yield strength (80,000 psi) and exposed 19,364 hr to the vapor phase above HRT solution at 300°C was found to have a stress-corrosion crack penetrating 80 percent of its thickness.

Pre-filming times of 50, 200, and 500 hr in boiling chloride-free HRT core solution were equally effective for preventing stress-corrosion cracking of type 347 stainless steel upon exposure in a similar environment containing 50 ppm chloride. Whereas in the absence of a pre-formed film, specimens generally cracked during the first 50 hr in the chloride-containing solution, the present tests with pre-filmed specimens have operated 500 hr, and, in one case, 2500 hr, without the occurrence of cracking.

In a study to determine the effect of the components in the HRT core solution, singly and in various combinations, at boiling temperatures on the stress-corrosion cracking behavior of type 347 stainless steel in the presence of chloride, some experimental data suggested that the uranyl ion may exert an appreciable effect in promoting cracking. Other data, however, were not in support of this effect.

The addition of sodium sulfite for removal of oxygen from chloride-containing distilled water at 300°C effectively prevented stress-corrosion cracking of type 347 stainless steel for 400 hr to date. In other tests, several prefilming methods in chloride-free environments at 300°C were unsuccessful in preventing cracking of type 347 stainless steel in chloride-containing water at 200°C.

Alternate materials including types 304, 304ELC, 309SCb, 316, 321, Carpenter 7-Mo, and Croloy 16-1 stainless steel as well as Incoloy and Nionel were subjected to stress-corrosion cracking tests at 300°C in distilled water with 100 ppm chloride at various pH levels. In general, the higher the nickel content of the alloy, the more resistant the alloy was to cracking. Nionel, an alloy containing 40% Ni, was fully resistant to cracking during test.

The corrosion behavior of electroless nickel plate on SAE 1045 carbon steel was excellent in distilled water at 300°C at adjusted pH levels of 2.5, 7.5, and 10.5. Corrosion rates were 1 mpy and less after 2000 hr. The presence of 50 ppm chloride did not affect the corrosion behavior.

The corrosion resistance of Incoloy was found to be comparable to that of type 347 stainless steel in HRT-related environments. Of special significance was the fact that the alloy was immune to cracking in boiling HRT core solution containing chloride whereas such is not the case for type 347 stainless steel.

Type AM-350 stainless steel in various heat-treated conditions exhibited excellent corrosion resistance in HRT core solution at boiling temperature and at 300°C; corrosion rates were less than 1 mpy. At 200°C, however, the corrosion rates ranged from 5 to 11 mpy. Tempered specimens of the alloy cracked in boiling HRT core solution containing 50 ppm chloride.

Stellites 1 and 3 and Rexalloy 33, materials of interest to the HRP injection-pump program, were corroded at rates of approximately 1 mpy and less by boiling HRT core solution. Stellite 98M2 corroded at a rate of 5 mpy in the same environment.

II. INTRODUCTION

The data presented in the following sections represent the detailed results obtained during the past quarter (October 31, 1957 to January 31, 1958) by the out-of-reactor solution corrosion group of the Homogeneous Reactor Project. A summary of the data has been reported in the Homogeneous Reactor Project Quarterly Progress Report for the Period ending January 31, 1958.

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

III. 100A LOOP PROGRAM (R. S. Greeley, S. R. Buxton, S. E. Bolt, W. C. Ulrich, H. C. Savage, J. C. Griess)

A. Corrosion of a Variety of Materials in Boiler Water at 300°C.

The series of tests to study corrosion for a number of materials in water as a function of water treatment and oxygen concentration was extended to 300°C. Previous results at 250°C have been reported.(1) Table I gives the conditions of the runs and the analytical data obtained. All runs lasted 200 hr.

Two sets of runs were made. In runs I-44 through 50 solution was continuously recirculated and no attempt was made to maintain a constant pH or phosphate concentration. Consequently in the runs with added oxygen, the chromium (VI) concentration increased as the run progressed due to oxidation of the chromium in the steel, and the pH of the solution decreased two or three units during the run. The phosphate concentration also decreased in these runs. In runs I-51 through 53 fresh solution of pH 9 to 11 containing about 60 ppm phosphate was continously added to the loop; the let-down stream was discarded, and in this way the solution composition was maintained as recommended for the HRT steam-system water.(2) The let-down system was described previously.(3)

Runs I-44 and I-47 were made with distilled water without added chemicals to establish a basis for comparison with runs using treated water. Deaeration in I-44 was accomplished by heating the water in the loop to 120°C and sparging with helium several times. The conductivity of the water was between 1.3 and 9.9 x 10^{-5} ohm-cm^{-1} during the runs. In run I-45 deoxygenation was accomplished by adding two 10-ml portions of 85% hydrazine hydrate solution to the water in the loop. In runs I-47 through 49 and I-51 through 53 oxygen concentrations were maintained by continuous feed and let-down; however, in I-49 the feed system did not operate properly and the oxygen concentration varied between 50 and 500 ppm. In run I-50, the let-down system was valved off and the run made with about 1000 ppm oxygen.

Table II lists the average corrosion rates observed in the first set of runs, I-44 through 50. Pins exposed at flow rates between 18 and 45 fps were averaged since little velocity effect was observed. Table III lists the average corrosion rates observed in the second set of runs, I-51 through 53. It should be noted that generally the corrosion rates listed would decrease with longer exposure times since all specimens were filmed over. The results are interpreted as follows:

1. Austenitic Stainless Steels:

   The several types of austenitic stainless steels tested (types 202, 304L, 316, 316L, 318, 347, Carpenter 20 and Carpenter 20 Cb) behaved very much alike and showed low corrosion rates. Very little effect of varying the oxygen concentration in the phosphate-containing water from 2 to 1500 ppm was evident. Corrosion rates in oxygen-free boiler water were roughly 5 times less.

2. Miscellaneous Stainless Steels and Nickel Alloys:

   Croloy 16-1, type 446, SRF-1132, Incoloy, and Nionel showed low corrosion rates generally similar to those of the austenitic stainless steels. Type 414 was less resistant than the austenitic

TABLE I

Conditions of Water Runs at 300°C (All Runs 200 hr)

Run No.	Solution Composition	PO_4[(a)] conc'n (ppm)	Oxygen conc'n (ppm)	pH	Final Conc'n of Ions (ppm) Ni	Cr (III)	Cr (VI)	Fe	Cl
I-44	H_2O	0	0	4 - 7	< 1	< 1	< 1	< 1	< 2
I-45	$H_2O + PO_4$ (hydrazine)	60 50	0	9 - 10	< 1	< 1	< 1	3	< 2
I-47	H_2O	0	7 - 11	4 - 6	< 1	< 1	< 1	< 1	2
I-48	$H_2O + PO_4$	$60 \rightarrow 25$	4 - 11	$9 \rightarrow 7$	< 1	< 1	21	3	< 2
I-49	"	$60 \rightarrow 30$	50 - 500	$9 \rightarrow 6$	< 1	< 1	27	< 1	< 2
I-50	"	$60 \rightarrow 30$	700 - 1500	$9 \rightarrow 6$	< 1	< 1	18	< 1	4
I-51[(b)]	"	60	10	8 - 10	5	< 1	< 1	< 1	< 2
I-52[(b)]	"	60	2	9 - 10	1	< 1	< 1	6	< 2
I-53[(b)]	"	60	4	9 - 10	1	< 1	< 1	1	< 2

(a) As trisodium phosphate

(b) Fresh solution added continously.

TABLE II

Average Corrosion Rates of Several Alloys in Water at 300°C

	CORROSION RATE (mpy)					
Run No.	I-44[a]	I-47[a]	I-45[b]	I-48[b]	I-49[b]	I-50[b]
Oxygen Conc., ppm	< 0.1	7-11	< 0.1	4-11	50-500	700-1500
Type Metal						
202	0.24	0.39	0.22	2.9	2.0	1.7
304L	0.42	0.37	0.36	1.2	2.2	2.2
316L	0.32	0.35	0.26	0.97	1.1	1.1
318	0.40	0.47	0.30	1.3	1.4	1.4
347	0.42	0.42	0.35	1.2	2.1	2.8
347 stress specimens	0.18	0.18	0.21	0.45	0.62	1.1
347 stress specimens[c]	0.22	0.40	0.24	0.53	0.77	0.61
Carpenter-20	0.08	0.47	0.30	0.64	0.68	0.34
Carpenter-20Cb	0.12	0.64	0.22	0.68	0.76	0.77
Average, Austenitic SS	0.27	0.41	0.27	1.1	1.3	1.3
414	2.2	0.86	1.8	2.1	3.0	1.7
Croloy 16-1	0.32	0.39	0.34	1.7	2.0	1.9
446	0.04	0.30	0.17	1.4	4.5 (1.9)[d]	1.2
SRF 1132	0.75	0.60	0.64	1.5	1.8	0.85
Armco Iron	6.5	5.1	4.1	8.6	17	6.5
A-212-B	8.7	13	13 (6.7)[e]	17	26	18
AISI C-1016	10	15	10	15	28	15
AISI C-1010	9.2	19	11	17	21	12
AISI C-1019 stress specimens	7.5	19	22	13	8.3	29
ASTM A-7 coupons	5.2	5.0	3.8	5.9	7.1	3.7
Titanium RC-55	f	0.15	1.3	0.31	0.69	0.39
Niobium	f	f	1.3	f	f	f
Zircaloy-2	f	f	f	f	f	f
Nickel-Plated Carbon Steel[g]	-	-	-	-	-	0.39

a. Distilled water
b. 60 ppm PO_4 as Na_3PO_4
c. Precracked by immersion 20 to 60 min in boiling 42% $MgCl_2$.
d. Omitting one value of 7.0 mpy at 44 fps.
e. Omitting one value of 33 mpy at 44 fps.
f. Specimen gained weight (after defilming).
g. Kanigen plated.

TABLE III

Average Corrosion Rates of Several Alloys at 300°C in Boiler Water Maintained at pH 9 to 10(a)

Material	Corrosion Rate (mpy)					
	I - 52		I - 53		I - 51	
	2 ppm Oxygen		4 ppm Oxygen		10 ppm Oxygen	
	5 to 18 fps	46 fps	5 to 18 fps	46 fps	5 to 18 fps	46 fps
202 SS	2.7	-	3.2	-	4.0	-
304L SS	1.4	2.3	1.4	2.3	1.4	2.1
316 SS	0.9	1.1	0.9	1.0	0.9	1.0
347 SS	1.4	2.5	1.6	2.4	1.6	2.3
347 SS(b)	1.2	-	0.4	-	-	-
347 SS stressed(b,c)	1.1	-	0.6	-	-	-
347 SS stressed(c)	0.8	-	0.5	-	0.8	-
Avg. Aus. SS	1.4	2.0	1.2	1.9	1.7	1.8
Armco Iron	10	-	12	-	15	-
A-212-B	12	25	15	24	22	33
AISI C-1010	11	17	14	20	18	24
AISI C-1016	12	24	15	23	20	29
Avg. Carbon Steel	11	22	14	22	19	29
Incoloy	0.5	0.9	0.5	0.7	0.3	0.5
Nionel	0.8	1.3	0.6	1.1	0.9	1.4
Ni-Plated Carbon Steel(d)	0.7	3.1	1.0	4.8	0.9	1.1
C-1010 stressed(c,e,f)	15	-	15	-	-	-
C-1010 stressed(c,e,g)	13, 6.7	-	16	-	-	-
C-1010 stressed(b,d)	16	-	24	-	45	-
ASTM A-7 coupons (10 to 100 fps)	-	7.1	-	6.9	-	8.3

(a) 60 ppm PO_4 as trisodium phosphate.

(b) Coupled to carbon steel.

(c) Stressed beyond elastic limit.

(d) Kanigen plated, 0.002 in. thick.

(e) Galvanically coupled to stainless steel through bolts and fulcrum.

(f) Formed crevice with stainless steel.

(g) Formed crevice with carbon steel.

stainless steels but the difference between the two was not as great as at 250°C.(1) Carbon steel AISI type C-1010, nickel plated to a thickness of about 0.002 in. by the Kanigen electroless process,(4) gave excellent results. Corrosion rates 5 to 10 times lower than for unplated specimens were observed.

3. Armco Iron and Carbon Steels:

Armco iron, carbon steel ASTM type A 212 B, and carbon steel AISI types C-1010 and C-1016 were exposed as pin specimens and all behaved similarly. Carbon steel ASTM type A-7 was exposed as flat coupon specimens and, perhaps due to a geometry effect, showed corrosion rates roughly half as great as the other types. All specimens showed a definite increase in corrosion rate with increasing oxygen concentration up to 50 ppm. Although corrosion rates appeared to decrease slightly at 1000 ppm oxygen, the change in pH and phosphate concentration and the build-up of chromium (VI) concentration (from the stainless steel loop) in solution may have affected the rates. The attack on the iron and steel specimens was irregular and, particularly at low flow rates in runs I-51, 52 and 53 (2 to 10 ppm oxygen), extensive pitting of the "oxygen cell"(5) type occurred. Since the corrosion rates listed in Tables II and III were determined from weight losses, true penetration rates on the pitted specimens were considerably greater. Penetration rates calculated from pit depths determined metallographically were 40 to 50 mpy. Figure 1 shows average corrosion rates, determined from weight losses, plotted against oxygen concentration. Since true penetration rates are larger than those shown, it is apparent that the oxygen concentration in the boiler water of the HRT must be maintained as low as possible.

4. Other Alloys:

Zircaloy-2 and niobium generally showed slight weight increases. Titanium RC-55 corroded only slightly in distilled water but in the treated water rates ranged from 0.3 to 1.3 mpy.

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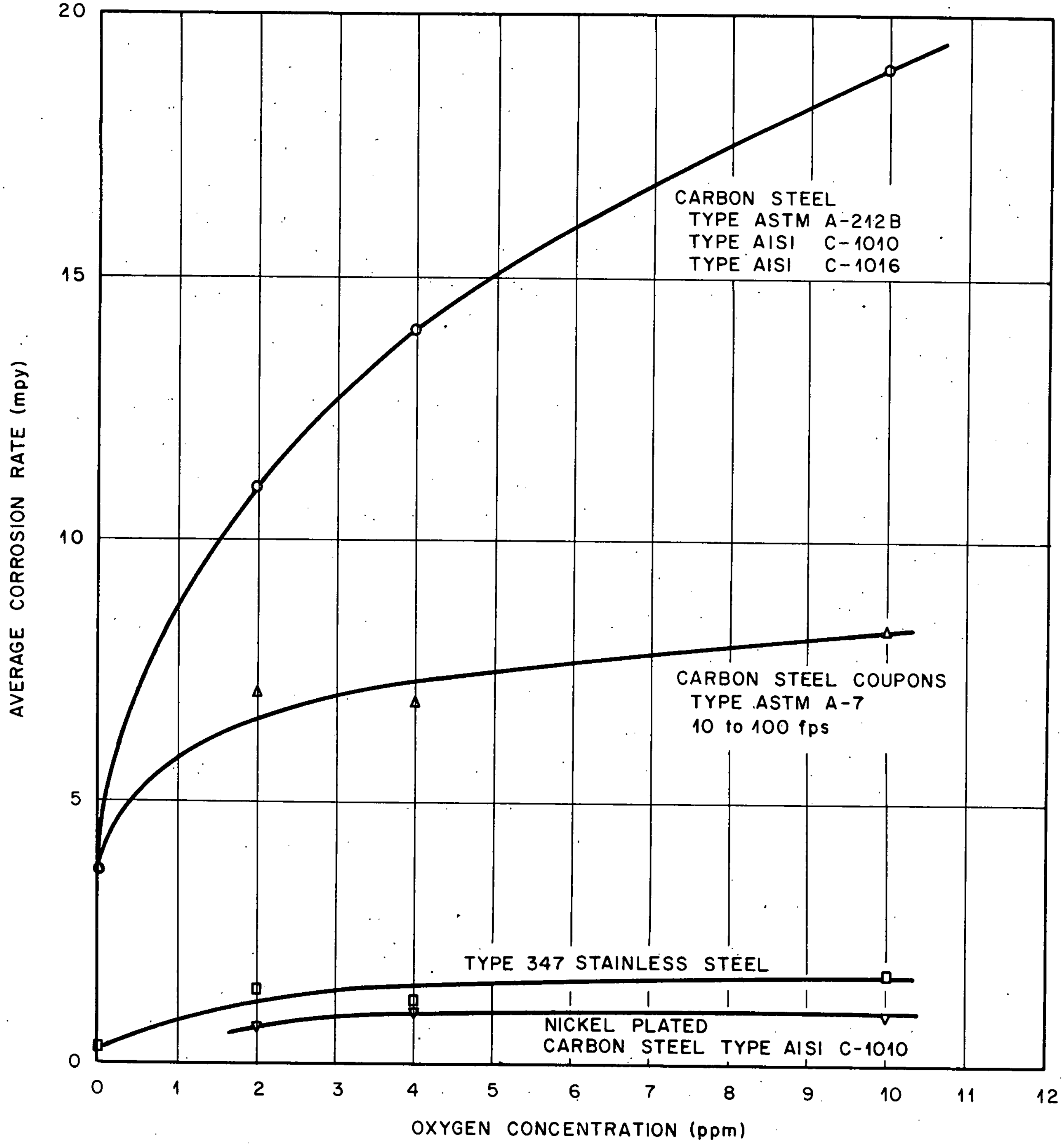

Fig. 1. Average Corrosion Rates of Carbon and Stainless Steels at 5 to 18 fps in Boiler Water at 300°C as a Function of Oxygen Concentration (200 hr. runs)

5. Stressed and Coupled Specimens:

In each run several type 347 stainless steel and several AISI type C-1010 carbon steel specimens were mounted on a special stress-specimen holder which was inserted in one of the main barrels of the loop. The stress applied was greater than the elastic limit and the flow rate of solution over the specimens was about 3 fps. None of the specimens showed stress-corrosion cracks, and no significant acceleration of general attack due to the applied stress was evident.

In runs I-52 and 53 specimens were mounted on top of one another in pairs to give stainless steel - carbon steel, stainless steel - stainless steel, and carbon steel - carbon steel couples with a crevice between the specimens. No significant effect of the coupling or of the crevice formed between the couples was noticed.

In runs I-44 through I-50, four type 347 stainless steel specimens were assembled in pairs, stressed over a single fulcrum inserted between them, and immersed 20 min to 1 hr in boiling 42% $MgCl_2$ prior to being fastened to the holder and placed in the loop. The purpose of this treatment was to determine whether stress-corrosion cracks once started in a chloride medium would continue to propagate in the absence of chloride in high temperature water. Each specimen was examined under a low-power microscope before and after the run in an attempt to determine whether the cracks had lengthened during the run. (The boiling 42% $MgCl_2$ treatment induced cracks about halfway across each specimen.) In no instance did the cracks propagate to give complete fracture of the specimen during the run. However, it was not possible to determine with certainty whether the cracks had propagated further during the run. It may have been that the stress was relieved by the cracking in the magnesium chloride solution so that no further propagation would have been expected.

B. Corrosion Resistance of Several Alloys at 200 to 295°C in 0.17 *m* UO_2SO_4.

The corrosion resistance of a number of alloys not previously tested and of three alloys hardened by appropriate heat treatment was compared with the resistance of the austenitic stainless steels in uranyl sulfate at 200 to 295°C. The uranyl sulfate concentration was 0.17 *m* in order to compare the results with previous tests.(6) Table IV lists the weight losses observed at 5 to 11 fps and at 21 to 43 fps. Weight losses of two to four pins of each type were averaged in each velocity range (except where noted) since there was little effect of velocity within each range.

At 200°C all of the alloys except Hastelloy B were covered with a partially protective film at all flow rates. At 250°C most of the alloys exposed at 5 to 11 fps developed protective coatings, but at the higher flow rates either no or only partial coating formed. Those alloys showing low weight losses at 295°C developed protective films whereas those showing high weight losses did not. If the weight losses of the alloys are compared to those of type 347 stainless steel it can be seen that, with few exceptions, equally good corrosion resistance was shown by the following: types 202, 302, 302B, 303, 304, 304L, 309SCb, 310S, 316, 316L, 321, 347 cast, 430, 431, 446, AM-350, and Croloy 16-1 stainless steel; Incoloy; Carpenter 10, 20 and 20 Cb; CD4MCu; Hastelloy R-235; Multimet, and Timken 16-25-6. The type 202 and the 300 series stainless steels are austenitic. The types 430, 446, and Croloy 16-1 are ferritic steels whereas the 414, 431, and AM-350 steels are martensitic and hardenable by appropriate heat treatment. Table V lists the heat treatments given the types 414, 431 and AM-350 steels and their resulting hardness. In the hardened condition, types 431 and AM-350 showed no difference in corrosion resistance from that shown in the annealed condition. Incoloy and the Carpenter alloys are alloys of possible use in the HR program. CD4MCu is an alloy which may be used as-cast or wrought and can be hardened by aging. The Hastelloy R-235, Multimet and Timken are high strength alloys of possible interest as bolt materials.

TABLE IV

Average Weight Loss of Different Alloys in 0.17 *m* Uranyl Sulfate Solution at 200, 250, and 295°C

Alloy	Average Defilmed Weight Loss (mg/cm^2) in 200 hr					
	200°C		250°C		295°C	
	5-11 fps	21-43 fps	5-11 fps	21-43 fps	5-11 fps	21-43 fps
202	13	16	14	97	2.0	3.3
302	4.6	5.1	19	65	1.9	1.8
302B	5.1	5.1	21	88	3.5	32
303	7.9	9.2	6.9	60	2.4	44
304	7.4	6.9	6.5	46	2.1	51
304L	4.4	4.4	11	69	2.3	45
309SCb	4.0	4.1	11	24	4.0	7.9
310S	2.9	3.4	16	60	4.6	9.3
316	3.9	4.5	21	70	4.6	140
316L	3.4	3.4	30	65	4.2	130
321	4.6	3.6	23	70	4.0	130
347	6.0	6.9	22	69	2.9	11
347 Cast	4.2	5.1	29	74	3.8	120
347 Cr PA(a)		0.87		5.5		120
347 Cr PB(b)		0.78		9.2		120
414 Annealed	20	33	21	23	23	27
414 Hardened	20	23	13	14	17	17
430	9.2	13	5.5	51	1.5	25
431 Annealed	9.7	9.7	5.1	6.4	4.0	2.9
431 Hardened	12	13	6.0	14	4.2	4.0
446	8.3	10	5.1	10	1.7	2.4
Croloy 16-1	6.4	10	2.8	6.4	1.5	1.7
Croloy 1515N	12	14	25	97	2.5	13
AM 350(1)(c)	5.1	6.9	5.5	16, 92(d)	1.8	2.9
AM 350(2)(c)	5.6	8.3	4.0	13, 120(d)	2.0	3.1
AM 350(3)(c)	4.6	6.9	5.5	5.5, 110(d)	2.0	2.3
AM 350(4)(c)	4.6	6.5	5.1	12	2.3	3.1
AM 350(5)(c)	4.6	6.5	4.6	17, 70(d)	1.7	2.8
CD4MCu	4.3	4.2	14	83	4.1	78
Carpenter 10	8.3	8.3	12	87	3.0	26
Carpenter 20	3.4	4.1	30	78	6.9	150
Carpenter 20Cb	3.7	3.7	16	60	9.2	92
Hastelloy B	> 2600	> 2600				
Hastelloy C	33	36	160	240	360	1100
Hastelloy R 235	6.9	6.4	35	110	13	130
Hastelloy X	8.7	11	64	120	43	270
Haynes 25	6.0	6.0	64	87	280	460
Incoloy	8.3	8.7	24	100	6.9	17
Multimet	6.9	7.4	29	120	7.4	190
Nionel	11	11	32	130	18	190
Timken 16-25-6	4.5	8.7	11	97	3.5	55

(a) Chrome plated 0.0002" by Electrolyzing Corp., Chicago Heights, Illinois.
(b) Chrome plated 0.0005" by Electrolyzing Corp., Chicago Heights, Illinois.
(c) See Table V.
(d) Each value is for 1 pin.

TABLE V

Heat Treatment and Hardness of Various Alloys

Alloy	Condition	Hardness (Rockwell C)
414 A	Annealed at 1250°F	35
414 H	Heated at 1850°F for 1 hr and quenched in oil	47
431 A	Annealed at 1250°F	30.5
431 H	Heated at 1850°F for 1 hr and quenched in oil	43
AM 350(1)	Annealed at 1750°F for 1/2 hr and air cooled	34.5
AM 350(2)	Annealed and subzero cooled (2 hr at -100°F)	38
AM 350(3)	Annealed and subzero cooled and tempered (2 hr at -100°F + 1 hr at 850°F)	43
AM 350(4)	Annealed and intermediate aged (1 hr at 1350°F)	32
AM 350(5)	Annealed and double aged (1 hr at 1350°F + 1 hr at 850°F)	37

Showing greater corrosion resistance than type 347 at 200 and 250°C but poorer resistance at 295°C were type 347 stainless steel specimens chromium plated to a thickness of 0.0002 and 0.0005 in. by an electrolyzing process. Showing slightly poorer resistance than type 347 at all temperatures were Nionel and Croloy 1515 N stainless steel; and showing considerable poorer resistance were the Hastelloys B, C, X, and 25, and stainless steel type 414. The compositions of several of the alloys have been listed in other reports.(7) Table VI lists the compositions of the rest of the materials tested.

The results showed that there are several alloys as resistant to 0.17 *m* uranyl sulfate as type 347 stainless steel.

C. Circulation of Uranyl Carbonate at 250 to 300°C.

Previous corrosion tests with lithium carbonate solutions containing dissolved uranium trioxide have shown very low corrosion rates at 250°C with many materials including carbon and stainless steels.(8,9) Similar tests have now been made at temperatures up to 300°C. The corrosion results are listed in Table VII.

It can be seen that corrosion rates at 17 fps were generally low, less than 5 mpy, for all of the materials tested. If one compares the data obtained at 300°C with that obtained at 250°C,(8) it is seen that the rates are essentially the same.

Unfortunately, the solutions were not stable. In the first run, J-91, uranium and lithium precipitated at 300°C from a solution initially containing 0.03 *m* UO_3 (about 8 g of uranium per liter) dissolved in 0.19 *m* Li_2CO_3 under 300 psi CO_2. Within 24 hr the solution contained only 0.002 *m* UO_3 (about 0.5 g of uranium per liter) and 0.06 *m* Li_2CO_3. Increasing the carbon dioxide partial pressure to 600 psi failed to increase the solubility. Since Marshall and Secoy indicated that more uranium would be soluble in higher concentration Li_2CO_3,(10) a second run was

TABLE VI

Compositions of Several Alloys Tested in 0.17 *m* UO_2SO_4

(%)

Alloy	Cr	Ni	C	Mn	Si	Mo	Fe	Other
302	17 - 19	8 - 10	0.08 - .20	2 max	1 max		Bal. Fe	0.03 S max 0.04 P max
302 B	17 - 19	8 - 10	0.008 - .20	2 max	2 - 3		Bal. Fe	0.04 P max
303	17 - 19	8 - 10	0.15 max	2 max	1 max		Bal. Fe	0.15-0.35 Se
309SCb	23.2	14.5	0.06	1.76	0.54		Bal. Fe	0.014 P, 0.020 S 0.89 Nb
310 S	24.8	19.7	0.08	1.76	0.57	0.22	Bal. Fe	0.080 P, 0.017 S 0.22 Cu
321	17 - 19	8 - 11	0.08 Max	2 max	1 max		Bal. Fe	Ti 5xC min
430	17 - 18	1 max	0.12 max	1 max	1 max		Bal. Fe	0.03 S max 0.04 P max
431	15 - 17	1.25-2.50	0.20 max	1 max	1 max		Bal. Fe	0.04 P max
Croloy 1515 N	15.1	15.7	0.088	1.34	0.75	1.44	Bal. Fe	0.011S, 0.013 P 1.07 W, 0.85 Nb
AM 350	17	4.2	0.08	0.60		2.75	Bal. Fe	
CD4MCu	25 - 27	4.7-7.0	0.04 max	1.0	1 max	1.75-2.25	Bal. Fe	2.75-3.25 Cu
Hastelloy B	< 1	62	0.12 max			26 - 30	4 - 6	
Hastelloy C	13 - 17.5	Bal. Ni				16 - 18	4.5-7	3.7-5.3 W
Hastelloy X	22	Bal. Ni	0.15 max			9	17 - 20	
Haynes 25	19.7	10.1	0.09	1.42	0.5	51.6	1.8	14.8 W
Incoloy	19	40	0.01	0.90	0.33	3.26	32	1.85 Cu
Nionel	21.9	40	0.05	0.61	0.60	2.97	31.28	1.55 Cu

Note: Ranges of values are given where only nominal values are available.

TABLE VII

The Corrosion of Several Alloys in Uranyl Carbonate Solutions

	Corrosion Rate (mpy)					
	J-91 (891 hr) 300°C 0.03 *m* UO_3 + 0.19 *m* Li_2CO_3		J-92 (200 Hr) 300°C 0.07 *m* UO_3 + 0.25 *m* Li_2CO_3		J-93 (511 hr) 250 to 280°C 0.03 *m* UO_3 + 0.15 *m* Li_2CO_3	
Material	19 fps	68 fps	19 fps	65 fps	17 fps	-
Armco Iron	2.6	2.5	4.3	3.7	-	
AISI C-1010	2.4	2.6	3.7	4.2	2.9	
AISI C-1016	2.5	2.8	4.1	6.3	4.7	
202	0.6	1.5	1.5	2.7		
304L	0.7	5.0	1.4	8.2		
309SCb	0.8	2.8, 29[(a)]	1.9	16		
347	0.3	2.1	1.1	10	3.2	
Carpenter 20 Cb	4.3	33	1.7	24		
Incoloy	3.2	27	1.6	18	5.2	
414	0.5	0.7	1.3	2.3		
Croloy 16-1	0.2	-	-	-	1.5	
430	-	0.5	1.3	2.6		
431	0.3	0.6	1.3	2.0		
446	-	0.7	-	2.7		
SRF 1132	-	11	-	-		
Stellite 98M2	-	21	-	67		
Ti RC-55	0.2	0.3	0.8	2.2		
Ti 4% Al, 4% Mn	-	0.4	-	2.4		
Ti 6% Al, 4% V	0.1	-	1.1	-		
Ti 3% Al, 5% Cr	-	0.3	-	1.7		
Niobium	-	-	-	-	0.5	
Nionel	-	-	-	-	1.4	
Crystal Bar Zr	-	-	-	-	0.1	
Zircaloy - 2	-	-	-	-	0.0	
347 SS Coupons (11-82 fps)	1.8		3.3		3.1	

(a) Each value is for one pin.

made at 300°C with 0.06 *m* UO_3 in 0.25 *m* Li_2CO_3 under 600 psi CO_2. Again uranium and lithium precipitated and within 150 hr the solution contained only 0.004 *m* UO_3 (1 g of uranium per liter) in 0.07 *m* Li_2CO_3. In order to determine at what temperature precipitation first occurred, a third run, J-93, was made at successively higher temperatures with 0.03 *m* UO_3 in 0.15 *m* Li_2CO_3 under 600 psi CO_2. Figure 2 is a plot of uranium and lithium concentration as a function of time in run J-93 and shows that the solution was stable for 150 hr at 250°C but was unstable at 260°C and above. Therefore, the uranyl carbonate system does not have adequate stability for operation above 250°C.

D. Corrosion Testing in Beryllium Sulfate Solutions.

1. Circulation of 0.04 *m* UO_2SO_4 Containing 0,04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$.

It was reported previously that corrosion rates of type 347 stainless steel in 0.04 *m* UO_2SO_4 containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$ were lower at 200 to 250°C than in HRT solution (0.04 *m* UO_2SO_4 + 0.02 *m* H_2SO_4 + 0.005 *m* $CuSO_4$), but that the specimens did not film over within 200 hr.(11) In order to determine whether stainless steel specimens would film over after longer exposure times, 500 and 1000 hr runs were made with the beryllium - containing solution at 200°C and 500 hr runs were made at 225 and 250°C. Table VIII lists the conditions of the runs. Figures 3, 4, and 5 illustrate the results obtained with type 347 stainless steel coupons.

In Figure 3, it can be seen that at 200°C the specimens filmed over and showed no additional weight loss between 500 and 1000 hr at flow rates up to a velocity of 15 to 20 fps. Figure 4 presents similar data obtained at 225°C and shows that little additional corrosion occurred after the 200 hr exposure up to flow rates of 15 to 20 fps. In both cases corrosion rates above the critical velocity were lower by a factor of five than rates in the standard HRT fuel solution at

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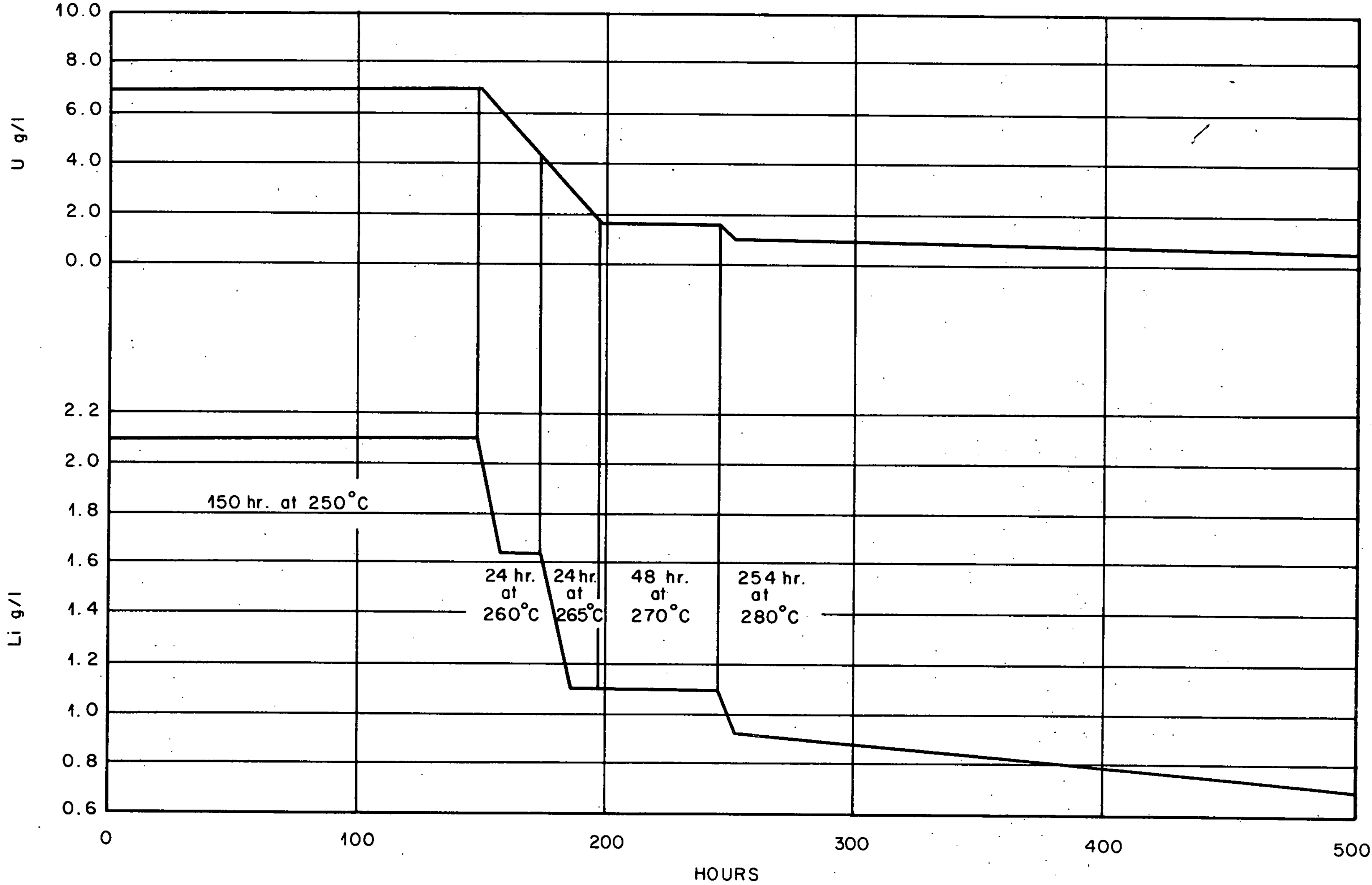

Fig. 2. Changes in Concentration of Uranium and Lithium at Various Temperatures in Run J-93 (Initially 0.03m UO_3 Dissolved in 0.15m Li_2CO_3 Under 600 psi CO_2 Pressure at 250°C)

TABLE VIII

Conditions of Runs with 0.04 *m* UO_2SO_4 Containing 0.04 *m* $BeSO_4$ and 0.005 *m* $CuSO_4$

Run No.	Time (hr)	Temp (°C)	Concentration U gm/l	Concentration Be gm/l	Concentration Cu ppm
0-19	500	200	10.2	0.46	310
0-20	500	225	10.0	0.39	295
0-21	510	250	10.9	0.32	300
0-23	1000	200	10.3	0.50	300
0-18	1000	300 (a)	9.8	0.40 (b)	280

(a) Thermally cycled twice at 200°C.

(b) Final concentration was 0.30 gm/l at 300°C.

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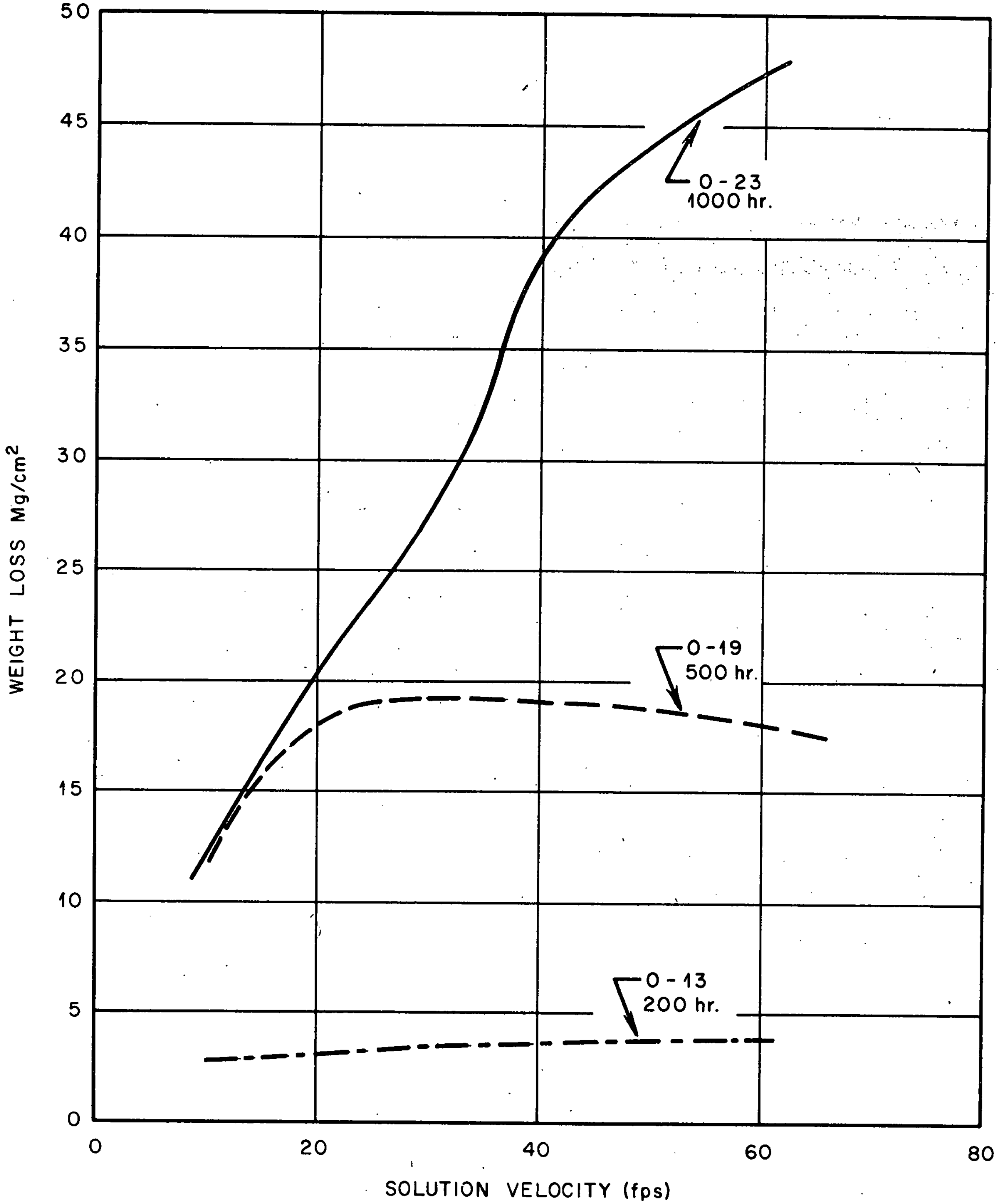

Fig. 3. Weight Losses of Type 347 Stainless Steel Coupons in $0.04m\ UO_2SO_4 + 0.04m\ BeSO_4 + 0.005m\ CuSO_4$ at 200°C

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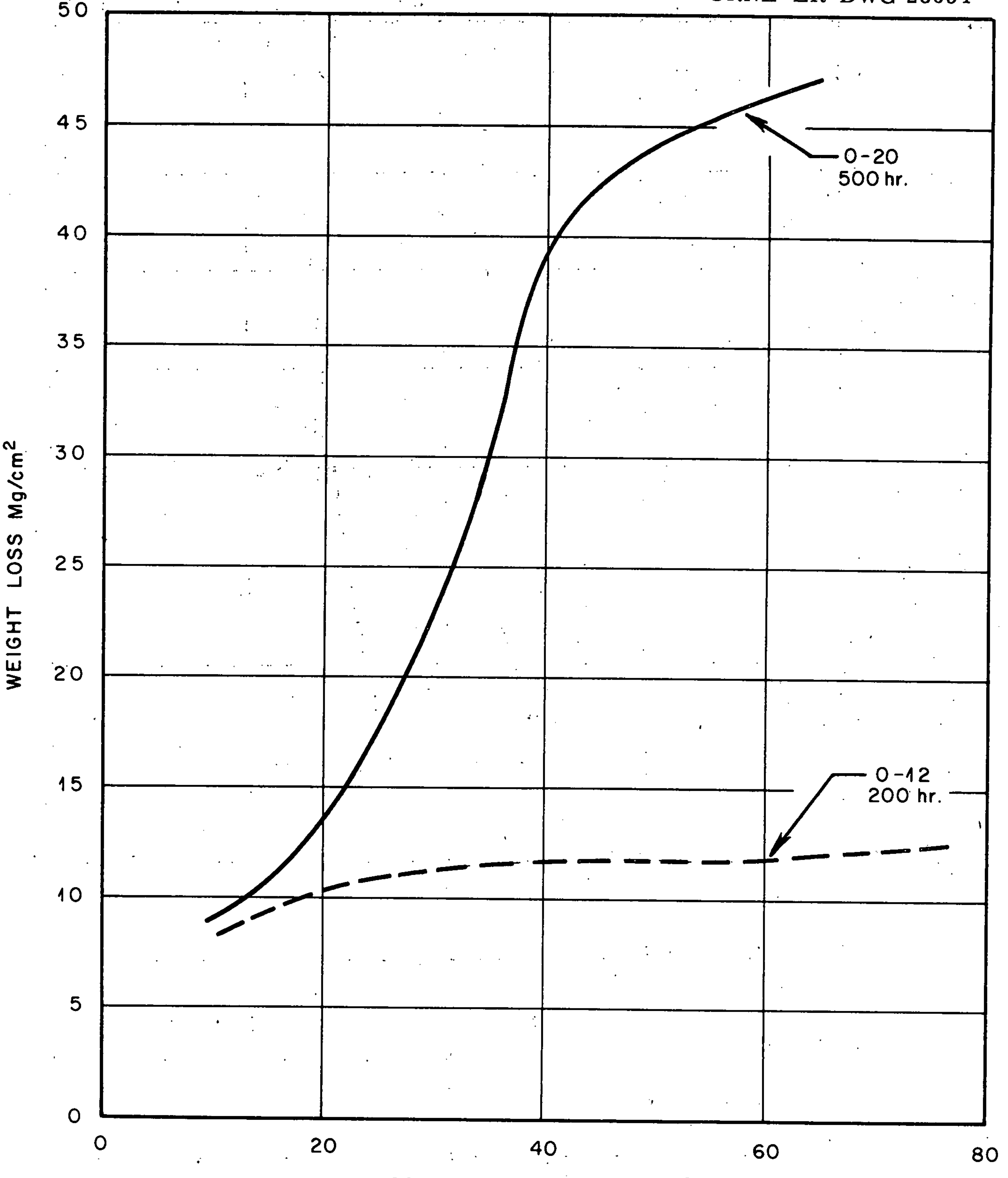

Fig. 4. Weight Losses of Type 347 Stainless Steel Coupons in 0.04m UO_2SO_4 + 0.04m $BeSO_4$ + 0.005m $CuSO_4$ at 225°C

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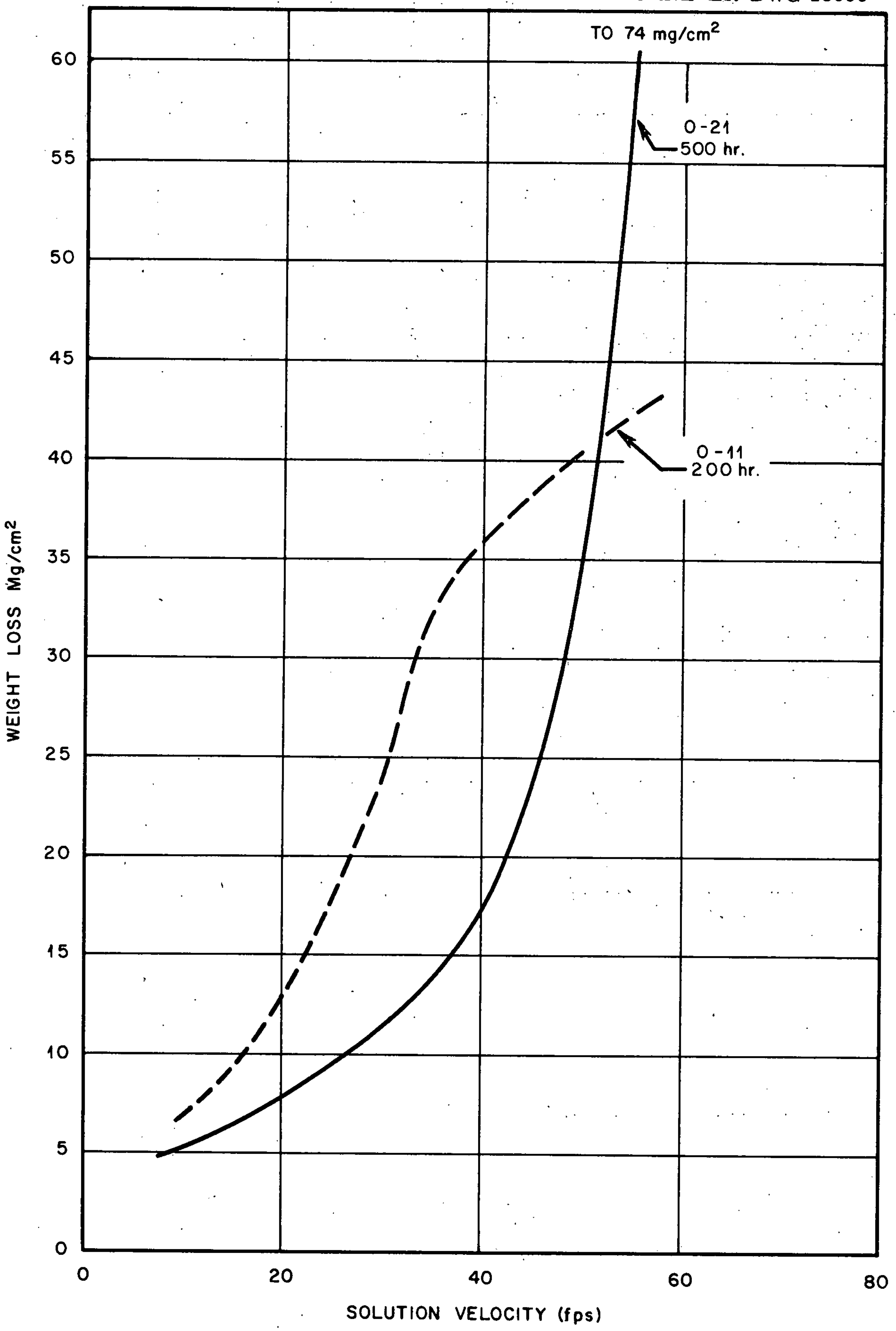

Fig. 5. Weight Losses of Type 347 Stainless Steel Coupons in 0.04m UO_2SO_4 + 0.04m $BeSO_4$ + 0.005m $CuSO_4$ at 250°C

the same temperature. At 250°C, as shown in Figure 5, the results were anomalous in that weight losses in the 500 hr run were lower, up to 52 fps, than in the 200 hr run. Although the reason for this is not known, it appeared that the coupons filmed over up to a critical velocity of 20 to 30 fps in both runs. The solutions were stable at 200, 225, and 250°C.

It was noticed that the corrosion rate of the type 347 pins and coupons at high velocity at 200°C was increasing with time and that the increase was proportional to the chromium (VI) concentration in solution. It has been postulated that the rate of film formation is directly proportional to the corrosion rate,(12) and hence the film formation at 200°C and perhaps at 225 and 250°C might have been dependent on the chromium (VI) concentration in solution. Since chromium (VI) is apparently not stable in radiation fields, it is questionable whether stainless steel specimens would film over in reactor experiments.

In order to determine the phase stability of the beryllium-containing solution, a 1000 hr run was made at 300°C. The loop was thermally cycled to 200°C twice to find out if any precipitates formed at the higher temperature would redissolve at the lower temperature. The uranium and copper concentrations were constant within ± 5 and ± 15%, respectively. However, beryllium precipitated at 300°C and redissolved at 200°C and the pH of the solution (measured at room temperature) changed reversibly from 2.0 at 300°C to 3.0 at 200°C. Therefore, the solution was not entirely stable at 300°C.

In view of the above results, it is possible that the dilute beryllium sulfate-uranyl sulfate solution may offer advantages over HRT solution from a corrosion standpoint. In-reactor tests have shown that added sulfate ion may inhibit radiation-induced corrosion of Zircaloy-2.(13) Therefore, in-reactor tests with added beryllium sulfate appear warranted to determine whether sulfate ions added as beryllium sulfate will inhibit radiation-induced corrosion of Zircaloy-2 and to determine whether stainless steel specimens will film over in a radiation field. Also both in-reactor and out-of-reactor tests of solution stability at temperatures between 250 and 300°C must be made.

2. Circulation of 0.075 *m* $BeSO_4$.

In the program of investigating corrosion of stainless steel by beryllium - containing solutions, it became desirable to test the corrosiveness of beryllium sulfate solutions only. Accordingly, 0.075 *m* $BeSO_4$ was circulated at 250°C for 200 hr with the results shown in Figure 6. The concentration was chosen to give roughly the same pH as 0.17 *m* UO_2SO_4. Both beryllium sulfate and uranyl sulfate give acid solutions at room temperature but the beryllium ion is not subject to reduction as is the uranyl ion. A comparison of the corrosion of type 347 stainless steel in beryllium sulfate with that of the same steel in 0.17 *m* UO_2SO_4 at 250°C shows that the solutions were equally corrosive at 8 to 15 fps but at higher flow rates the beryllium sulfate solution was considerably less corrosive. The coupons were filmed over up to 48 fps in the beryllium sulfate solution. The beryllium sulfate solution was less corrosive than the uranyl sulfate solution, possibly because the beryllium sulfate solution contains less free acid at 250°C or because the uranyl ion accelerates corrosion. Interestingly enough, the 0.075 *m* beryllium sulfate solution was not stable at 250°C. The beryllium concentrations fell at a constant rate from 0.075 to 0.043 *m* and the pH of the solution (measured at room temperature) decreased from 2.6 to 2.0 during the 200 hr run.

3. 0.75 *m* $BeSO_4$ Containing 0.25 *m* UO_3 (dissolved).

A previous run ("O"-6) with 1.0 *m* $BeSO_4$ containing 0.36 *m* dissolved UO_3 gave remarkably low corrosion of type 347 stainless steel at 250°C.(14) In attempting to duplicate those results, the solution inadvertently contained only 0.25 *m* UO_3 and 0.75 *m* $BeSO_4$. The solution was circulated for 200 hr at 250°C ("O"-24) and the corrosion results obtained with type 347 stainless steel are shown in Figure 7. Rather

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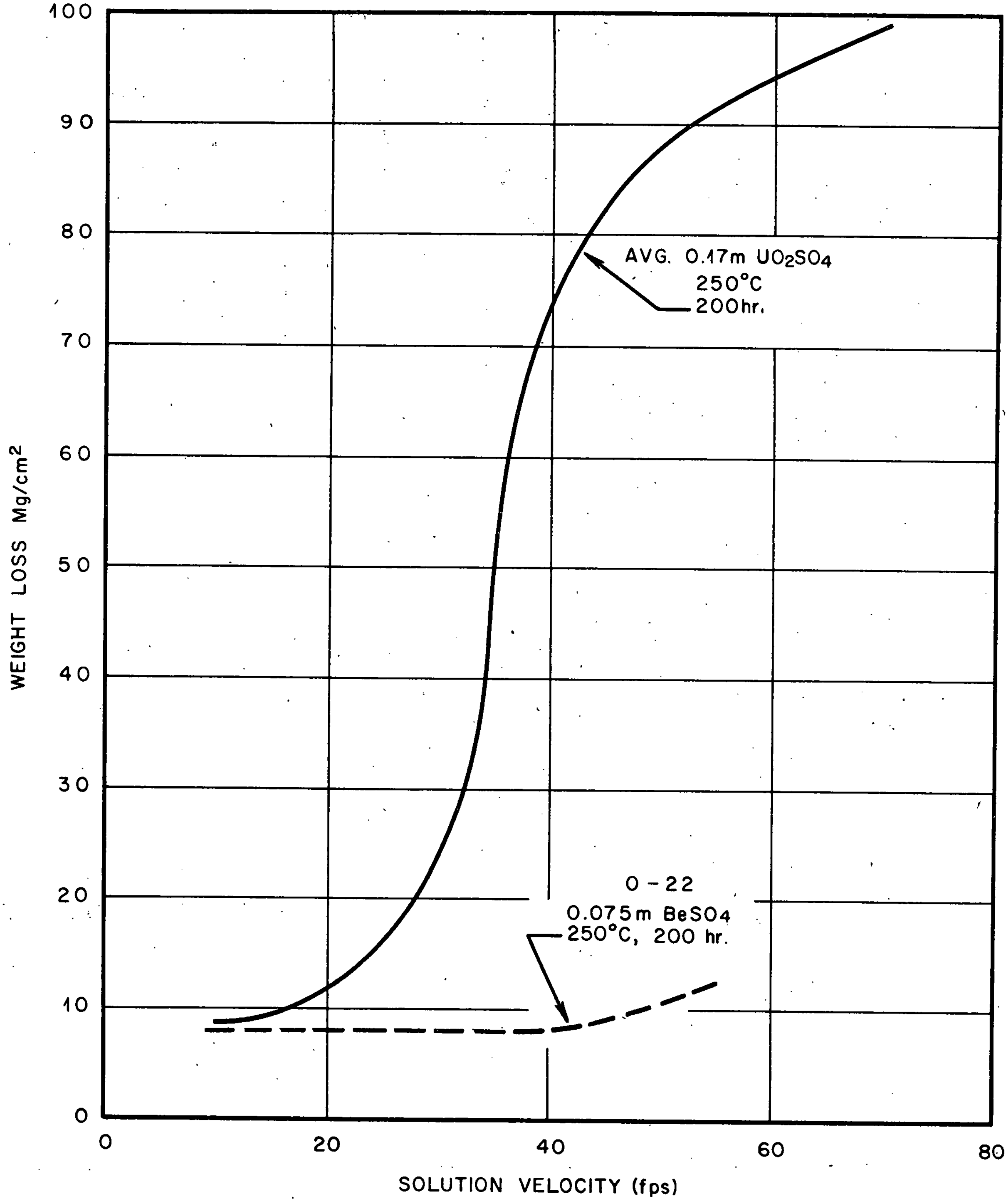

Fig. 6. Weight Losses of Type 347 Stainless Steel Coupons in 0.075m $BeSO_4$ at 250°C

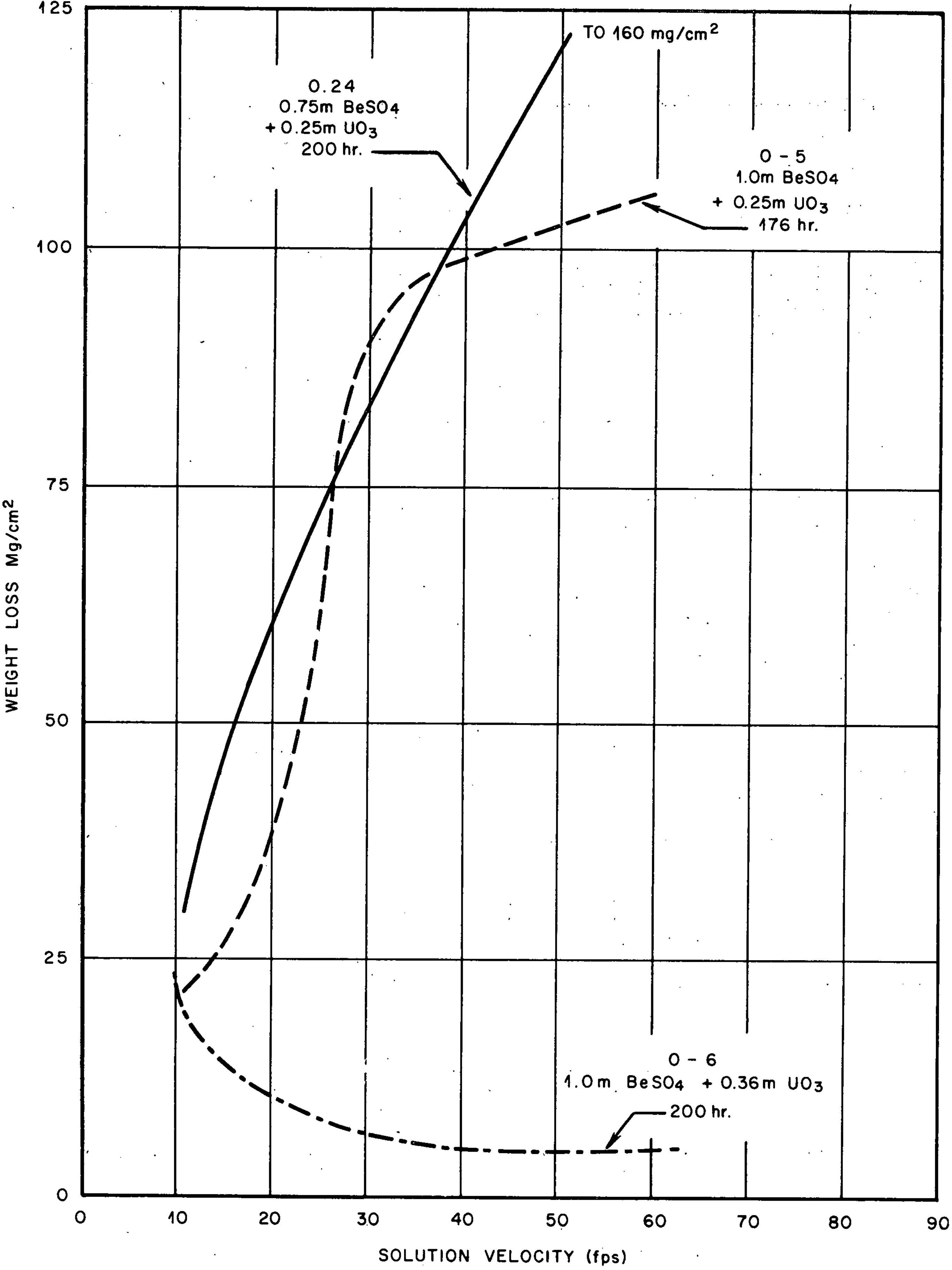

Fig. 7. Weight Losses of Type 347 Stainless Steel Coupons in 0.75m $BeSO_4$ Containing 1.25m UO_3 (Dissolved)

than very low corrosion, a sharp velocity effect and relatively high corrosion occurred. As shown in Figure 7, the results were very similar to another previous run ("0"-5) with 1.0 m $BeSO_4$ containing 0.25 m UO_3 at 250°C.(11) Therefore, the very low rates observed previously could not be duplicated.

E. Stability and Corrosiveness of Dilute Uranyl Sulfate Solutions at 300°C.

Previous work has shown that about 0.02 m H_2SO_4 must be added to 0.04 m UO_2SO_4 containing 0.005 to 0.01 m $CuSO_4$ to prevent hydrolytic precipitation of uranium and/or copper at 300°C.(15) In order to determine whether decreasing the uranium concentration or increasing the copper concentration would affect solution stability, four runs were made (in light water solution) with 0.02 m UO_2SO_4 containing 0.02 or 0.03 m $CuSO_4$ and various amounts of sulfuric acid. Conditions of the runs and results are listed in Table IX.

A 0.02 m UO_2SO_4 solution containing 0.03 m $CuSO_4$ and 0.02 m H_2SO_4 was stable for 1000 hr at 300°C in run N-34, whereas 0.02 m UO_2SO_4 solutions containing 0.02 or 0.03 m $CuSO_4$ with 0.006 to 0.01 m H_2SO_4 were not stable within 1000 hr at 300°C. Therefore, since approximately as much sulfuric acid (0.02 m) is needed to stablize these solutions as those studied previously, there appears to be no significant effect on solution stability of decreasing the uranium concentration a factor of two or of increasing the copper concentration a factor of four to six.

Corrosion of type 347 stainless steel coupons in these runs increased slightly with increasing acid and copper concentration. A comparison of weight losses in 0.02 m UO_2SO_4 containing 0.02 m H_2SO_4 and 0.03 m $CuSO_4$ (run N-34) with those in 0.04 m UO_2SO_4 containing 0.02 m H_2SO_4 but different amounts of copper sulfate (runs A-88 and N-10) is shown in Figure 8. It can be seen that the critical velocity was slightly lower with the 0.02 m UO_2SO_4 solution than with the solutions containing 0.04 m UO_2SO_4. However, below 30 fps weight losses were somewhat lower in the solution containing the lower uranium concentration. Therefore at 300°C, at least,

TABLE IX

Conditions and Results of Solution Stability Runs

(300°C)

Run No.	Nominal Composition	Time (hr)	pH Initial-Final	Uranium Conc (gm/l) Initial	Uranium Conc (gm/l) Final	Copper Conc (gm/l) Initial	Copper Conc (gm/l) Final	Remarks
N-32	0.02 *m* UO_2SO_4 0.01 *m* H_2SO_4 0.02 *m* $CuSO_4$	200	1.9 - 1.7	5.9	5.7	1.3	1.2	Unstable
N-33	0.02 *m* UO_2SO_4 0.006 *m* H_2SO_4 0.03 *m* $CuSO_4$	517	1.9 - 1.8	5.5	5.1	1.8	1.3	Unstable
N-34	0.02 *m* UO_2SO_4 0.02 *m* H_2SO_4 0.03 *m* $CuSO_4$	1000	1.6 - 1.6	5.4	5.3	1.9	1.8	Stable
M-34	0.02 *m* UO_2SO_4 0.01 *m* H_2SO_4 0.03 *m* $CuSO_4$	1000	1.9 - 1.6	5.8	5.1	2.0	1.7	Unstable

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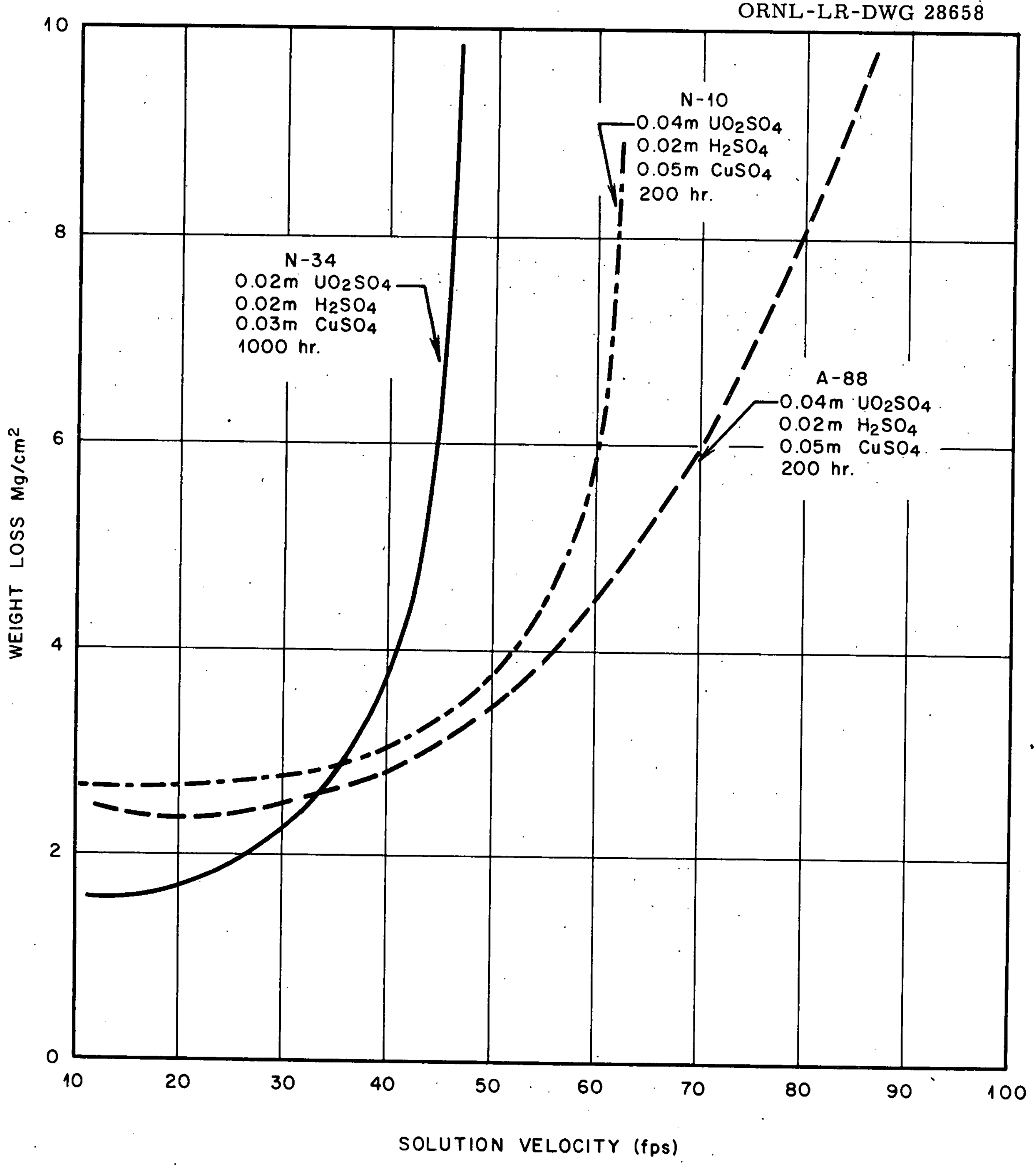

Fig. 8. Weight Losses of Type 347 Stainless Steel Coupons in Dilute Uranyl Sulfate Solutions Containing Sulfuric Acid and Copper Sulfate at 300°C

it is necessary for either 0.02 or 0.04 *m* UO_2SO_4 solutions with copper sulfate to contain 0.02 H_2SO_4 for chemical stability; and with this amount of acid, both solutions are about equally corrosive.

F. Effect of Oxygen Concentration in 0.17 *m* UO_2SO_4 at 250°C.

The effect of oxygen concentration on corrosion of stainless steel in uranyl sulfate has been studied previously(16) but in the stainless steel loops used for testing there has always been the problem of the building up of chromium (VI) concentration in solution which affected the results. Therefore, several runs were made in an all-titanium loop to avoid large changes in chromium (VI) concentration during the test. The results are plotted in Figure 9. All runs were made at 250°C for 100 hr with 0.17 *m* UO_2SO_4. Two type 347 stainless steel pins were exposed at 13 fps and two at 68 fps in each run. The corrosion rates plotted as the ordinate in Figure 9 are the average rates for the 100 hr runs. It should be pointed out that at the low flow rate (13 fps) the specimens developed films and with further exposure would show no additional corrosion. Hence, the rates are only relative. On the other hand, those specimens exposed at the high flow rate did not develop films and those corrosion rates would remain the same regardless of the exposure time.

It can be seen that at 70 fps in the presence of 200 ppm chromium (VI) added as potassium dichromate corrosion rates decreased with decreasing oxygen concentration. When no chromium (VI) was added, corrosion rates did not vary with the oxygen concentration. The 5 ppm chromium (VI) came from oxidation of chromium in the stainless steel pins. At 13 fps there was little, if any, effect of oxygen concentration either in the presence or absence of added chromium (VI). The explanation of these results may be that in the absence of a protective film on the steel at high flow rates the 200 ppm chromium (VI) accelerates the corrosion rate to the point where the rate controlling step involves oxygen. This step could be either the diffusion of oxygen to the metal surface, the adsorption of oxygen on the surface, or the reaction of oxygen with the metal. In the absence of chromium (VI) some other process not involving oxygen would be the rate controlling step.

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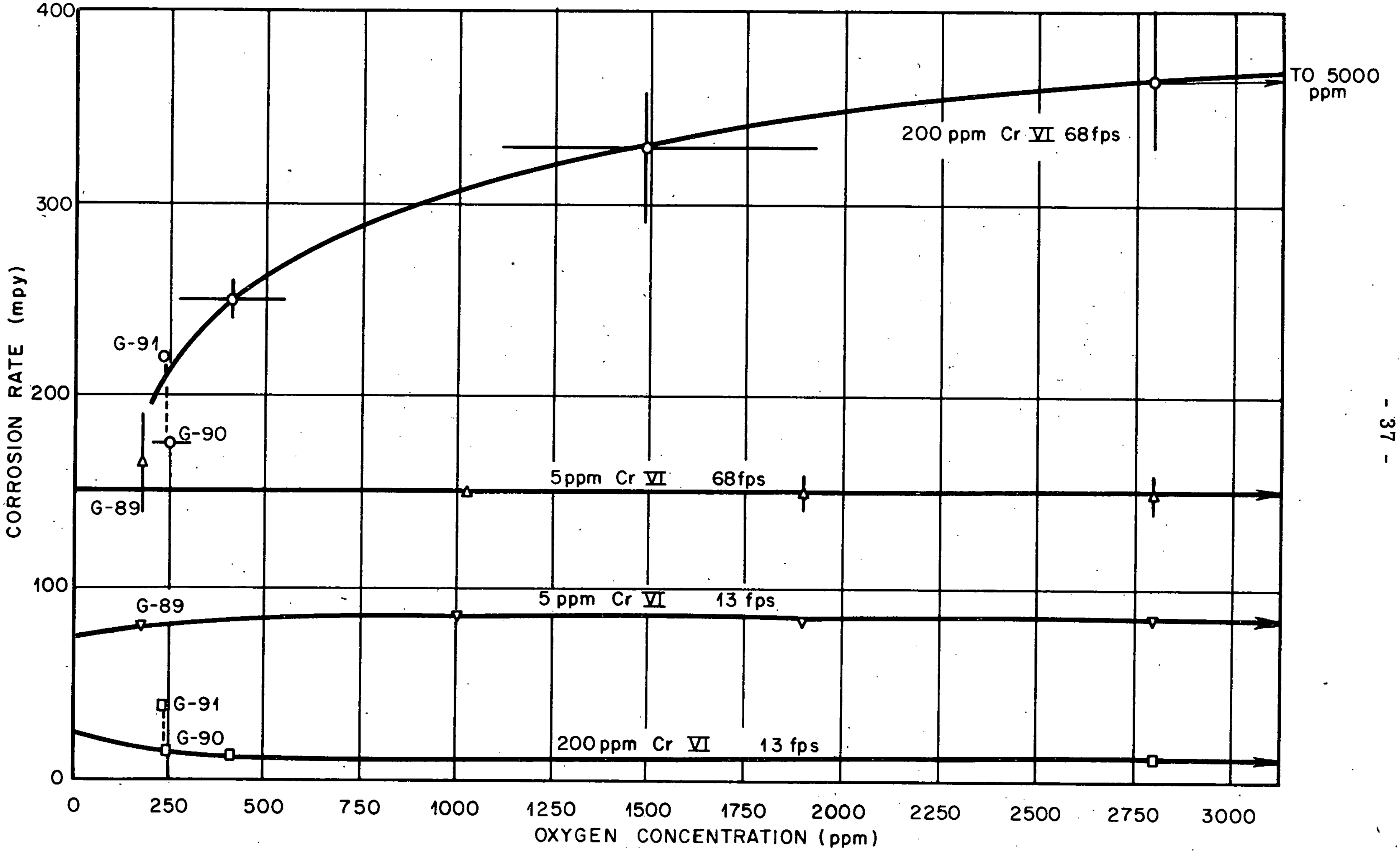

Fig. 9. Effect of Oxygen Concentration on the Corrosion of Type 347 Stainless Steel Pins in 0.17m UO_2SO_4 at 250°C (Titanium Loop 100hr. Runs)

G. The Corrosion of Stainless Steel in Dilute Sulfuric Acid at 250°C.

It has been felt that a study of corrosion of stainless steel in dilute sulfuric acid at high temperatures might help interpret the mechanism of corrosion of stainless steel in high temperature uranyl sulfate solutions. Previous studies(17) have been made in stainless steel loops but they were complicated by the build-up in solution of corrosion products originating from the large surface area of stainless steel in the loops. To circumvent this difficulty, an all-titanium loop was used in the present investigation. Runs were made with 0.05, 0.025, and 0.015 m H_2SO_4 at 250°C with two type 347 stainless steel pins exposed at 13 fps and two at 68 fps. The data obtained at 68 fps are plotted versus the calculated pH of the solution in Figure 10. The pins exposed at 13 fps gave erratic results and are not included in the present discussion.

Lietzke and Stoughton have given a method by which the pH of a sulfuric acid solution may be calculated at 250°C using the equation of Young for the change in the bisulfate dissociation constant as a function of temperature.(18) The pH of the solutions used in this study was so calculated and the values obtained are the ones used in Figure 10.

The line connecting the points in Figure 10 was drawn with a slope of -2. The excellent fit of the data to such a slope is strong evidence that the rate determining reaction in the corrosion of stainless steel at 68 fps in dilute sulfuric acid involves two hydrogen ions. Two possibilities of such a reaction are:

$$(1) \quad (Fe, Cr, Ni) + 2H^+ \longrightarrow (Fe^{++}, Cr^{++}, Ni^{++}) + H_2$$

$$(2) \quad (Fe, Cr, Ni) + 1/2\ O_2 + 2H^+ \longrightarrow (Fe^{++}, Cr^{++}, Ni^{++}) + H_2O$$

Since oxygen is consumed in the corrosion reaction, equation (2) seems the more probable, although equation (1) may be the rate determining precursor to catalytic combination of hydrogen and oxygen on the steel surface. Further work will involve determining the role of uranyl ions in changing the above reactions.

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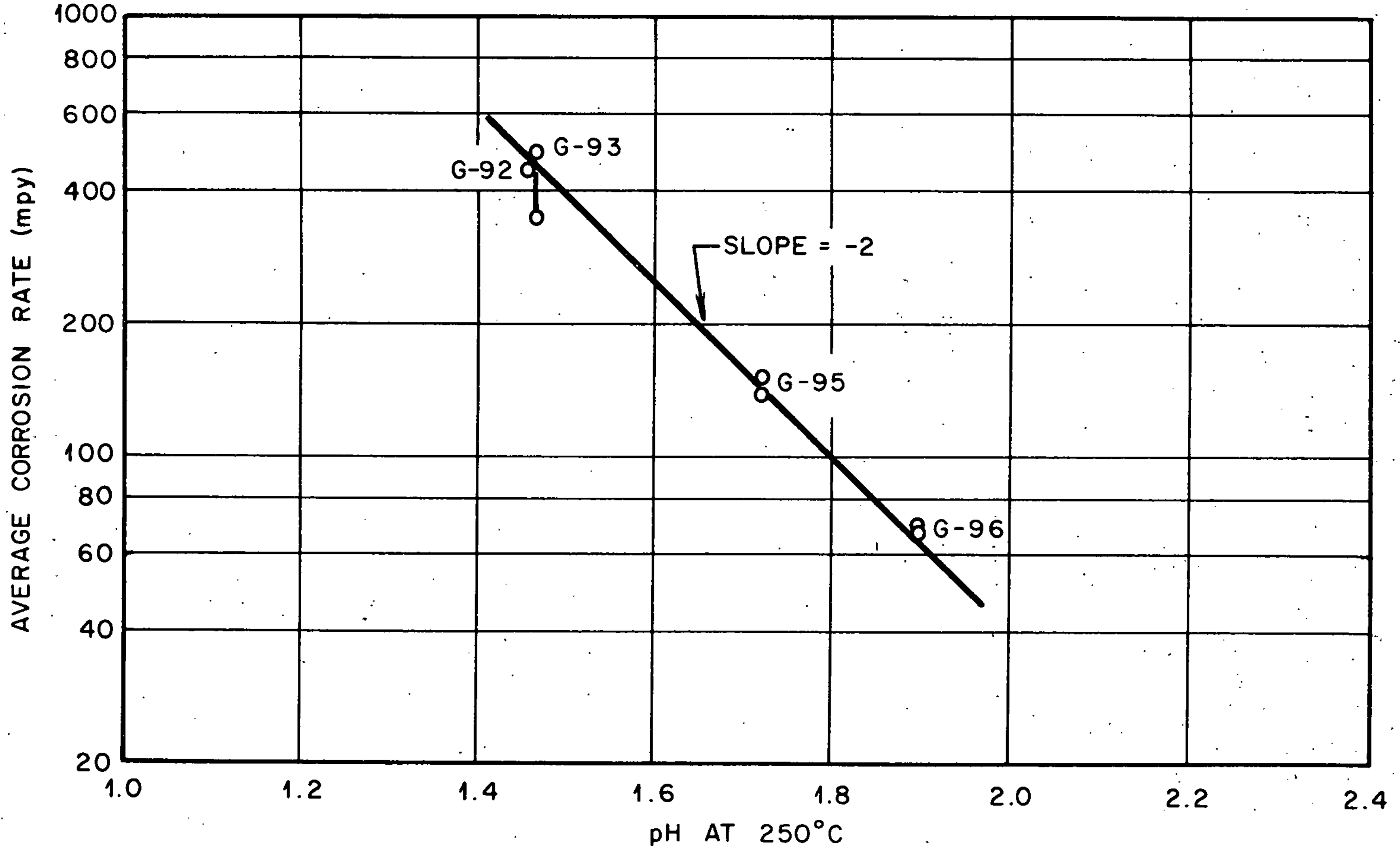

Fig. 10. Effect of Hydrogen Ion Activity (pH) on the Corrosion of Type 347 Stainless Steel Pins at 68fps in H_2SO_4 at 250°C (Titanium Loop, 200 hr. Runs)

H. Ignition of a Titanium Fitting in Oxygen at Room Temperature.

Recently in preparing an all-titanium loop for a run, a piece of Teflon used as a gasket became wedged in a Ti-75A nipple. The loop was pressurized with about 175 psig oxygen at room temperature in an effort to force the Teflon from the loop. When this failed to remove the Teflon, a file was used to pry the Teflon loose. Apparently the file scratched the surface of the nipple and immediately the titanium nipple caught fire.

Figure 11 illustrates the remainder of the burned nipple and for comparison shows a new nipple identical to the one that burned. As can be seen, about 3/8 in. of titanium was consumed by the fire. The incident underscores the possibility of titanium-oxygen reactions even at moderate pressures at room temperatures. Work being performed on subcontract to the Laboratory is investigating these reactions in more detail.(19)

I. Metallographic Examination of Stress Specimens Exposed in Simulated HRT Fuel Solution at 300°C.

It was reported previously that metallographic examination of stress specimens exposed in simulated HRT fuel solution (0.04 m UO_2SO_4 containing 0.01 to 0.025 m H_2SO_4 and 0.005 to 0.01 m $CuSO_4$) for 12,543 hr at 200°C and of specimens exposed for 13,385 hr at 250°C revealed no stress-corrosion cracks.(20) Since then, metallographic examination of stress specimens exposed 14,364 hr in simulated HRT fuel solution at 300°C has been carried out. The specimens examined included types 309 SCb, 347, 17-4 PH, and hardened AM-350 stainless steel and titanium alloys 110AT and 130AM. All specimens were initially stressed to 75 percent of their room temperature yield strengths; and one specimen of each type was exposed in the vapor phase and one to three specimens of each type were exposed in the liquid phase.

Metallographic examination of the 17-4 PH specimen stressed to 80,000 psi and exposed in the vapor above HRT solution at 300°C disclosed a stress-corrosion crack which penetrated about 80 percent of the 1/8 in.

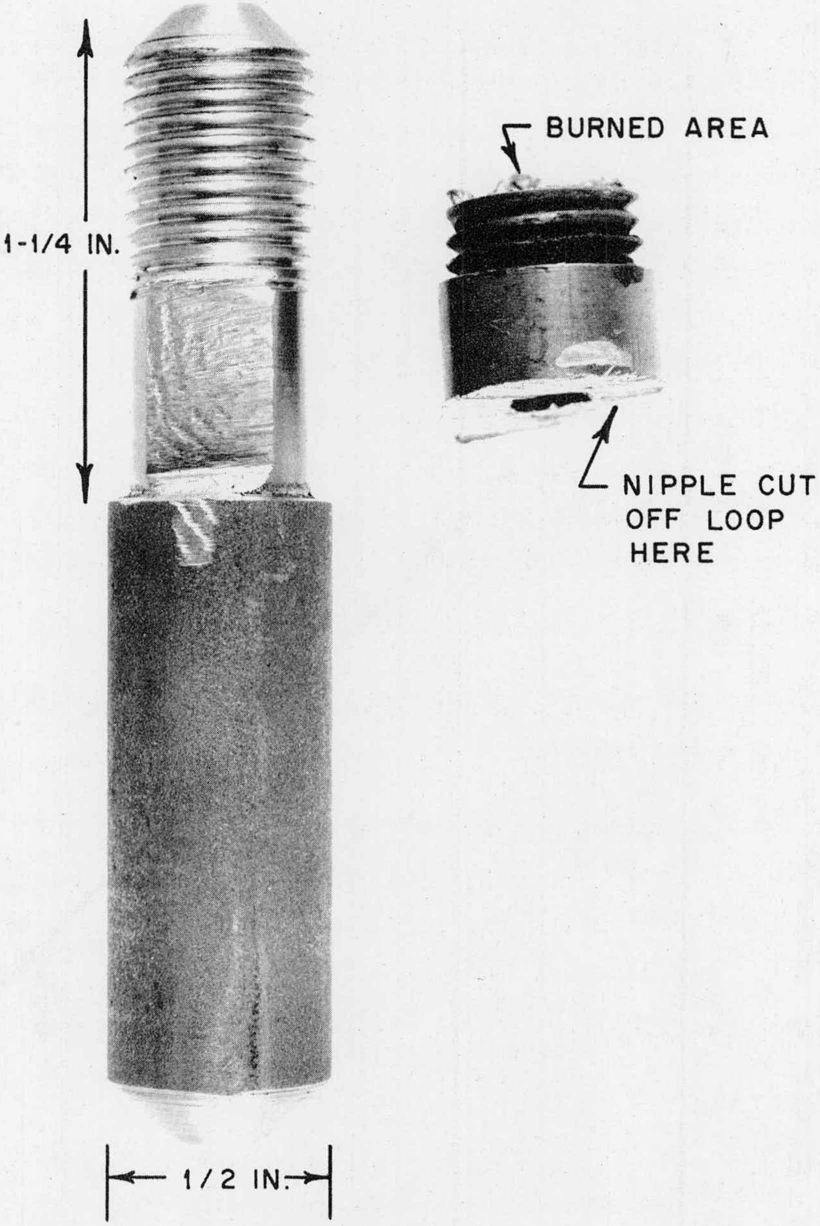

Fig. 11. The Burned Titanium Nipple (right) and a New Nipple (left) Identical to the Burned Nipple. (2054-1 Plate)

thickness of the specimen. The crack is shown in Figure 12. No cracks were found in the area of maximum stress on the three other 17-4 PH specimens stressed similarly but exposed in the liquid. No cracks were found on the other types of stressed materials simultaneously exposed.

The hardness of all of the 17-4 PH stress specimens exposed at 300°C was about Rockwell C-43 at the end of the test. However, the specimens presumably were only partially hardened to Rockwell C-38 prior to the test (identical specimens exposed 13,385 hr at 250°C and 12,543 hr at 200°C still exhibited a Rockwell C-38 hardness after the test). Therefore, somehow the specimens at 300°C became hardened during the test to the fully hardened condition of Rockwell C-43. It is known that 17-4 PH stressed specimens will crack when exposed to uranyl sulfate in the fully hardened condition.(21) However, the reason for the specimens exposed in the liquid and spray regions not cracking is not known.

J. Composition of Scale Formed on Platinum Pins Exposed in 0.17 *m* UO_2SO_4 at 200 to 295°C in Stainless Steel Loops.

During the runs discussed in Part B of this report, gold and platinum pins were also exposed. The gold pins collected a very loose scale at 200 and 250°C which flaked off. The platinum pins collected a tightly adhering scale which was dissolved off with fuming perchloric acid and analyzed chemically for iron, chromium, nickel, and uranium. The results obtained from the platinum pins are given in Table X in which the analyses have been converted to percent of the oxide in the scale. The scale weight on each pin was only about 1 mg, so the accuracy of the data is at best only about ± 10 percent of the values listed. Pins were exposed during two runs at both 250 and 300°C. Both sets of data are listed in Table X for 250° but at 295°C a significant amount of scale was collected in only one run. The reason that scale was collected in one run at 295°C and not in the other is that several alloys which corroded severely and put a much higher concentration of corrosion products into solution were included in the former run. These corrosion products collected on all surfaces.

Fig. 12. Stress-Corrosion Crack in a 17-4 PH Stress Specimen Exposed 14, 364 hr in the Vapor above HRT Solution at 300°C. (T13938)

TABLE X

Composition of Scale Formed on Platinum Pins in 0.17 *m* UO_2SO_4

Temp. (°C)	Flow Rate (fps)	Film Wt. (mg)	Fe_2O_3 (%)	Cr_2O_3 (%)	NiO (%)	UO_3 (%)	Total (%)
200	5	1.4	88.9	10.1	0.2	29.2	128
	11	1.2	63.5	5.1	0.1	11.8	81
	21	1.4	97.0	11.0	0.2	2.9	111
	40	1.3	88.3	9.8	0.1	2.6	101
250	5	0.7	77.4	9.4	1.0	13.0	101
	11	2.1	56.2	9.3	0.6	6.0	69
	21	1.6	98.8	8.9	1.6	8.2	118
	40	1.9	99.6	8.5	1.0	18.9	128
250	5	1.4	87.3	11.3	2.5	< 1	101
	24	1.8	90.6	11.8	1.5	11.6	116
	43	2.2	84.3	10.5	1.5	23.3	120
295	5	1.5	48.0	9.6	2.5	13.3	71
	10	1.5	79.0	11.4	2.0	14.3	107
	24	2.0	68.5	15.8	3.5	8.3	96
	43	2.2	67.7	11.3	1.6	9.1	90
Averages			79.5	10.3	1.3	11.5	103

Several interesting facts are apparent from consideration of Table X:

1. Little significant difference in scale composition was caused by differences in flow rate or temperature. Even chromium, which at 295°C is appreciably oxidized to the soluble chromium (VI), was present to about the same extent at all temperatures.

2. The uranium content of the scale was appreciable, about 12%. This result is surprising since many previous analyses of the scale formed on platinum pins in 0.17 *m* UO_2SO_4 have consistently shown only about 1% uranium in the film. This discrepancy in results has not been resolved.

3. The nickel content of the scale was almost negligible.

4. The iron-chromium ratio in the scale was about 80:10 whereas in the metal it is about 75:18; the scale appeared to be enriched in rion.

The manner of transport of the corrosion products to the platinum surface is not known, but it is likely that ferric and chromic ions oxidized from a corroding steel surface hydrolyze to colloidal-size particles. These particles are swept along by the circulating solution until they meet a surface with an appropriate electric charge (depending on the zeta potential of the colloid and the streaming potential of the surface) which flocculates and collects them. Evidently gold does not have as appropriate a potential as platinum. Since chromium is oxidized to the trivalent state more easily than iron, presumably the chromium would more likely be oxidized and hydrolyzed very close to the steel surface whereas the iron would tend to be swept away. Nickel, of course, remains essentially soluble and forms few, if any, hydrolyzed particles. The uranium in the film, if uniformly distributed over all the stainless steel surfaces of the loop in the same proportion as on the platinum pins (assuming the 12% value is correct), amounts to about 0.8 g. That is, about 0.2% of the uranium in solution is either in colloidal form and collected by the platinum as discussed above or is occluded by the scale as it grows.

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

A. Stress-Corrosion Cracking of Type 347 Stainless Steel

1. Effect of Pre-Formed Films in Uranyl Sulfate Solution.

Continuation of a study to determine the effectiveness of pre-formed films for eliminating the susceptibility of type 347 stainless steel to stress-corrosion cracking in boiling, chloride-containing uranyl sulfate solution was made during the past quarter. Previous work showed that a film formed on type 347 stainless steel stress specimens by treatment in boiling, chloride-free HRT core solution (0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$) did protect the specimen from stress-corrosion cracking exposure in a similar environment containing 50 ppm chloride.(22,23) It was also found that the pre-formed film was equally effective whether the U-bend was formed before or after pretreatment. An improvement in the general corrosion resistance of type 347 stainless steel in the boiling chloride-containing uranyl sulfate solution was also attributed to the presence of the pre-formed film.

Recent studies were concerned with the incidence of stress-corrosion cracking as a function of the prefilming time. Elastically-stressed U-bend specimens of type 347 stainless strel in triplicate were exposed for periods of 50,100 and 500 hr in boiling and aerated, chloride-free HRT core solution. With several exceptions, the specimens were stressed before the prefilming operation. After prefilming the specimens were returned to a similar environment to which 50 ppm of chloride were added as potassium chloride. Results appear in Table XI.

In a total of 17 U-bend specimens, no cracking was found during exposure periods of 500 hr and 2500 hr. Previous work showed that in a similar environment but with no prefilming of surfaces 75% of the U-bend specimens tested cracked during the initial 50 hr; 85% of the specimens cracked during the first 400 hr of the test. The 500-hr tests listed in Table XI are being continued.

TABLE XI

Effect of Pre-formed Film on Stress-Corrosion Cracking of Type 347 Stainless in Boiling and Aerated HRT Core Solution(1) Containing 50 ppm Chloride

Prefilming Time(2) (hr)	No. of Specimens	Total Hr	Observations
50	3	500	No Cracking
200	3	500	No Cracking
500	3	500	No Cracking
500(3)	8	2500	No Cracking

(1) 0.04 *m* UO_2SO_4 containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$.

(2) Pre-filmed in boiling chloride-free HRT core solution.

(3) Specimens were prefilmed both before and after stressing.

On the basis of the preliminary experimental data, it appears that if chloride ions inadvertently were introduced into the low pressure system of a homogeneous reactor, the presence of a pre-formed film previously formed under conditions of chloride-free operation would be of considerable benefit in protecting against stress-corrosion cracking. Future work with pre-formed films will be concerned with the effect of prefilming temperature on the effectiveness of the film in minimizing stress-corrosion cracking of type 347 stainless steel.

2. Effect of HRT Core Solution Components.

Since laboratory tests demonstrated that a boiling and aerated solution consisting of 0.04 m UO_2SO_4, 0.02 m H_2SO_4, 0.005 m $CuSO_4$ and 25 to 500 ppm chloride could induce stress-corrosion cracking in type 347 stainless steel, it was of interest to examine the effect of the components of the solution (except chloride), either singly or in combination, on the stress-corrosion process. All test solutions contained 50 ppm chloride added as potassium chloride. In several instances, potassium ions were substituted for uranyl ions.

Test specimens consisted of elastically-stressed U-bends prepared from annealed and pickled 0.025-in. thick type 347 stainless steel strip. Edges of specimens were mechanically polished before stressing. Each test was run with two, three, or four stress specimens. The results are included in Table XII.

In the control tests with a solution containing uranyl sulfate, copper sulfate, sulfuric acid and 50 ppm chloride, cracking was observed on 5 specimens during a 400-hr exposure. Four of the 5 specimens exhibited cracks during the initial 50 hr. When the uranyl ions were replaced by potassium ions in two cases (K_2SO_4-H_2SO_4-$CuSO_4$ and K_2SO_4-H_2SO_4), no cracking of specimens occurred during a 2500-hr exposure. Similarly, no cracking was observed in the following chloride-containing solutions after exposure periods ranging from 300 to 1500 hr: 0.04 m UO_2SO_4-0.02 m H_2SO_4; 0.04 m UO_2SO_4-0.005 m $CuSO_4$; 0.02 m H_2SO_4; and 0.005 m $CuSO_4$. However, in the 0.04 m UO_2SO_4 solution, 3 of 8 specimens showed cracks after 500 hr.

TABLE XII

Effect of HRT Core Solution Components on Stress-Corrosion Cracking Behavior of Type 347 Stainless Steel: Atmospheric Boiling with Air Aeration and 50 ppm Chloride

Solution	Number of Specimens	Total Hr	Observations
0.04 *m* UO_2SO_4 0.02 *m* H_2SO_4 0.005 *m* $CuSO_4$	5	400	Cracking observed on all specimens; 4 of 5 specimens cracked during initial 50 hr
0.04 *m* K_2SO_4 0.02 *m* H_2SO_4 0.005 *m* $CuSO_4$	2	2500	No cracking
0.04 *m* K_2SO_4 0.02 *m* H_2SO_4	2	2500	No cracking
0.02 *m* UO_2SO_4 0.02 *m* H_2SO_4	2	1500	No cracking
0.04 *m* UO_2SO_4 0.005 *m* $CuSO_4$	3	500	No cracking
0.02 *m* H_2SO_4	2	1500	No cracking
0.005 *m* $CuSO_4$	3	300	No cracking
0.04 *m* UO_2SO_4	8	500	Cracking observed on 3 specimens

Thus, the initial experimental evidence on the effect of various components in the HRT core solution on the stress-corrosion cracking behavior of type 347 stainless steel suggests that under conditions of atmospheric boiling and in the presence of chloride, the uranyl ion is an important factor in the mechanism of the cracking process. Of the different solution systems tested thus far, only two were capable of producing cracks; namely, the 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ solution and the 0.04 *m* UO_2SO_4 solution.

Some additional information on the role of the uranyl ion was obtained with U-bend specimens removed from the 2500-hr test in the boiling 0.04 *m* K_2SO_4 solution containing 0.02 *m* H_2SO_4, 0.005 *m* $CuSO_4$ and 50 ppm chloride. Upon completion of the test, the specimens were pickled in HNO_3-HF solution to remove surface films and returned to the original solution. Uranyl sulfate was added to make the solution 0.04 *m* and the test continued. During the initial 200 hr one of the duplicate specimens exhibited a crack. However, no further cracking developed during an additional 1300 hr of exposure.

In a second test, contradictory results were obtained in the presence of the uranyl ion. Duplicate U-bend specimens, after 2500 hr in boiling 0.04 *m* K_2SO_4 solution containing 0.02 *m* H_2SO_4 and 50 ppm chloride, were pickled to remove surface films and then exposed in boiling 0.04 *m* UO_2SO_4 solution containing 0.02 *m* H_2SO_4, 0.005 *m* $CuSO_4$ and 50 ppm chloride. Whereas, generally, cracking of type 347 stainless steel U-bend specimens occurs within a period of 400 hr, the present duplicate stress specimens have shown no evidence of cracking during 1500 hr of test.

Future work will deal with a more comprehensive study to define the effect of the uranyl ion on the stress-corrosion cracking process. Of special interest will be a study on the effect of uranium concentration as affecting cracking in boiling uranyl sulfate solutions.

3. Behavior in Chloride-Containing Water at Elevated Temperatures.

Previous laboratory studies have shown that stress-corrosion cracking in type 347 stainless steel exposed in distilled water at pH values of 2.8, 6.5, and 10.5 and containing from 25 to 100 ppm chloride can occur at temperatures of 150, 200, 250 and 300°C.(24,25) It was also demonstrated that the incidence of cracking was independent of the dissolved oxygen content in the range of approximately 10 to 1200 ppm under similar conditions of chloride concentration, water pH and temperature. Furthermore, no evidence of cracking was observed in stressed type 347 stainless steel after 3000 hr in pH 2.8 distilled water containing 50 to 500 ppm chloride at atmospheric boiling with air-aeration of the test solutions. However, at 100°C in distilled water containing 100 ppm chloride at pH values of 2.8 and 10.5, cracking was produced in seven of eight specimens in 400 hr or less when the environments were initially pressurized with 150 psi of oxygen at room temperature.

In order to determine the susceptibility of type 347 stainless steel to cracking in chloride-containing distilled water in the absence of oxygen, tests were run at 300°C in solutions containing 100 ppm chloride at adjusted pH values of 2.8, 6.5 and 10.5. After the U-bend stress specimens and solutions were placed in stainless steel autoclaves, a double freezing-vacuum degassing treatment was used to remove oxygen. After 400 hr, four of the six stress specimens in solutions with initial pH values of 2.8 and 10.5 had cracked. No cracks were observed after 400 hr in specimens exposed to the pH 6.5 solution.

Since some doubt exists regarding the efficiency of the degassing operation, it cannot be stated with certainty that cracking occurred in the absence of oxygen. Tests are being run in which sodium sulfite has been added to solutions as an oxygen scavenger. The amount of sodium sulfite used in each test was double the amount of oxygen theoretically present. To date, no cracking has been observed after 400 hr of test. Residual sulfite concentrations of 15 to 80 ppm at the end of each 100 hr period indicate the complete removal of oxygen. These data are in support of the recent work reported by the Bettis Plant of Westinghouse Electric Corporation in Pittsburgh.(26) In the Bettis studies, no cracking of type 347 stainless steel was obtained at 260°C in synthetic boiler water containing 50 ppm chloride and sodium sulfite. However, when the chloride content was increased to 500 ppm, cracking was observed in solutions containing low residual concentrations of sodium sulfite.

Preliminary studies (reported in a preceding section) showed that a film formed on type 347 stainless steel by exposure in boiling, chloride-free HRT core solution effectively eliminated cracking sensitivity when chloride was added to a similar environment. Therefore, the use of a pre-formed film was investigated as a means for combatting stress-corrosion cracking in chloride-containing distilled water at 200°C. Prefilming of stress U-bend specimens was accomplished by two methods: (1) heating in chloride-free distilled water for 100 hr at 300°C, and (2) heating for 100 hr at 300°C in distilled water containing 500 ppm chromate added as sodium chromate. The filmed specimens were then placed in distilled water at 200°C which contained 100 ppm chloride. The 200°C temperature was chosen because previous work showed that the time to cracking was shorter and the frequency of cracks was considerably greater than was observed at other temperatures.

All of the prefilmed stress specimens cracked in 100 hr or less. Further testing is planned to determine if films formed in boiling uranyl sulfate solution will resist cracking in chloride-containing water at elevated temperatures.

B. Stress-Corrosion Cracking of Alternate Alloys.

In addition to type 347 stainless steel, the stress-corrosion cracking behavior of a number of other alloys was examined at 300°C in water containing 100 ppm chloride. Adjusted initial pH values of 2.8, 6.5 and

10.5 were used in the tests; pH adjustments were made with either hydrochloric acid or sodium hydroxide. No adjustment was made on the pH 6.5 water. The materials subjected to test included types 304, 304 ELC, 309 SCb, 316, 321, Carpenter 7-Mo and Croloy 16-1 stainless steels as well as Incoloy and Nionel. A summary of the results obtained thus far appears in Table XIII. All tests were run or are being continued in the presence of oxygen.

All of the austenitic 300 series stainless steels with the exception of type 309SCb cracked within a period of 300 hr and less. In the case of the type 309SCb stainless steel, the accumulated test time of 200 hr may not be sufficiently long to produce cracking. The test is being continued. Type 304 stainless steel was tested in both annealed and sensitized condition in order to determine if the nature of the cracking process was similar in each case. Figures 13 and 14 are photomicrographs of the annealed and sensitized alloy, respectively, that were made upon completion of the tests. In both conditions, the nature of the cracking was predominantly transgranular. It is of interest to note, however, that the width of the cracks in the sensitized condition was appreciably greater than that of the cracks in the annealed condition.

Carpenter 7-Mo stainless steel was found to crack in both annealed and full-hard conditions when exposed in the chloride-containing water with an initial pH of 2.8. However, when the initial water pH was increased to 10.5, no cracking occurred during a 300-hr test period in the annealed condition and during a 100-hr test in the full-hard condition. The tests are being continued.

Of particular interest in the stress-corrosion cracking study was the behavior of the three alloys, Croloy 16-1 stainless steel, Incoloy and Nionel. Croloy 16-1 is similar in composition to low-carbon type 431 stainless steel and contains 16% Cr and 1% Ni. No cracking occurred on U-bend stress specimens of the material during periods up to 600 hr at 300°C in water containing 100 ppm chloride at initial pH values of 2.8, 6.5, and 10.5. The alloy exhibited a pronounced susceptibility to pitting

TABLE XIII

Stress-Corrosion Cracking Behavior of Various Alloys at 300°C in Distilled Water with 100 ppm Chloride (Saturated with Air at Room Temperature)

Alloy Type	Condition	Solution pH	Time (hr)	Observations
304	Annealed	2.8	100	Cracked
304	Annealed	10.5	100	Cracked
304	Sensitized	2.8	100	Cracked
304	Sensitized	10.5	100	Suspected cracks
304ELC	Annealed	2.8	300	Surface crazing. Few pits.
309SCb	Annealed	2.8	200	No cracks
316	Annealed	2.8	200	Cracked
321	Annealed	2.8	200	Cracked
321	Annealed	10.5	200	No cracks
Carp. 7-Mo	Annealed	2.8	300	Suspected cracks. Moderate general corrosion.
Carp. 7-Mo	Annealed	10.5	300	No visible cracks. Thin hard film.
Carp. 7-Mo	Full Hard	2.8	100	Cracked. Moderate general corrosion.
Carp. 7-Mo	Full Hard	10.5	100	No visible cracks.
Croloy 16-1	Annealed	2.8	600	Severe pitting. Thick scale. No cracks.
	Annealed	6.5	200	Severe pitting. No cracks.
	Annealed	10.5	400	Severe pitting. No cracks.
Incoloy	Annealed	2.8	500	Severe pitting. Heavy corrosion, cracked.
	Annealed	6.5	100	Light general corrosion. No cracks.
	Annealed	10.5	300	Few small pits. Light corrosion. No cracks.
Nionel	Annealed	2.8	200	Heavy loose scale. No cracks.
	Annealed	6.5	100	Deep pits. Thick scale. No cracks.
	Annealed	10.5	100	Light general corrosion. No cracks.

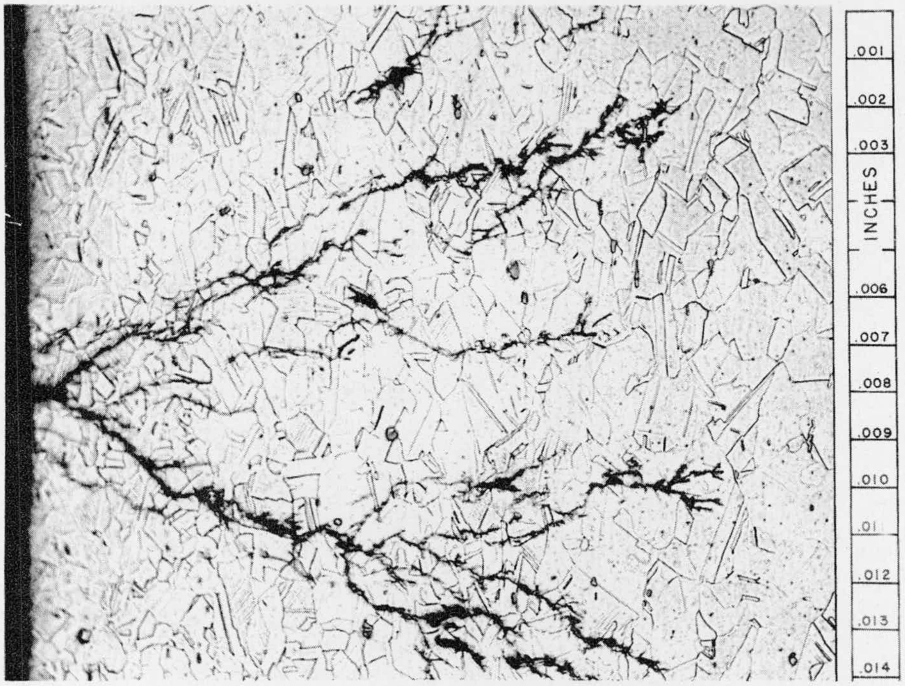

Fig. 13. Photomicrograph of Stress-Corrosion Cracking in Annealed Type 304 Stainless Steel After 100-hr Exposure to Distilled Water Containing 100 ppm Chloride at pH 2.8. Magnification 250X. (T13919)

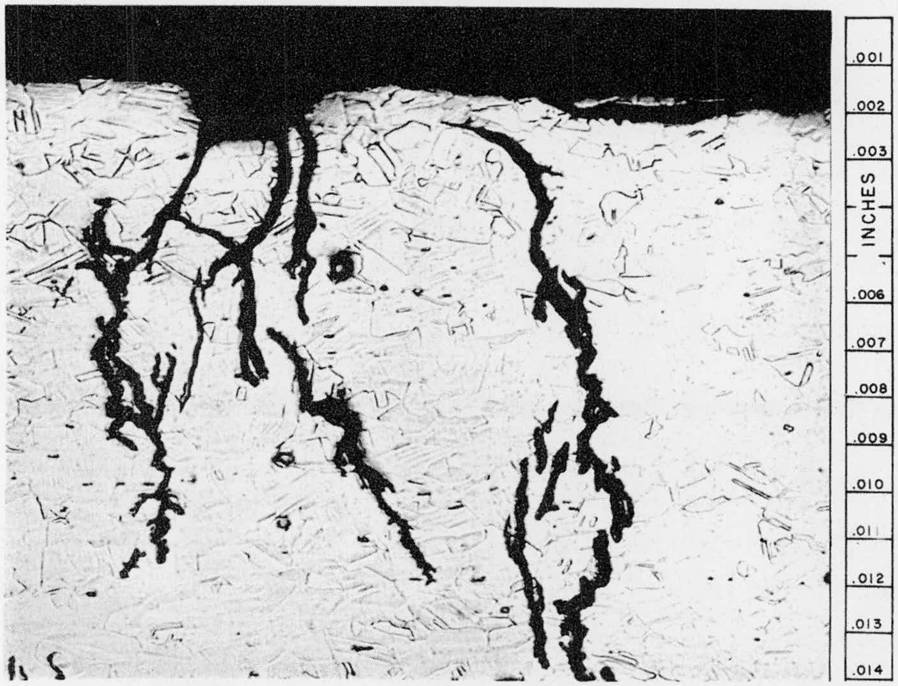

Fig. 14. Photomicrograph of Stress-Corrosion Cracking in Sensitized Type 304 Stainless Steel after 100-hr Exposure to Distilled Water Containing 100 ppm Chloride at pH 2.8. Magnification 250X. (T14242)

attack in all environments, however. In addition to the distilled water environments, tests were made in boiling 42% $MgCl_2$ solution. No cracking was visible at 15X magnification after 100 hr. However, metallographic examination at higher magnification disclosed two cracks that were transgranular in nature. A photomicrograph of the cracks is shown in Figure 15.

Incoloy, an alloy containing 20% Cr, 32% Ni plus Co, and balance iron, developed small cracks after 500 hr at 300°C in 100 ppm chloride-containing water at an initial pH of 2.8. The transgranular nature of the cracks is illustrated by photomicrographs in Figures 16 and 17. No cracking has been found after 100 and 300 hr, respectively, in the chloride-containing environment at initial pH values of 6.5 and 10.5. The tests are being continued.

Nionel, with a composition of 19% Cr, 40% Ni and balance iron, has resisted cracking in all environments shown in Table XIII. However, accumulated test times, thus far, are relatively short, 200 hr. The alloy was found more resistant to general corrosion and pitting attack than either Incoloy or Croloy 16-1 stainless steel.

The results obtained to date in the chloride-containing distilled water at 300°C substantiate cracking data that were obtained in boiling 42% $MgCl_2$ solution, particularly for the austenitic stainless steels. Increased nickel contents in the various alloys tested appeared to reduce the susceptibility to cracking and in the case of Nionel with a nickel content of 40%, no cracking has been observed to date.

C. Corrosion Behavior of Electroless Nickel Plate.

The corrosion resistance of carbon steel in oxygenated steam or in water can be markedly improved by deposition of a thin layer of nickel on the surface of the steel. A technique of nickel deposition by a non-electrolytic process has been developed by the National Bureau of Standards.(27) Coupons of SAE 1045 carbon steel plated to a thickness of 2 mils by this method were tested at 300°C in distilled water under various pH conditions. A graph of weight losses as a function of exposure time for the different

Fig. 15. Photomicrograph of Stress-Corrosion Cracks in Croloy 16-1 Stainless Steel after 100-hr Exposure to Boiling 42% $MgCl_2$. Magnification 250X. (T13645)

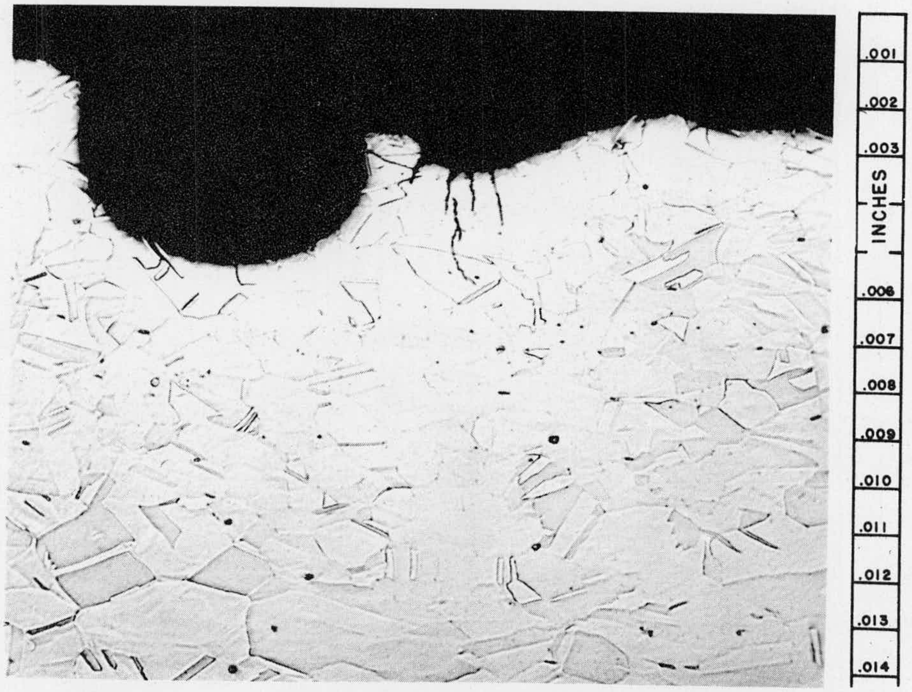

Fig. 16. Photomicrograph of Stress-Corrosion Cracking in Incoloy after 500-hr in Distilled Water at 300°C Containing 100 ppm Chloride at pH 2.8. Magnification 250X. (T-13569)

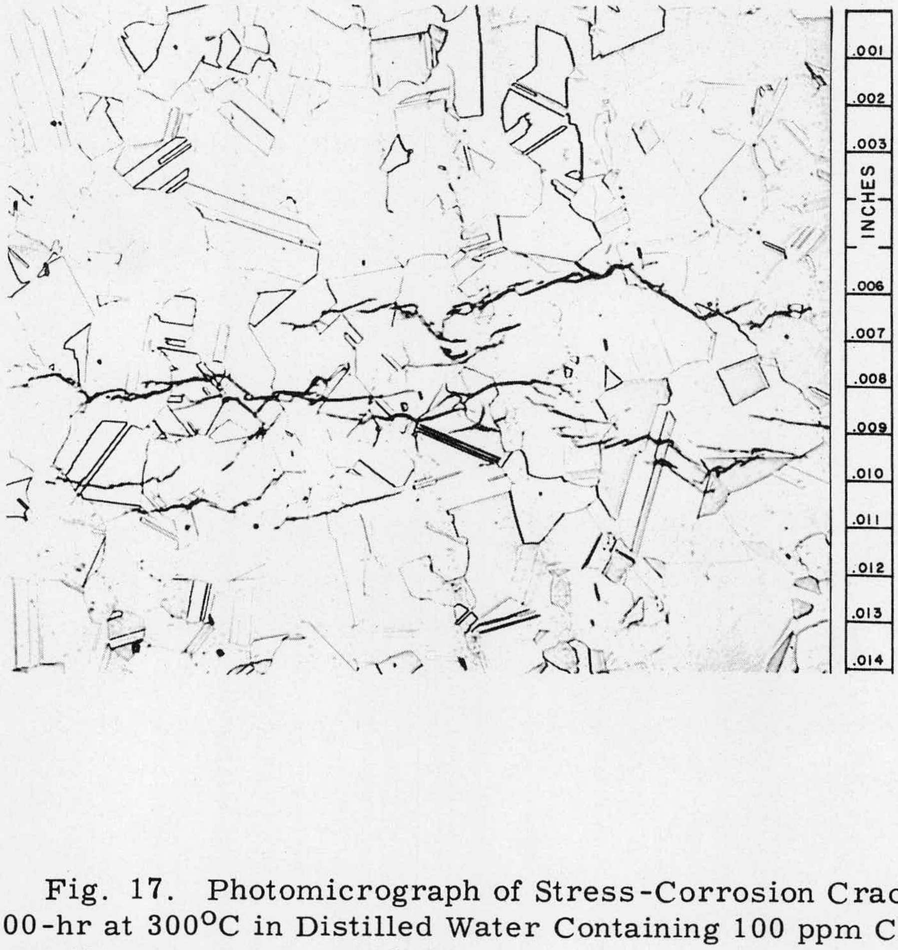

Fig. 17. Photomicrograph of Stress-Corrosion Cracking in Incoloy after 500-hr at 300°C in Distilled Water Containing 100 ppm Chloride at pH 2.8. Magnification 250X. (T13568)

test conditions appears in Figure 18. The superior corrosion behavior was exhibited by specimens exposed in water adjusted to pH 10.5 with trisodium phosphate; the corrosion rate remained constant at a value not greater than 0.4 mpy during the 2000-hr test. In water adjusted to a pH of 2.5 by the addition of sulfuric acid, the initial 100-hr rate was appreciably high, 10 mpy. The rate decreased with time, however, to a value of 1 mpy after 200 hr. The addition of 50 ppm chloride to the same environment resulted in a similar corrosion behavior except that the initial 100-hr corrosion rate was somewhat lower, 7 mpy. The 2000-hr rate was approximately 1 mpy.

Good corrosion resistance was also obtained in pH 7.5 water that was adjusted with trisodium phosphate. After an initial 100-hr rate of approximately 1 mpy, the rate decreased to 0.2 mpy after 2000 hr.

No significiant pitting attack was observed on any of the specimens but in a few instances, the plate was chipped off sharp corners emphasizing the necessity of careful design and preparation of parts to be protected by this method. The exposed areas of steel underwent a shallow pitting attack.

The ability of the nickel plate to withstand thermal cycling was demonstrated by tests in which specimens were heated in air to 300°C, maintained at this temperature for 2 hr, and then cooled in air to room temperature. After 25 such cycles, there was no indication of a separation between the nickel plate and the carbon steel base metal.

D. Miscellaneous Corrosion Tests.

On the basis of their physical and mechanical properties, a number of materials could find use in homogeneous reactors provided they were sufficiently corrosion resistant to the environments to which they would be exposed. A resume of the results of corrosion tests on some possible useful materials follows.

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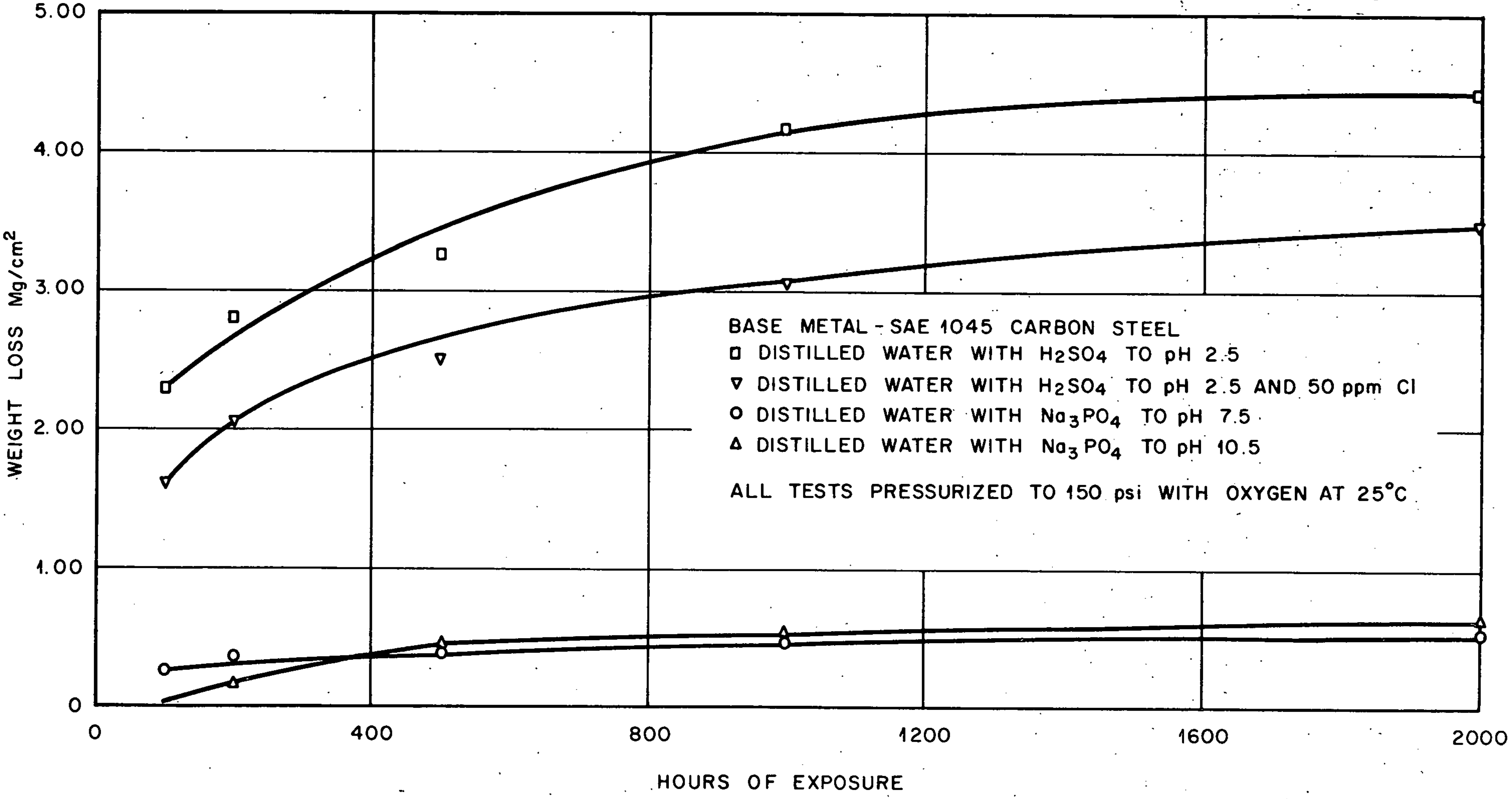

Fig. 18. Weight Losses of Electroless Nickel Plate at 300°C

1. Incoloy.

The general corrosion behavior of Incoloy, a high-nickel alloy, was examined in several HRT-related environments, namely, 5% HNO_3 solution and HRT core solution consisting of 0.04 *m* UO_2SO_4, 0.02 *m* H_2SO_4, and 0.005 *m* $CuSO_4$. Of considerable interest was the stress-corrosion cracking behavior of the alloy in boiling HRT core solution containing 50 ppm chloride and in boiling 42% $MgCl_2$ solution.

Material was procured as cold-rolled, annealed, and pickled 1/8 in.-thick plate having a hardness of 64 Rockwell B. The actual chemical composition of the Incoloy was as follows: 0.04% C, 20.7% Cr, 32.5% Ni, 0.8% Mn, and balance iron plus small amounts of copper and silicon.

Results of the corrosion tests appear in Table XIV. The corrosion resistance of the alloy in the uranyl sulfate and nitric acid solutions was excellent at all temperatures; observed rates were 1 mpy and less for 1000-hr tests. Stress specimens were exposed in boiling 42% $MgCl_2$ solution, in HRT core solution at 300°C, and in boiling HRT core solution containing 50 ppm chloride as potassium chloride. In no case was there any positive indication of stress-corrosion cracking. At the end of the 100-hr test in the magnesium chloride solution, examination at 90X magnification disclosed what appeared to be a superficial crazing. Positive identification as to the existence of actual cracks will be determined by metallographic examination.

In summary, the general corrosion behavior of Incoloy in static systems is quite comparable to that of type 347 stainless steel exposed to similar conditions. In chloride environments Incoloy demonstrated a remarkable resistance to stress-corrosion cracking.

2. Type AM-350 Stainless Steel.

Type AM-350 stainless steel is a precipitation-hardenable alloy and could conceivably be used in the Homogeneous Reactor Program for such applications as check valves in injection-type pumps, valve trim, bolting

TABLE XIV

Corrosion of Incoloy by Various Environments
(1000-hr Tests)

Specimen Type	Environment	Temp (°C)	Corrosion Rate (mpy)(1) and Remarks
Coupon	HRT Core Solution(2)	Boil	0.1
Coupon	HRT Core Solution	200	1.0
Coupon	HRT Core Solution	300	0.8
Coupon	5% HNO_3	Boil	0.1
U-bend(3)	42% $MgCl_2$	154	No cracks
U-bend	HRT Core Solution	300	No cracks (0.7 mpy)
U-bend	HRT Core Solution plus 50 ppm Chloride	Boil	No cracks

(1) Determined from defilmed weight losses

(2) 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$

(3) 100-hr test

material, etc. Accordingly, corrosion tests were conducted to evaluate the corrosion behavior of the alloy in a number of heat-treated conditions in reactor-related environments. The nominal composition of the alloy is 0.08% C, 17% Cr, 4% Ni, 2.7% Mo, 0.87% Mn, and balance iron.

The corrosion resistance was examined in four heat-treated conditions in a solution containing 0.04 *m* UO_2SO_4, 0.02 *m* H_2SO_4, and 0.005 *m* $CuSO_4$ at temperatures of 100, 200, and 300°C and in boiling 5% HNO_3 solution. Stress-corrosion cracking behavior of the alloy was examined in the former solution containing 50 ppm chloride at its boiling point.

Prior to heat treatment, all test specimens were subjected to an annealing treatment in air for 2 hr at 1950°F followed by air cooling. The subsequent heat-treating operations resulted in hardness values up to 49 Rockwell C. Heat treatment of annealed specimens consisted of the following:

a. Cooled 2 hr at -100°F (39 Rockwell C)
b. Cooled 2 hr at -100°F and tempered 1 hr at 750°F (49 Rockwell C)
c. Aged 1 hr at 1350°F (32 Rockwell C)

Corrosion - test results for the type AM-350 stainless steel are summarized in Table XV. In the uranyl sulfate solution at 100°C and at 300°C, observed corrosion rates were 0.6 mpy or less, indicative of excellent corrosion behavior throughout the 1000-hr tests. There was no apparent effect of heat-treatment on corrosion resistance in the two environments. At 200°C, however, corrosion rates were appreciably higher, ranging from 5 to 11 mpy. The highest rate was observed on an annealed specimen. Considerable filming of specimens occurred in the 200°C tests.

The corrosion resistance of both annealed and subzero cooled specimens in boiling 5% HNO_3 solution was high with rates not in excess of 0.5 mpy. In the aged condition (1 hr at 1350°F), however, the rate increased to 3 mpy. Some shallow pitting was noted on annealed specimens.

TABLE XV

Corrosion Behavior of Type AM-350 Stainless Steel in Reactor-Related Environments (1000-hr Tests)

Heat Treatment	Hardness	Corrosion Rate (mpy)(1) 5% HNO_3 (100°C)	HRT Core Solution (100°C)	(200°C)	(300°C)
Annealed	92 Rockwell B	0.5	< 0.1	11.0	0.4
-100°F, 2 hr	39 Rockwell C	0.3	0.1	4.8	0.6
-100°F, 2 hr 750°F, 1 hr	49 Rockwell C(2)	-	0.5	-	-
1350°F, 1 hr	32 Rockwell C	3.0	0.3	6.5	0.3

(1) Determined from defilmed weight losses.

(2) Observed value higher than literature-reported value of 41 Rockwell C.

Stress specimens in the cooled and tempered condition (2 hr at -100°F followed by 1 hr at 750°F) were exposed in a boiling 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ solution containing 50 ppm chloride. Both specimens cracked during the first 50 hr. The corrosion rate, 0.5 mpy, was identical with the rate obtained in a similar chloride-free environment.

Additional testing of type AM-350 stainless steel consisted of determining the corrosion behavior of the alloy in the cooled and tempered condition and welded to type 347 stainless steel. Two types of welds were examined, butt and seal welds. Both were made with heliarc without using filler rod. The specimens were exposed for 1000 hr in the boiling 0.04 *m* UO_2SO_4 solution containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$. Assuming that the type 347 stainless steel underwent negligible attack in the environment, the corrosion rate on the butt-welded type AM-350 stainless steel was 0.7 mpy whereas the seal-welded specimen corroded at a rate of 1.5 mpy. Neither specimen showed any evidence of localized attack in the heat-affected zone of the AM-350 alloy.

3. Stellites 1, 3, and 98M2; Rexalloy 33.

Four materials of interest to the HRP injection-pump program were tested in boiling and aerated 0.04 *m* UO_2SO_4 solution containing 0.02 *m* H_2SO_4 and 0.005 *m* $CuSO_4$. The materials included Stellites 1, 3, and 98M2 and Rexalloy 33. The form of the specimens as received was as follows: (1) a check valve seat of deposited Stellite 1; (2) a check valve seat of cast Stellite 3; (3) rectangular blocks of cast Stellite 98M2; and (4) a check valve ball of cast Rexalloy 33, a product of Crucible Steel Company of America. The nominal chemical compositions, hardnesses, and observed corrosion rates for the four materials are reported in Table XVI. Stellite 98M2 was corroded at the highest rate, 5 mpy, for the 1000-hr test. The other three alloys corroded at rates ranging from 0.5 to 1.3 mpy. The specimens were not defilmed since with one exception, they acquired no visible film during the course of the tests. The surfaces of the Stellite 98M2 specimens were uniformly

TABLE XVI

Corrosion of Stellites and Rexalloy 33 by Boiling HRT Core Solution*

(1000-hr Tests)

Material	Nominal Composition (wt %)	Hardness (Rockwell C)	Corrosion Rate (mpy)
Stellite 1	2.5 C, 12 W, 30 Cr balance cobalt	55	1.3
Stellite 3	2.5 C, 12.5 W, 30.5 Cr, 3 Fe, 3 Ni, 47 Co, 1.5 others	57	0.5
Stellite 98M2	2 C, 18 W, 30 Cr, 38 Co, 2 Fe, 3.5 Ni, 1 Mo, 5.51 others	63	5.0
Rexalloy 33	2.25 C, 17 W, 33 Cr, 44 Co, balance iron	61	0.8

*0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m $CuSO_4$

coated with golden-colored crystals, the major constituent of which was determined to be tungsten by spectrographic analysis. Hence, all of the above materials with the possible exception of Stellite 98M2 showed adequate corrosion resistance to the static uranyl sulfate solution at approximately 100°C.

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