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I. SUMMARY:

A number of loop runs have been made to determine the chemical stability of possible fuel solutions, and the results obtained from these runs have been compared with data obtained by others. A solution containing 0.04 m UO_2SO_4 , 0.03 m CuSO_4 , 0.03 m NiSO_4 and 0.023 m D_2SO_4 in heavy water was not completely stable at 175°C or at other higher temperatures. About 7% of the copper was lost at 175°C to 275°C, and an additional 9% was lost when the temperature was increased to 300°C. In the same solution the nickel solubility decreased by 40% up to 200°C and then increased up to 275°C and at 300°C again decreased. Throughout the run no uranium was lost from solution.

A second solution containing 0.01 m UO_2SO_4 , 0.02 m D_2SO_4 , 0.01 m CuSO_4 and 850 ppm nickel in heavy water was stable at 300°C. However, when an additional 450 ppm of nickel was added to the solution, about 10% of the uranium, 6% of the copper, and 20% more nickel than was added in the final addition precipitated from solution.

Several other runs were made in which 0.04 m UO_2SO_4 solutions containing 0.025 m D_2SO_4 , 0.03 m CuSO_4 and 0.04 m alkali or alkaline-earth metal sulfates were circulated at 300°C in a titanium loop. Solutions containing lithium and rubidium sulfate lost 30 and 15% of their copper, respectively. The loss of copper from solutions containing either beryllium or magnesium sulfate was no greater than 5%. Other runs with the latter two solutions in stainless steel loops showed that the beryllium-containing solution was more corrosive and the magnesium-containing solution less corrosive than the same solution without the added sulfate salt.

Previous runs in stainless steel loops have shown that the removal of oxygen from uranyl sulfate solutions results in the precipitation of uranium and severe corrosion of the stainless steel. An attempt was made to minimize corrosion in such cases by the addition of magnesium sulfate to the solution prior to precipitation. No beneficial effect due to the presence of magnesium sulfate was observed.

Experiments designed to determine the corrosiveness of the heavy-liquid phase of a uranyl sulfate solution above its separation temperature showed that titanium and Zircaloy-2 were only very slightly attacked by the heavy phase. Type 347 stainless steel, on the other hand, was attacked at a high rate.

Tests that were previously reported showed that the rate of attack of carbon steel by boiler water at 300°C was proportional to the oxygen concentration in the range of < 1 to 10 ppm. Runs made under identical conditions except the solution containing 50 ppm of chloride have shown the chloride ions to be without effect on the corrosion of carbon steel. However, some stress-corrosion cracking of austenitic stainless steel specimens was observed in the presence of chloride ions. ↑

The ability of ruthenium, either as a salt, oxide, or metal, to catalyze the oxidation of chromium (III) to chromium (VI) in sulfuric acid solutions was demonstrated. Since chromium (VI) inhibits corrosion in sulfuric acid solutions, ruthenium can be classed as a corrosion inhibitor although its action is an indirect one. Previously the same effect of ruthenium was demonstrated in uranyl sulfate solutions. Whether ruthenium functions in the same manner during in-pile corrosion tests remains to be seen.

The removal of oxygen from chloride-containing water at 300°C has prevented cracking of type 3A7 stainless steel during 2000-hr tests. With oxygen present in similar environments, 100% of the specimens tested underwent cracking in 500 hr or less.

The pre-exposure of type 3A7 stainless steel stress specimens in boiling, chloride-free uranyl sulfate solution was 100% effective in preventing stress-corrosion cracking in a similar environment containing 50 ppm of chloride. In the absence of the pre-exposure, 55% of the specimens tested in the chloride-containing environment cracked. Prefilming in uranyl sulfate solution at 125, 150, 175, and 200°C has also been completely effective in preventing cracking in the boiling, chloride-containing solution.

The corrosion resistance of Nichel was nearly comparable to that of type 3A7 stainless steel in several reactor-related environments. Its apparent immunity to cracking in chloride-containing uranyl sulfate makes its use especially attractive.

Flame-Plate, a hard-facing material, and also type 202 stainless steel in a sensitized condition were found to be unsatisfactory for service in uranyl sulfate solutions. The corrosion resistance of CD-4MCu, a cast, age-hardenable alloy, was excellent in reactor-related environments. The alloy was tested in a number of heat-treated conditions, and in all cases corrosion rates were 0.7 mpy or less. Of particular interest was the fact that the alloy was not subject to cracking in boiling uranyl sulfate solution containing 50 ppm of chloride. ↓

II. INTRODUCTION

The data presented in the following pages represent the detailed results obtained during the past quarter (April 30, 1958, to July 31, 1958) by the out-of-reactor Solution Corrosion Group of the Homogeneous Reactor Project. A summary of the data has been given in Homogeneous Reactor Project Quarterly Progress Report for the quarters ending April 30, 1958, and July 31, 1958.

The data presented in this report 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. Burton, S. E. Bolt, W. C. Ulrich, E. S. Snively, N. E. Wisdom,* H. C. Savage, J. C. Griess)

A. Stability and Corrosiveness of Dilute Fuel Solutions

1. 0.04 m UO_2SO_4 Containing Initially 0.023 m D_2SO_4 , 0.03 m CuSO_4 , and 0.03 m NiSO_4 at Various Temperatures

The addition of nickel sulfate to dilute fuel solutions has been shown to cause partial precipitation of copper and nickel at 300°C.¹ In order to determine the effect of temperature on the amounts precipitated, a run was started with 0.04 m UO_2SO_4 containing initially 0.023 m D_2SO_4 , 0.03 m CuSO_4 , and 0.03 m NiSO_4 (1800 ppm Ni) in heavy water at 175°C. The temperature was then raised to 300°C in increments of 25°C with several days of circulation at each temperature. Table I lists the compositions of the solutions which were stable for the short periods of circulation at each temperature. As can be seen, some of the copper and nickel precipitated on startup. The copper concentration fluctuated around 1800 ppm up to 275°C and then more precipitated at 300°C. The nickel concentration decreased up to 200°C, then showed an increasing solubility up to 275°C, and finally more precipitated at 300°C. No uranium was lost from solution at any temperature during the run. At 300°C the nickel and copper concentrations were 1200 and 1600 ppm, respectively.

* Summer employee.

Also listed in Table I is the molality of the sulfate ion found in solution, the molality of the deuterium ion present in solution, and two ratios called the "Marshall" and "Modified Marshall" ratios, respectively. The Marshall ratio is defined as $1/2 U + Cu + Ni/SO_4$ with each ion concentration being in units of molality. The Modified Marshall ratio is $1/2 U + Cu + Ni/\sum \text{cations}$ ($\sum \text{cations} = D^+ + U + Cu + Ni$), again the units being molal.

Marshall and coworkers have found that in heavy water solutions of uranyl sulfate containing sulfuric acid, copper sulfate, and nickel sulfate at $300^\circ C$ in the range of total sulfate from 0.01 to 0.1 m, the solubilities of the various ions may be treated in the first approximation as acting independently.² They have determined the solubilities of uranium, copper, and nickel independently and together in the above range, and have shown that the Marshall ratio calculated and observed lies between 0.5 and 0.6. The observational points for the mixture lie within $\pm 5\%$ of the best line through the data, each point representing the combination of four analyses. In essence, the treatment of the data considers each cation as being tied up with a bisulfate ion and the uranium existing as a dimer, possibly $U_2O_5^{++}$. Nickel sulfate monohydrate has been identified by Marshall as one of the solid phases in equilibrium with the solution at $300^\circ C$. Antlerite ($3 CuO \cdot SO_3 \cdot 3 H_2O$) is suspected to be the other solid phase.

The Modified Marshall ratio is based on Marshall's treatment but was altered on the basis of empirical data from the LOOA loops. Since acid can form in a solution circulating at high temperature in a stainless steel loop from the oxidation of chromium to the hexavalent state and from the hydrolytic precipitation of basic sulfate salts, or oxides, it was felt necessary to include the acid concentration explicitly. In this case the acid concentration is entered as molality of deuterium ion (i.e., for $0.025 \text{ m } D_2SO_4$ this would be $0.05 \text{ m } D^+$).

The meaning of these ratios, beyond the very interesting and important significance attached by Marshall to his values at $300^\circ C$, is strictly a relative one. The values at each temperature will have to be related to those from other solutions in which the uranium, copper, nickel, and acid concentrations are varied widely. In this way

after the accumulation of sufficient empirical ratios, a given solution could be listed as probably stable or unstable at the temperature of interest if the calculated ratio were less than or greater than, respectively, the average empirical ratio for other solutions at that temperature.

Looking at the value of the Marshall ratio at 300°C in Table I (the only one for which other data exist for comparison), it appears very slightly higher than the 0.5 to 0.6 value expected. This could represent either an effect of uranium concentration (Marshall has only worked at uranium concentrations up to 0.02 m) or a nonequilibrium value. However, the ratio of 0.649 at room temperature would certainly be indicative of a solution which would be unstable at 300°C.

The Modified Marshall ratio will be discussed below. None of its values can at this point be related to solution stability.

Table I. Steady State Concentrations and Concentration Ratios of Ions in Heavy Water Solution Initially Containing 0.04 m UO_2SO_4 , 0.023 m D_2SO_4 , 0.03 m CuSO_4 and 0.03 m NiSO_4 at Several Temperatures

Temp. (°C)	Time (hr)	Concentrations					Marshall Ratio $\frac{1/2 \text{ U} + \text{Cu} + \text{Ni}}{\sum \text{SO}_4}$	Modified Marshall Ratio $\frac{1/2 \text{ U} + \text{Cu} + \text{Ni}}{\text{U} + \text{Cu} + \text{Ni} + \text{D}}$
		U^{+6} m	Cu^{++} ppm	Ni^{++} ppm	$\sum \text{SO}_4^{--}$ m	D^{+} m		
Init. Sol'n.		0.04	1900	1800	0.115	0.045	0.649	0.535
175	260	0.04	1750	1600	0.107	0.041	0.647	0.532
200	140	0.04	1800	1050	0.099	0.041	0.624	0.503
225	120	0.04	1800	1100	0.099	0.041	0.630	0.505
250	120	0.04	1750	1350	0.104	0.043	0.628	0.509
275	170	0.04	1750	1600	0.108	0.043	0.642	0.524
300	240	0.04	1600	1200	0.100	0.046	0.609	0.480

2. 0.01 m UO_2SO_4 Containing 0.02 m D_2SO_4 , 0.01 m CuSO_4 , and Various Amounts of NiSO_4 at 300°C

Since the HRT is currently being operated with uranyl sulfate solution in the blanket at a concentration roughly one-third that in the core, viz., about 0.01 m, it was of interest to investigate the phase stability of such dilute solutions. The solution chosen, 0.01 m UO_2SO_4 + 0.02 m D_2SO_4 + 0.01 m CuSO_4 in heavy water, was one shown to be stable in quartz tube tests.³ It should be noted that the acid and copper concentrations in this solution were greater than those in the blanket of the HRT.

The solution was circulated for 200 hr at 300°C and was entirely stable. Two batch additions of nickel sulfate in heavy water were made 14 days apart, each calculated to add about 450 ppm nickel to the solution. The solution remained stable for 500 hr with up to 890 ppm nickel. A third addition of nickel sulfate, however, caused precipitation of about 10% of the uranium, 6% of the copper, and about 20% more nickel sulfate than was added the third time.

Table II shows the analytical values for uranium, copper, nickel, sulfate, and deuterium ions at several stages during the run. The final row shows the values after equilibrium with the solid phases of the uranium, copper, and nickel precipitates had presumably been attained. The final two columns give the Marshall and Modified Marshall ratios (see above). The original value of the Marshall ratio, 0.345, being much less than 0.5 to 0.6, suggests that the solution would be stable at 300°C, as it was. Again, after the first nickel addition the value of 0.460 is enough lower than 0.5 to give evidence of stability. However, after the second nickel addition the value of 0.514 indicates the solution was close to saturation. Peculiarly enough, the value after the third addition, 0.466, was so low as to suggest that either (a) the large amount of nickel that precipitated carried down uranium and copper and that equilibrium between the solids and solution was not maintained, or (b) the solution was supersaturated prior to the third addition. Also, of course, errors in analysis could have caused the discrepancy. The Modified Marshall ratios will be discussed as follows:

Table II. Concentrations and Concentration Ratios of Ions in Heavy Water Solution Initially 0.01 m UO_2SO_4 Containing 0.02 m D_2SO_4 and 0.01 m CuSO_4 upon Additions of Nickel Sulfate at 300°C

Solution	U^{+6} m	Cu^{++} ppm	Ni^{++} ppm	SO_4^{--} m	D^+ m	Marshall Ratio	Modified Marshall Ratio
Original	0.010	580	0	0.042	0.040	0.345	0.238
After first nickel add'n.	0.010	580	470	0.048	0.040	0.460	0.329
After second nickel add'n.	0.010	580	890	0.057	0.040	0.514	0.395
After third nickel add'n.	0.009	550	700	0.055	0.041	0.466	0.365

3. 0.04 m UO_2SO_4 Containing Initially 0.025 m D_2SO_4 , 0.03 m CuSO_4 , and 0.04 m Alkali or Alkaline-Earth Metal Sulfate

In addition to the above tests, four runs were made in a titanium loop to study stability of solutions containing added alkali or alkaline earth-metal sulfates. The results are shown in Table III (runs G-105, 107, 108, and 109). The solutions containing lithium and rubidium sulfate lost 30 and 15% of their copper, respectively, and the solutions containing beryllium and magnesium lost 5% of their copper. Since wide variations were present in the copper analyses, the loss of copper from the beryllium and magnesium-containing solutions was within analytical error. All solutions produced small amounts of solids containing up to 15% uranium, which were collected in a hydroclone underflow pot attached to the loop. The total amount of solids collected, however, was not enough to affect significantly the concentration of uranium in solution. The solution containing magnesium sulfate produced the least amount of solids and these contained only 3% uranium as determined by spectrographic analysis.

Further tests were made with the beryllium and magnesium-containing solutions. A corrosion test was made with the beryllium-containing solution (0.04 m UO_2SO_4 + 0.025 m H_2SO_4 + 0.01 m CuSO_4 + 0.04 m BeSO_4) in light water for

200 hr at 300°C. The weight losses of type 347 stainless steel coupons are plotted as a function of flow rate in Figure 1. For comparison, the results from a run with a similar solution not containing beryllium sulfate ($0.04 \text{ m } \text{UO}_2\text{SO}_4 + 0.025 \text{ m } \text{H}_2\text{SO}_4 + 0.01 \text{ m } \text{CuSO}_4$) are shown. As can be seen, the beryllium-containing solution was much more corrosive. The reason for the increased corrosiveness may be that the beryllium ions partially hydrolyzed at the high temperature and formed additional acid which intensified the attack on stainless steel.

Two corrosion tests were made with the magnesium-containing solution in light water ($0.04 \text{ m } \text{UO}_2\text{SO}_4 + 0.025 \text{ m } \text{H}_2\text{SO}_4 + 0.03 \text{ m } \text{CuSO}_4 + 0.04 \text{ m } \text{MgSO}_4$) for 200 hr at 250°C. The results are shown in Figure 2 in which the weight losses of type 347 stainless steel coupons are plotted versus flow rate. Again shown for comparison is a similar run without magnesium sulfate ($0.04 \text{ m } \text{UO}_2\text{SO}_4 + 0.025 \text{ m } \text{H}_2\text{SO}_4 + 0.01 \text{ m } \text{CuSO}_4$). In this case corrosion was much less in the magnesium-containing solution. However, the results from the two runs with magnesium sulfate did not agree. It appeared that chromium (VI) concentration increased to a greater extent in N-37 than in J-94 and provided increased corrosion inhibition. The reason for the greater chromium (VI) build-up in N-37 is not known.

A further solution stability test was made with the magnesium-containing solution in order to study the effect of nickel sulfate. Run J-95 was started with $0.04 \text{ m } \text{UO}_2\text{SO}_4 + 0.025 \text{ m } \text{H}_2\text{SO}_4 + 0.03 \text{ m } \text{CuSO}_4 + 0.035 \text{ m } \text{MgSO}_4$ in heavy water at 300°C and two batch additions of nickel sulfate dissolved in heavy water were made, each calculated to add 500 ppm Ni to the solution. The results are shown in Table III. Nickel, copper, and magnesium but not uranium precipitated after each addition. The nature of the precipitates was not determined. Even though the solution was not stable, the fact that nickel precipitated was significant. Nickel has a fairly high thermal neutron capture cross-section (4.6 barns) and its removal from solution would be desirable. Therefore, if nickel could be caused to precipitate as nickel sulfate simply by the addition of magnesium sulfate, the length of time between fuel processings could be increased with subsequent lower fuel costs.

Fig 1 Weight Losses of Type 347 Stainless Steel Coupons in Solutions With and Without Beryllium Sulfate Each Run 200 hr at 300°C

Fig. 2. Weight Losses of Type 347 Stainless Steel Coupons in Solutions With and Without Magnesium Sulfate. All Runs 200 hr. at 250°C

The Marshall ratios are not listed in Table III since Marshall's work has not been extended to include alkali and alkaline-earth sulfate additions. The Modified Marshall ratios are listed, however, having been calculated on the following basis:

$$\text{Alkali Sulfates; Ratio} = \frac{1/2 U^{+6} + 1/2 (Li^{+} \text{ or } Rb^{+}) + Cu^{++} + Ni^{++}}{\sum \text{ cations}}$$

$$\text{Alkaline-Earth Sulfates; Ratio} = \frac{1/2 U^{+6} + Mg^{++} \text{ or } Be^{++} + Cu^{++} + Ni^{++}}{\sum \text{ cations}}$$

The calculations were based on the premise that each cation unites with a bisulfate ion and that the uranium species is dimeric. Looking at Table III and back to Tables I and II at the values of the Modified Marshall Ratio at 300°C, it appears that the equilibrium value is 0.4 to 0.5. The most striking regularity is in the last value in Table I (0.48) and the last three values in Table III (0.50). That is, the ratio changed very little from 0.5 for magnesium concentrations from zero to 0.035 m and for nickel concentrations from zero to 1200 ppm. If the ratio numerator is multiplied by two, the ratio value becomes equal to 1.0, and hence multiplying through by the denominator and subtracting out equal terms, the result is that

$$D^{+} = Cu + Ni + Mg$$

That is, the amount of deuterium ion to be added to achieve a stable heavy water solution at 300°C is roughly the sum of the copper, nickel, and (if present) magnesium. Following this principle further, beryllium requires slightly less acid (ratio = 0.53) but lithium and rubidium require somewhat more acid (ratio = 0.38 and 0.41, respectively). Obviously further solutions must be studied and a range of temperatures investigated in order to confirm the above ratios and to establish the temperature dependence of the ratios.

Of the solutions investigated, the magnesium-containing one (0.04 m UO_2SO_4 + 0.025 m D_2SO_4 + 0.03 m $CuSO_4$ + 0.035 m $MgSO_4$) appeared most promising, both from a stability and from a corrosion standpoint.

Table III. Final Concentrations of Solutions Initially Containing
 $0.04 \text{ m } \text{UO}_2\text{SO}_4$, $0.025 \text{ m } \text{D}_2\text{SO}_4$, 0.035 m
 Added Sulfate and $0.03 \text{ m } \text{CuSO}_4$ (1900 ppm Cu)
 in Heavy Water Circulated for 200 Hr at 300°C

Run No.	UO_2SO_4 m	D_2SO_4 m	Added Sulfate m	Copper ppm	Nickel ppm	Modified Marshall Ratio
			Li_2SO_4			
G-108	0.04	0.033	0.035	1300	< 30	0.38
			Rb_2SO_4			
G-109	0.04	0.026	0.021	1600	< 30	0.41
			BeSO_4			
G-107	0.04	0.025	0.035	1800	< 30	0.53
			MgSO_4			
G-105	0.04	0.029	0.035	1800	< 30	0.50
			MgSO_4			
J-95 after first NiSO_4 add'n.	0.04	0.029	0.028	1650	250 ^b	0.50
			MgSO_4			
J-95 after second NiSO_4 add'n.	0.04	0.026	0.020	1400	500 ^b	0.50

a) No rubidium was lost.

Through an error the original Rb_2SO_4 concentration was 0.021 m.

b) Nickel added batchwise as nickel sulfate in an amount calculated to give 500 and 1000 ppm, respectively, in the two parts of the run.

B. Oxygen Exhaustion Studies Concluded

The previous report discussed at length runs made at 250 and 280°C with 0.04 m $\text{UO}_2\text{SO}_4 + 0.025 \text{ m H}_2\text{SO}_4$ in the absence of oxygen.⁴ During the present quarter, another run was made at 250°C similar to the previous one except 0.04 m MgSO_4 and 0.01 m CuSO_4 were added to the solution. The magnesium sulfate was added to determine if it would suppress the corrosiveness of the sulfuric acid solution resulting from the reduction and precipitation of uranium. The copper sulfate was added to determine whether copper would precipitate in the absence of oxygen.

The run was started in the presence of a 4:1 helium-hydrogen atmosphere with oxygen excluded. Similar to previous runs, the uranium concentration dropped to less than 0.5 g per liter within 4 hr. The copper concentration also dropped from 0.66 to 0.20 g per liter in 4 hr. This was interpreted as a reduction of copper to the metal. The free-acid concentration increased from 0.025 to 0.050 m. The presence of the magnesium sulfate did not inhibit the corrosion of stainless steel; a rate of about 250 mpy was deduced from the increase in nickel concentration with time. After 6 hr 200 psi oxygen was added, the uranium and copper reappeared in solution within 20 min, and the corrosive attack leveled off at less than 1 mpy.

C. Corrosion of Stainless Steel, Titanium, and Zircaloy-2 in the Heavy Second Liquid Phase of Uranyl Sulfate Solution

Controlled studies of the attack by the heavy phase of two liquid-phase uranyl sulfate solution at elevated temperatures have not been made previously, although instances of drastic attack on stainless steel by the heavy phase have occurred.⁵ Since hot spots which could cause two-phase separation could conceivably occur in a reactor, further investigation was desirable. An all-titanium loop was modified to include a 1/4-in. titanium bypass line into which could be inserted with "Swagelok" fittings a 1/4-in. OD, 6-in. long, weighed tubing specimen. The tubing specimen was encased with a close-fitting aluminum jacket around which was wound a 300-watt heater. A 1500-watt preheater was installed in the 1/4-in. titanium

line preceding the specimen. During operation, the main circulating stream was controlled at 295 to 300°C, while the bypass line was heated to 310 to 312°C. The latter temperature was above the second liquid phase temperature of the 0.17 m UO_2SO_4 solution used in these runs. Boiling was prevented by gas pressurizing the system to 1700 psig. The bypass line was tilted slightly in relation to the horizontal in order that any heavy liquid phase which formed in the preheater would run down into the tubing specimen and cause local corrosion there. The solution flow rate through the specimen was about 3 fps.

A preliminary run was made without the special bypass in which the 0.17 m UO_2SO_4 solution was circulated at 310°C for 200 hr. Titanium and zirconium alloy pins were exposed at 17 and 70 fps to the solution which presumably was in the two-liquid phase state. That the phases did not mix was evident from solution samples which showed a sharp decrease in uranium concentration (from 40 to 34 g per liter) and a sharp drop in pH (from 2.5 to 2.1) when the temperature was raised from 300 to 310°C. Therefore, the pins were exposed to the "light" phase only; the "heavy" phase presumably collected in droplets along the bottom of the piping. The corrosion rates of the pins were in all cases less than 0.3 mpy.

Following this run the special bypass was installed and successive runs made with a type A-55 titanium, a Zircaloy-2, and a type 347 stainless steel specimen. The runs made with the titanium and Zircaloy specimens produced no localized attack. The corrosion rate from the weight loss of the tubing specimen was 1.6 mpy for the titanium and 0.7 mpy for the Zircaloy-2. Visually, the attack was very slight and completely uniform.

During the first run with the stainless steel specimen, the bypass orifice became plugged, the specimen overheated and its aluminum jacket melted, and drastic attack and rupture of the specimen occurred. Metallographic examination indicated that alloying of the aluminum with the steel occurred throughout the thickness of the stainless steel tube.⁶ Evidently a very high temperature was reached, possibly because of arcing by the heater wires. In any case, the failure of the specimen could not be attributed to localized attack by the solution. However, the failure emphasizes the need for high-temperature cut-out relays on aluminum-jacketed or cast heaters.

A second run was made with a type 347 stainless steel specimen. This time no plugging occurred. The specimen corroded uniformly at 76 mpy. Visually, no localized attack could be observed.

The corrosion rates of the titanium, Zircaloy-2, and stainless steel would suggest that heavy phase was present on the tubing walls during the run. However, the absence of localized attack would indicate that the heavy phase, if present, was swept past the tubing by the flowing solution, even though it has been observed in quartz tubes that heavy phase strongly wets the three metals tested.⁷ It was concluded that heavy-phase attack was severe only on the stainless steel and was not as catastrophic as has been observed in static systems⁵ so long as the solution flow rate was at least 3 fps. However, since the results were not conclusive, a different experimental arrangement was designed and will be tested later.

D. Corrosion of Stainless and Carbon Steels at 300°C in Chloride-Containing Boiler Water

In a continuation of the study of corrosion of materials by boiler water,⁸ the effect of chloride contamination was investigated. Three runs, I-55, 56 and 57, were made at 300°C, one each with < 0.1, ~ 4, and ~ 9 ppm oxygen in solution. The solution was maintained at pH 10 to 10.5 with 60 ppm phosphate as trisodium phosphate by continuous addition and letdown. The chloride concentration was 50 to 60 ppm as potassium chloride, and all other ions were less than 1 ppm. In I-55, oxygen was removed from the solution by adding 150 ml of 85% hydrazine hydrate to roughly 200 liters of solution in the addition supply barrel each time the barrel was filled and continuously sparging the barrel with nitrogen. In I-56, carbon dioxide-free air was bubbled through the barrel to give roughly 4 ppm oxygen in solution and in I-57, oxygen was bubbled through the barrel to give roughly 9 ppm oxygen in solution.

Table IV is a summary of the corrosion results. The results obtained at 5 and 15 fps were averaged since little velocity effect was observed in this region.

It should be noted that the corrosion rates listed in Table IV are average rates for the run and, except for the carbon steels in the presence of oxygen, would decrease with time.

Table IV. Average Corrosion Rates (mpy) at 300°C in Boiler Water^a Containing 50 ppm Chloride

Run No.	I-55		I-56		I-57	
	< 1 ppm O ₂		~ 4 ppm O ₂		~ 9 ppm O ₂	
O ₂ Concentration						
Flow Rate	3-18 fps	46 fps	3-18 fps	46 fps	3-18 fps	46 fps
Material						
202 SS	0.3	---	4.2	---	3.3	---
304L SS	0.4	0.5	1.7	2.6	1.7	2.8
316 SS	0.5	0.4	1.0	1.1	1.0	1.4
347 SS ^b	0.4	0.4	1.7	2.6	1.7	2.6
347 SS ^b	0.5	---	0.8	---	0.7	---
347 SS stressed ^c	0.5	---	0.9	---	0.7	---
347 SS stressed ^d	0.4	---	0.7	---	0.8	---
Average Aus. SS	0.4	0.4	1.7	2.1	1.4	2.2
Armco Iron	5.4	---	12	---	13	---
A212B	9.3	18	16	29	28	36
AISI C-1010	8.2	13	14	24	20	18
AISI C-1016	8.9	17	15	28	22	26
Average Carbon Steel	8.0	16	14	27	21	27
Incoloy	0.3	0.3	0.5	0.7	0.4	0.9
Niobel	0.1	0.2	0.4	0.6	0.5	1.0
Ni-plated carbon steel ^e	0.8	7.7	1.1	7.7	0.7	3.6
C-1010 stressed ^{f,i}	13	---	16	---	26	---
C-1010 stressed ^{g,i}	13	---	13	---	19	---
C-1010 stressed ^{h,i}	24	---	21	---	26	---
C-1010 stressed ⁱ	18	---	13	---	24	---
ASTM A-7 Coupons (10 to 100 fps)	3.0		7.7		14	

a) Water containing 60 ppm PO₄ as Na₃PO₄.

b) Coupled to carbon steel.

c) Stressed beyond elastic limit and coupled to carbon steel.

d) Stressed beyond elastic limit.

e) Kanigen electroless plated 0.002-in. thick.

f) Stressed beyond elastic limit and formed crevice with stainless steel.

g) Stressed beyond elastic limit and formed crevice with carbon steel.

h) Stressed beyond elastic limit. No crevice.

i) Galvanically coupled to stainless steel through bolts and fulcrum.

The variation in corrosion rate with oxygen concentration for the various alloys tested was very similar to that reported previously for the same system in the absence of chloride.⁸ In fact, the presence of 50 ppm chloride had very little effect on the corrosion rates of any of the alloys tested. Table V compares the corrosion rates of the austenitic stainless steels and the carbon steels in the presence and absence of chloride at several oxygen concentrations.

Table V. Comparison of Corrosion Rates of Steels in Boiler Water at 300°C with and without Chloride

		Oxygen Concentration, ppm		
		< 1	~ 4	~ 10
< 1 ppm Chloride	Average Austenitic Stainless Steels	0.4 mpy	1.6 mpy	1.8 mpy
	Average Carbon Steels	12	18	24
50 ppm Chloride	Average Austenitic Stainless Steels	0.4	1.9	1.8
	Average Carbon Steels	12	21	24

Stress-corrosion cracks were found on two of the type 347 stress specimens exposed in run I-57 (~ 9 ppm oxygen).⁹ One of these specimens was stressed on top of a carbon steel specimen, forming a galvanic couple over its entire length, and the other was stressed over another type 347 stainless steel specimen. Obviously, any galvanic action failed to prevent cracking. However, only a total of three cracks were found metallographically, and the deepest of these was about 0.010 in. Hence, the phosphate ion present in the solution may have acted as a partial inhibitor for stress-corrosion cracking.

As noted previously, there was little difference among the austenitic stainless steels. Corrosion rates of these steels increased a factor of 4 to 5 with oxygen added to the water over rates in the absence of oxygen, but the rates did not vary with oxygen concentration. The various carbon steels tested pitted in the presence of oxygen, and the corrosion rates reported would be two or three times greater if the pitting attack rate rather than the general attack rate were given. Nickel plating the carbon steel by the electroless nickel-plating technique gave excellent results. Corrosion rates were two to ten times less on

plated than on unplated specimens. Monel and Incoloy were also very corrosion resistant. No significant effect of stress, crevice, or galvanic action was noted on the general corrosion rates of the carbon and stainless steels tested except for the cracking noted above.

E. Effect of Ruthenium on the Chromium (VI) Concentration in Dilute Sulfuric Acid Solution

The ability of ruthenium as the nitroso complex to catalyze the formation of hexavalent chromium in dilute uranyl sulfate solutions was pointed out previously.¹⁰ It was of interest to determine whether ruthenium would have the same catalytic activity in dilute sulfuric acid solutions. Normally when sulfuric acid solutions are circulated in a stainless steel loop, no chromium (VI) is formed, regardless of oxygen concentration or temperature.

A 40-hr run was made at 250°C with 0.025 M H_2SO_4 containing initially 100 ppm ruthenium as the nitroso complex and about 1000 ppm oxygen. At the end of the run the chromium (VI) concentration was 110 ppm. Evidently ruthenium was very effective in catalyzing the oxidation of chromium to the hexavalent state even though 90% of the ruthenium was lost from solution within 3 hr. Over half of the chromium (VI) must have come from the oxide scale already present on the loop walls since the extent of corrosion during the run would account for only about 40 ppm Cr(VI). Interestingly enough, as the ruthenium precipitated the chloride concentration in solution increased from 2 ppm at the start of the run to 20 ppm after 3 hr. It appeared that the ruthenium nitroso complex, which was made from ruthenium trichloride, retained some chloride in an inner coordination complex, and at room temperature this chloride was not precipitated by silver nitrate during analysis. At 250°C, as the ruthenium precipitated, the complex was broken up and the free chloride appeared.

The precipitated ruthenium could not be rinsed from the loop after the above run. In a second run with 0.025 M H_2SO_4 at 250°C, in which no more ruthenium was added, the system retained its ability to catalyze the oxidation of chromium to the

hexavalent state. Within 30 hr 70 ppm Cr(VI) was formed, and at the end of the 87-hr run the concentration was 140 ppm. Chemical analysis showed about 8 ppm ruthenium in solution, presumably from dissolution of the previously precipitated ruthenium metal or dioxide.

Two additional runs, one 70-hr and the other 180-hr long, were made at 250°C without adding more ruthenium, and in both cases chromium (VI) again built up in solution. The solution for these runs was 0.05 m H_2SO_4 . In the second of these runs the chromium (VI) concentration leveled off at 160 ppm after 100 hr. Evidently all of the chromium had been leached from the oxide scale and the amount coming from corrosion was negligible. Therefore, a chromic sulfate solution was pumped into the loop while in operation so as to give 200 ppm chromium (III) in solution. Immediately the chromium (VI) concentration increased and within 80 hr reached 320 ppm. Since 80% of the chromium (III) added was oxidized in 80 hr, the catalytic ability of the ruthenium was clearly shown.

In the absence of chromium (VI) the acid solutions discussed above are quite corrosive to stainless steel.¹¹ In the presence of ruthenium and the attendant increase in chromium (VI) concentration, corrosion was markedly inhibited at flow rates less than about 40 fps. This is shown in Figure 3, in which weight losses of type 347 stainless steel coupons are plotted against solution flow rate for runs in 0.025 m H_2SO_4 with and without ruthenium present. The inhibiting agent appeared to be the chromium (VI) which averaged 100 ppm in the run with ruthenium and was less than 1 ppm in the run without ruthenium.

Further runs will be made to determine the reason for the catalytic activity of the ruthenium and to measure the rate of oxidation of chromium (III) to chromium (VI) at several temperatures.

IV. LABORATORY CORROSION STUDIES (J. L. English, D. W. Hess, P. D. Neumann, J. C. Griess)

A. Stress-Corrosion Cracking of Type 347 Stainless Steel

Fig. 3. Weight Losses of Type 347 Stainless Steel Coupons in 0.025m H₂SO₄ With and Without Ruthenium at 250°C

1. Stress-Corrosion Cracking by High-Temperature Chloride-Containing Water

Tests have been run to determine the stress-corrosion cracking behavior of type 347 stainless steel at 300°C in water containing 100 ppm of chloride in the absence of oxygen. The oxygen removal was achieved by the addition of sodium sulfite in an amount double that needed to remove the oxygen present initially in the test system. Residual sulfite concentrations at the completion of test runs indicated complete oxygen removal.

The test specimens were elastically stressed U-bends that were prepared from annealed 0.025-in.-thick type 347 stainless steel strip. Tests were run with specimens completely immersed in distilled water containing 100 ppm chloride at initial pH values of 6.5 and 10.5. The latter value was obtained by adjustment with sodium hydroxide.

Eight specimens were exposed for 2000 hr (4 specimens at each pH value). No cracking occurred. Under similar conditions with approximately 10 ppm or higher of oxygen present, 100% of type 347 stainless steel specimens tested developed cracks during exposure periods of 500 hr or less. Thus it may be concluded that in chloride-containing water at pH values of 6.5 or 10 the removal of oxygen from the system is an effective means of preventing stress-corrosion cracking of type 347 stainless steel and presumably other austenitic stainless steels.

2. Stress-Corrosion Cracking by Chloride-Containing Uranyl Sulfate Solution

An evaluation of the effectiveness of preformed films for preventing stress-corrosion cracking of type 347 stainless steel in a chloride-containing uranyl sulfate solution at its atmospheric boiling temperature

has been continued. Preliminary results of the evaluation have been reported.^{12,13,14} Prefilming of elastically stressed U-bend specimens was accomplished by immersion in chloride-free 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m $CuSO_4$ at temperatures of 100, 125, 150, 175, and 200°C. At temperatures of 125 and above, the prefilming solution was pressurized with oxygen. The test specimens consisted of elastically stressed U-bends that were prepared from annealed and pickled 0.020-in.-thick type 347 stainless steel strip. The edges of the specimens were mechanically abraded to remove sheared surfaces. After prefilming, the stressed specimens were tested in boiling and aerated 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m $CuSO_4$ solution containing 50 ppm of chloride as potassium chloride.

Initial studies concerned with prefilming in boiling (100°C) chloride-free uranyl sulfate showed that pre-exposure times of either 50, 100, or 500 hr were completely effective in preventing cracking when the specimens were subsequently exposed to the chloride-containing environment. In a total of 17 prefilmed specimens, no cracking occurred during exposure periods up to 2500 and 3000 hr. In the case of the 500-hr pretreatment, specimens were stressed before and after the prefilming. In neither case was cracking observed after an exposure of 3000 hr in the chloride-containing environment. In the absence of the pretreatment, more than half of the specimens would have cracked in 500 hr or less in the latter environment.

Other studies were concerned with the effectiveness of preformed films formed at temperatures above the atmospheric boiling point of the solution (125 to 200°C) in eliminating cracking susceptibility of type 347 stainless steel when subsequently exposed to boiling and chloride-containing uranyl sulfate solution. Stressed specimens were exposed for an arbitrarily selected period of 100 hr at temperatures of 125, 150, 175, and 200°C in chloride-free 0.04 m UO_2SO_4 - 0.02 m - 0.005 m $CuSO_4$ solution. The pretreatment of specimens at the elevated temperatures produced films which increased in thickness

as the prefilming temperature was increased. The prefilmed specimens were then placed in a similar solution (except at 100°C) containing 50 ppm of chloride. Results of the tests appear in Table VI.

Table VI. The Effect of Prefilming Temperature on the Stress-Corrosion Cracking Behavior of Type 347 Stainless Steel in Boiling and Aerated Uranyl Sulfate Solution^a Containing 50 ppm Chloride

<u>Prefilming^b Temperature (°C)</u>	<u>Number of Specimens</u>	<u>Test Time (hr)</u>	<u>Observations</u>
125	9	2000	No cracking
150	9	1500	No cracking
175	9	1000	No cracking
200	9	500	No cracking

- a) 0.04 m UO_2SO_4 with 0.02 m H_2SO_4 and 0.005 m CuSO_4 .
b) Prefilmed in the above chloride-free solution.

No cracking in any of the specimens pretreated at 125 to 200°C (a total of 36) has been observed thus far during exposure periods of 500 to 2000 hr in the chloride-containing environment. As mentioned earlier, slightly more than one-half of the specimens would have cracked in 500 hr or less in the absence of the pretreatment.

Thus the experimental evidence to date clearly shows the beneficial effect of preformed films in preventing stress-corrosion cracking of type 347 stainless steel in boiling, chloride-containing uranyl sulfate solution. A grand total of 53 stress specimens has been pretreated at temperatures between 100 and 200°C in chloride-free uranyl sulfate solution. No cracking has occurred on any of the specimens exposed in a similar solution containing 50 ppm of chloride during exposure periods of 500 to 3000 hr.

The effectiveness of films preformed at temperatures up to 300°C in preventing cracking will be examined in chloride-containing uranyl sulfate solution at the boiling temperature and above during the next quarter.

B. MISCELLANEOUS CORROSION TESTS

A number of corrosion tests have been made on materials of possible interest to the Homogeneous Reactor Project. The materials included Nionel, type 202 stainless steel, Flame-Plated stainless steel, and CD-4MCu stainless steel.

1. Nionel. Nionel, an alloy which contains approximately 40% Ni, 20% Cr, 30% Fe, 3% Mo, 1.75% Cu, and 0.05% C, was exposed in a number of reactor-related environments. The observed hardness of annealed 1/8-in.-thick test specimens was 72 Rockwell B. The environments tested and the average corrosion rates for duplicate specimens are reported in Table VII. In all cases good agreement between rates for the duplicate specimens was obtained.

With the exception of the 200 and 300°C tests in uranyl sulfate solution, the corrosion resistance of Nionel was excellent with observed rates less than 0.1 mpy. In the uranyl sulfate solution at 200 and 300°C, the rates were 2 mpy or slightly less. Although these rates are an order of magnitude greater than those observed on type 347 stainless steel under similar conditions, the general corrosion resistance of the alloy is considered acceptable.

A significant feature of the corrosion behavior of Nionel was its resistance to stress-corrosion cracking in boiling uranyl sulfate solution containing 50 ppm of chloride and in boiling magnesium chloride solution. In comparison, more than 50% of type 347 stainless steel stress specimens are cracked in less than 500 hr in the former solution and in a few hours in the latter environment.

Table VII. Corrosion of Nionel by Several
Reactor-Related Environments

Environment	Temp. (°C)	Total Time (hr)	Corrosion Rate (mpy)	Observations
5% HNO ₃	Boiling	1000	< 0.1	Negligible attack
42% MgCl ₂ ^a	154	100	-	No cracks
UO ₂ SO ₄ Solution ^b	Boiling	1000	< 0.1	Negligible attack
	Boiling	1000	< 0.1 ^c	Very shallow pitting, < 0.5 mil
	200	1000	1.7	Numerous shallow pits, < 0.5 mil
	300	1000	2.0	Mild attack along polish lines
	300	1000	2.0 ^a	No cracking
UO ₂ SO ₄ Solution plus Chloride ^d	Boiling	1000	< 0.1	Negligible attack
	Boiling	2500	< 0.1 ^a	No cracking

a) Stress-corrosion cracking test with U-bend specimen.

b) 0.04 M UO₂SO₄ - 0.02 M H₂SO₄ - 0.005 M CuSO₄.

c) Specimens heated for 1 hr in air at 677°C (1250°F).

d) 0.04 M UO₂SO₄ - 0.02 M H₂SO₄ - 0.005 M CuSO₄ with 50 ppm chloride as KCl.

One possible objection to the use of the alloy for reactor applications, however, is the fact that its high nickel content (40%) would mean a fourfold increase of nickel in the fuel solution compared with the nickel contribution from type 347 stainless steel corroding at the same rate.

2. Type 202 Stainless Steel. A number of low-nickel, high-manganese austenitic stainless steels whose physical and mechanical properties as well as corrosion resistance are reported to compare favorably

with the conventional 18-8 (300 series) stainless steels have been developed. Inasmuch as these steels conceivably could have usefulness in homogeneous reactor applications, a typical steel of this class, type 202, was subjected to test in several reactor-related environments. The nominal chemical composition of type 202 stainless steel is 17-19% Cr, 4-6% Ni, 7.5-10% Mn, 0.15% C max., and balance iron. The results of corrosion tests on the annealed material have been reported previously.¹⁵

Present tests dealt with the behavior of the alloy in the sensitized condition. The sensitizing treatment consisted of heating specimens for 1 hr in air at 677°C (1250°F) followed by air cooling. Table VIII shows the environments in which the specimens were tested and the observed corrosion rates. For comparison the results obtained in the same environments with annealed specimens are also shown in Table VIII.

Table VIII. Corrosion of Type 202 Stainless Steel in
Annealed and Sensitized^a Conditions by
Several Reactor-Related Environments
(Test Time - 1000 Hr)

Environment	Temp (°C)	Corrosion Rate (mpy)	
		Annealed	Sensitized
5% HNO ₃	Boiling	0.1	18
UO ₂ SO ₄ Solution ^b	Boiling	< 0.1	2, 22
	200	0.9	2
	300	0.4	0.4
UO ₂ SO ₄ Solution ^c	Boiling	< 0.1	-

a) Heated 1 hr in air at 1250°F; air cooled.

b) 0.04 m UO₂SO₄ - 0.02 m H₂SO₄ - 0.005 m CuSO₄.

c) 1.33 m UO₂SO₄.

In the annealed condition, the corrosion resistance of the type 202 stainless steel compared favorably with that of type 347 stainless steel exposed in similar environments. The corrosion resistance of type 202 stainless steel, however, was lowered by the sensitizing treatment. This was particularly true in the boiling 5% HNO_2 and the boiling uranyl sulfate solutions. The behavior of sensitized specimens in the latter solution was very erratic. In one case, severe blistering of the metal and reduction of copper from solution were observed while specimens corroded at a rate of 22 mpy. A repeat test with specimens from the same source resulted in a corrosion rate of 2 mpy; neither metal blistering nor copper reduction occurred. A vacuum fusion analysis on one of the sensitized specimens that blistered showed a hydrogen content of 100 ppm, whereas the hydrogen content of the unexposed material was 3 ppm. For comparative purposes, sensitized type 302 stainless steel specimens were exposed for 1000 hr in the boiling uranyl sulfate solution. The specimens underwent negligible attack and showed no blistering phenomenon as was experienced by the sensitized type 202 stainless steel specimens.

Welded specimens of the type 202 stainless steel were exposed in the as-welded and in the welded-and-annealed condition in oxygenated $0.04 \text{ } m \text{ } \text{UO}_2\text{SO}_4 - 0.02 \text{ } m \text{ } \text{H}_2\text{SO}_4 - 0.005 \text{ } m \text{ } \text{CuSO}_4$ solution at its atmospheric boiling temperature, 200 and 300°C and in boiling 5% HNO_3 solution. Type 308 stainless steel rod was used for the welding. The agreement between the results of 1000-hr tests for as-welded and welded-and-annealed specimens was excellent. Corrosion rates, with one exception, were 0.6 mpy or less. The exception was the uranyl sulfate solution at 200°C; observed corrosion rates were 2.0 and 1.5 mpy, respectively, for as-welded and welded-and-annealed specimens. No evidence of localized corrosion attack resulting from sensitization during welding was observed on the as-welded specimens or on the specimens that were annealed after welding.

The stress-corrosion cracking behavior of annealed type 202 stainless steel was examined in boiling $0.04\text{ }m\text{ }UO_2SO_4 - 0.02\text{ }m\text{ }H_2SO_4 - 0.005\text{ }m\text{ }CuSO_4$ solution containing 50 ppm of chloride as potassium chloride. Cracking of both unstressed control specimens and stressed specimens occurred around the edges of drilled holes during 1000 hr. The control specimens were also subject to blistering.

In view of the unreliable behavior of the type 202 stainless steel, particularly in the sensitized condition, it appears unlikely that the alloy would be suited for homogeneous reactor applications. The results also indicate that the 200 series stainless steels would probably have no major advantage over the corresponding 300 series but may have serious disadvantage in reactor-related environments.

3. Flame-Plated Stainless Steel. One of the problems associated with various homogeneous reactor applications has been finding a corrosion-resistant hard-facing material for use in shaft seals, pump bearings, valve trim, etc. Recently, tests were completed with a hard-facing material designated as Flame-Plate, a product of the Linde Company. The plate composition is reported to be 64% W, 23% Ni, 6% Cr, and 7% C. The deposited plate, after surface finishing, has an average hardness of 930 DPH (~ 68 Rockwell C).

Test specimens of type 347 stainless steel, Flame-Plated to a depth of 0.003 in. on one side, were exposed in deionized water, nitric acid, and oxygenated uranyl sulfate solutions. The results of the tests are shown in Table IX. Corrosion rates were based on the Flame-Plated surface area only; attack on type 347 stainless steel is only several tenths of an mpy or less in all environments tested.

Table IX. Corrosion of Flame-Plate on Type 347 Stainless Steel
by Several Reactor-Related Environments
(Test Time - 1000 Hr)

Environment	Temperature (°C)	Corrosion Rate (mpy) ^a
Deionized H ₂ O	300	19
5% HNO ₃	Boiling	2
UO ₂ SO ₄ Solution ^b	Boiling	4
	200	3
	300	20

a) Based upon Flame-Plated surface only.

b) 0.04 m UO₂SO₄ - 0.025 m H₂SO₄ - 0.01 m CuSO₄

The corrosion resistance of the Flame-Plate was generally poor in all environments. Observed rates for 1000-hr tests ranged from 2 mpy in boiling 5% HNO₃ solution to 20 mpy in oxygenated uranyl sulfate solution at 300°C. In deionized water at 300°C, the rate was 19 mpy. The attack on the deposit was characterized by heavy granulation. Therefore, Flame-Plate cannot be recommended for use in any of the environments tested.

4. CD-4MCu Stainless Steel. A new age-hardenable alloy designated as CD-4MCu stainless steel has been subjected to a series of corrosion-evaluation tests. The alloy was specifically developed as a cast high-strength material for the Alloy Casting Institute by the Corrosion Research Laboratories of Ohio State University. The nominal composition of the cast alloy is 25-27% Cr, 4.75-6% Ni, 1.75-2.25% Mo, 2.75-3.25% Cu, 1% Si max., 1% Mn max., 0.04% C max., and balance iron. A small amount of cerium (~ 0.1%) is added to improve the rolling characteristics of the alloy in the production of wrought material. Five different heat-treated conditions of the alloy were examined. A

description of the heat treatments and observed hardness values are shown in Table X. The maximum hardness for any application is recommended not to exceed 34 Rockwell C. Beyond this value, appreciable loss in ductility of the alloy is encountered.

Table X. Heat Treatments and Hardness Values
for CD-4MCu Stainless Steel

Heat Treatment	Hardness (Rockwell C)
1. As cast	26
2. Cold rolled and aged 3 hr at 900°F	43
3. Hot rolled at 1870°F, water quenched, annealed 1 hr at 1950°F, water quenched	25
4. Hot rolled and annealed as per (3), aged 4 hr at 850°F, air cooled	33
5. Hot rolled and annealed as per (3), aged 2 hr at 900°F, air cooled	34

The as-cast material was exposed for 1000 hr in boiling 5% HNO_3 and in boiling 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 solution; the observed rates were less than 0.1 mpy. In the latter solution at 300°C with oxygen overpressure, the rate was 0.6 mpy. In all cases, corrosion attack was uniform. A test to determine if the as-cast material is subject to galling has been run in oxygenated 0.04 m UO_2SO_4 - 0.025 m H_2SO_4 - 0.01 m CuSO_4 solution at 300°C. A machined 3/8-16 bolt was initially stressed to 18 to 20 ft-lb (approximately 40,000 psi) in an assembly that consisted of a ferrule, washer and a stainless steel bolt containing a hardened thread insert. The assembly was dismantled three times during a 500-hr exposure and the torque required to release the stress was measured. Each time the measured torque was not appreciably different from the initially applied torque, indicating that severe galling had not occurred. The as-removed corrosion rate for the CD-4MCu bolt was 0.3 mpy.

Cold rolled and aged specimens (1/64-in. thick) of the alloy (No. 2 in Table X) were butt-welded by a fusion process to type 347 stainless steel and exposed for 1000 hr in boiling 5% HNO_3 and in boiling 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 solution. Assuming negligible attack on the type 347 stainless steel, observed corrosion rates for the CD-4MCu were 0.4 mpy or less. There was no evidence of preferential corrosion in the heat-affected zone.

The same age-hardened material was stressed and placed in boiling 42% MgCl_2 solution; cracking occurred within 2 hr. Two elastically stressed U-bends and unstressed control specimens were exposed for 2500 hr in boiling 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 solution containing 50 ppm of chloride as potassium chloride. No cracking was observed during this period and corrosion rates were less than 0.1 mpy. Under similar conditions, 55% of 0.025-in.-thick elastically stressed type 347 stainless steel U-bend specimens were subject to cracking. After the stress-cracking test, one of the CD-4MCu specimens was cathodically defilmed; the other was left in the filmed condition. Both specimens, still in a stressed condition, were placed in boiling 42% MgCl_2 solution; both cracked within 1 hr.

Annealed specimens (No. 3 in Table X) and specimens age-hardened at 850 and 900°F (No. 4 and 5, respectively, in Table X) were exposed for 1000 hr at 300°C in oxygenated 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 solution. In no case did the corrosion rates exceed 0.7 mpy. There was no significant difference between the behavior of the annealed and the age-hardened materials. Elastically stressed U-bends of the age-hardened materials were exposed for periods up to 2000 hr at atmospheric boiling in a similar uranyl sulfate solution with and without 50 ppm of chloride. No cracking occurred on specimens in either environment. With chloride present, the corrosion rates were 0.5 mpy or less; in the absence of chloride, the corrosion rates were less than 0.1 mpy.

On the basis of the experimental data, CD-4MCu stainless steel appears to be a material worthy of more extensive testing and evaluation for reactor applications. Its corrosion resistance compares very favorably with that of type 347 stainless steel under similar conditions of exposure. Its low nickel content (5 to 6%) would be less objectionable from a neutron-poisoning viewpoint in fuel systems than the nickel content in type 347 stainless steel (9 to 12%). Furthermore, its high strength and indicated immunity to stress-corrosion cracking in boiling, chloride-containing uranyl sulfate solution make its use especially attractive.

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