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DISCLAIMER

Reports previously issued in this series are as follows:

ORNL CF 56-1-167	Period Ending January 31, 1956
ORNL CF 56-4-138	Period Ending April 30, 1956
ORNL CF 56-7-52	Period Ending July 31, 1956
ORNL CF 56-10-13	Period Ending October 31, 1956
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ORNL CF 58-7-132	Period Ending July 31, 1958
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I. SUMMARY

A number of tests were made during the quarter to study the deposition of uranium, copper, and nickel sulfates from dilute simulated fuel solutions circulated through a heated Zircaloy-2 pipe section in a 100A pump loop. With the heated pipe mounted in a nearly horizontal position, loss of salts from solution was observed in all cases when boiling of the solution occurred. When most of the gas was removed and the system was hydraulically pressurized, loss of salts from solution was still observed when bulk boiling of the solution in the bypass occurred.

When the orientation of the heated Zircaloy-2 bypass was changed from its nearly horizontal position, used in the initial series of tests, to a vertical position with the solution entering either from the top or from the bottom, no salts were lost from solution even under conditions of vigorous boiling and at metal wall temperatures in excess of 400°C.

Observations in a glass mockup of the bypass indicate that the tube wall is continuously wet when in the vertical position; whereas in the horizontal position a vapor space formed in the upper part of the tube which prevented its being wetted by the solution. Thus deposited solids or liquids would be washed away in the vertical arrangement but could build up on the heated, unwetted part of the pipe in the horizontal arrangement.

Additional out-of-pile tests were carried out in an in-pile loop in which the metal wall of the core section was heated. This loop is approximately 1 liter in volume and contains a 5-gpm canned-rotor pump. For conditions of fluid flow and core wall temperature at which boiling occurred

at the core wall, loss of salts from solution by deposition on the core wall was observed. At 280°C, increasing the sulfuric acid concentration inhibited the deposition which could still be made to occur at higher heat fluxes. At 225°C, deposition occurred regardless of the acid concentration, although there were indications that the rate and extent of deposition were decreased at higher acid concentrations.

Two different hydroclone mountings on a 100A loop have been tested to determine the effectiveness of each mounting in removing corrosion products from the loop. In one case the inlet to the hydroclone was joined to the main loop piping by a perpendicular tee near the pump discharge. In the second case the inlet to the hydroclone was attached to the bottom of the pressurizer so that particles could "fall" into the hydroclone. In each case only about 10% of the corrosion products originating from the corrosion in the loop were collected in the hydroclone underflow pot. Most of the corrosion products collected as a tightly adhering film on all interior surfaces of the loop.

Chemical stability tests were run at 300°C on a solution containing 0.025 m UO_2SO_4, 0.2 m Li_2SO_4, 0.1 m D_2SO_4 and 0.02 m $CuSO_4$, and on one identical to the first except diluted by a factor of 3. Both solutions were unstable during 200-hr loop runs; the concentrated solution lost 80% of its copper and none of its uranium, whereas the dilute solution lost 90% of its copper and 60% of its uranium. In a third run 0.2 m $MgSO_4$ was substituted for the 0.2 m Li_2SO_4 of the first solution. The resulting solution lost 20% of its copper and 6% of its uranium during circulation at 300°C. Increasing the acid concentration would result in greater solution stability, but tests showed that the increased acid made the solution very corrosive, particularly in crevice areas.

The effectiveness of fluoride ions as an additive to oxygen- and chloride-containing phosphate-treated boiler water for the suppression of stress-corrosion cracking was found to be essentially nil.

The pretreatment of U-bend specimens of type 347 stainless steel in a solution containing 0.04 *m* UO_2SO_4, 0.02 *m* H_2SO_4, and 0.005 *m* $CuSO_4$ at temperatures ranging from 100 to 300°C gave substantial protection to the specimen against stress-corrosion cracking when subsequently exposed to the same solution containing chloride ions. Specimens from one heat of the alloy which cracked 50% of the time without pretreatment were completely resistant to cracking after pretreatment; specimens from a different heat of the same alloy which cracked 100% of the time in the absence of pretreatment cracked only 15% of the time after pretreatment.

Preliminary tests with cast type 347 stainless steel have shown the material to be more resistant to chloride-induced stress-corrosion cracking than similar wrought material. However, cracking was readily observed on cast materials that had been cold-worked as a result of forming the metal into U-bends. In high-temperature water only one small crack has been observed to date, and that was found on a stress specimen exposed to a solution containing 100 ppm chloride and oxygen at 300°C. Under the same conditions wrought type 347 stainless steel specimens develop many, much deeper cracks during tests of 500 hr or less.

Tests to determine the corrosiveness of the heavy phase of a high-temperature uranyl sulfate solution to Zircaloy-2 have indicated that Zircaloy-2 is practically unaffected by it. The presence of copper in the heavy phase did not make it more corrosive.

In 100-hr tests at 250°C, titanium was not corroded significantly by oxygen-free uranyl sulfate solutions, and no definite evidence of solution instability was observed.

The corrosion rate of Incoloy 804 was found to be tolerable but greater than type 347 stainless steel in uranyl sulfate solutions in the temperature range of 100 to 300°C. Tests with Electrolyzed coatings on type 304 stainless steel (a proprietary process for depositing a hard, chromium-rich deposit on metal surfaces) have shown that the deposited layer dissolves from the surface in high-temperature, oxygenated, aqueous environments and hence is of little value in high-temperature fuel systems. However, at 100°C in the absence of chloride ions, the Electrolyzed coating is stable and could conceivably be useful where a hard surface is necessary.

II. INTRODUCTION

The data presented in the following pages represent the detailed results obtained during the quarter ending January 31, 1959, by the Solution Materials Section of the Reactor Experimental Engineering Division. A summary of the data has been given in the Homogeneous Reactor Project Quarterly Progress Report for the quarter ending January 31, 1959.

This report represents a progress report, and hence the conclusions drawn from the data must be considered preliminary and subject to possible change as further experimentation is completed.

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

A. Deposition of Uranium from Dilute Uranyl Sulfate Solutions in a Heated Bypass

1. 100A Loop H Tests

(a) Hydraulic Pressurization Tests.--In the previous report, experiments were described in which uranium, copper, and nickel sulfates were caused to deposit in a heated, Zircaloy-2 bypass installed horizontally on a titanium loop.[1] The basic reason for the deposition and the exact nature of the deposits were not determined, however; thus additional tests were carried out.

The loop was modified to allow hydraulic pressurization rather than gas pressurization as used previously. The loop was operated full of solution and about 50 ml/min were cooled and let down to a reservoir. The solution in the reservoir was saturated at room temperature and atmospheric pressure with oxygen and then pumped back into the loop with a diaphragm-feed pump. In this way the gas concentration in the circulating solution was maintained at about 20 ppm oxygen. The hydraulic pressurization system has been described previously.[2] The solution circulated was 0.025 m UO_2SO_4 containing 0.015 m D_2SO_4, 0.01 m $CuSO_4$, and 0.004 m $NiSO_4$ in D_2O.

Under these conditions with the loop main-stream at 280°C and loop pressure maintained at 1570 psia, heat to the bypass was increased to obtain outlet temperatures of 290, 300, and 312°C. The solution flow rate through the bypass was about 0.3 fps as in the previous tests. No deposition occurred. Under gas pressurization, deposition did occur at the latter two outlet temperatures.[3] Finally the heat was increased until the temperature of the emerging solution was equal to the boiling point at 1570 psia. Boiling and flashing of solution in the bypass was apparent, since a thermocouple on the bypass inlet occasionally indicated a temperature higher than the prevailing loop temperature. Under these conditions deposition of about 20% of the uranium, copper, and nickel occurred. When deposition was at a maximum, the loop pressure was increased to 1775 psia to prevent boiling. Within 90 min the uranium and copper concentrations in the main-stream had returned to their original values.

Therefore deposition was obtained under hydraulic pressurization as well as under gas pressurization, but the conditions required under hydraulic pressurization were more drastic. It appeared that deposition did not occur under hydraulic pressurization during conditions of nucleate, subcooled boiling, but did occur when volume-boiling occurred such that the bypass was partially filled with vapor. Since the bypass would become partially filled with vapor more easily when the solution contained a high gas concentration than with a low gas concentration, the fact that deposition occurred more easily with gas pressurization than with hydraulic pressurization was perhaps explained. The above experiment did not rule out the possibility that a heavy second-liquid phase formed and caused the loss of uranium from the main-stream. However, subsequent tests in a different system showed that deposition could occur at temperatures much below the second-liquid-phase temperature (~334°C).[4]

Throughout these runs it was apparent that the thermocouples located under the heater on the bypass were not indicating the wall temperature of the heated section of the bypass. However, it was possible to estimate the inside wall temperature of the Zircaloy-2 by conventional heat-transfer calculations assuming laminar flow through the bypass. In this way a film coefficient of 200 Btu/hr·ft^2·°F was obtained,[5] and the Zircaloy-2 wall temperatures listed in Table I were calculated. Deposition of uranium and copper occurred under all of the conditions listed. Also, it was calculated that the highest wall temperature was above the boiling point of the solution in each case. However, it can be seen in Table I that under two of the conditions the highest wall temperature was below the second-liquid-phase temperature of 334°C.

Table I. Inside Wall Temperatures of Heated Zircaloy-2 Bypass During Uranium Deposition

Bypass Inlet Temperature (°C)	Bypass Outlet Temperature (°C)	Calculated Highest Bypass Wall Temperature (°C)
285	319(a)	363
285	312(a)	349
282	302(a)	328
284	302(a)	326
251	297(a)	357
250	290(a)	342
274	318(b)	376

(a) See reference 1 for discussion of these tests.

(b) Hydraulically pressurized.

Several solution samples were removed from the bypass, and all contained several hundred milligrams of tan-colored solids. These solids were identified as ZrO_2 by X-ray diffraction analysis and contained 61% Zr, 0.8% U, 0.1% Ni, 1.25% Cu, 1.2% Fe, and 0.05% Cr by chemical analysis. The presence of such a large amount of ZrO_2 indicated severe attack of the Zircaloy-2 bypass.

The bypass was removed from the loop and sectioned for microscopic and metallographic examination. The examination showed that a general pitting type of attack had taken place on the top half of the heated section, leaving a porous appearance.[6] The bottom half of the heated section was covered with a pale, yellow scale underneath which little attack was visible. The scale consisted of 11% U, 34% Zr, 0.3% Cu, 0.1% Ni, and 0.7% Ti by chemical analysis. Demarcation between the upper and lower halves of the bypass was sharp; and it was postulated that at low flow rates when boiling occurred, vapor filled the top half and the solution ran along the bottom half of the pipe, which was mounted on about a 15-deg decline. A glass mockup of the bypass operated at room temperature with water and air at low pressure to simulate solution and vapor showed that such a sharp demarcation was likely to occur at low flow rates (0.3 fps) with a ratio of water to air of about 4:1.

Hence the deposition of uranium and the attack of the Zircaloy-2 on the upper portion of the tube could be explained as follows: the boiling solution splashed up onto the hot, dry pipe wall in the vapor space; the droplets flashed into steam, leaving a deposit of the uranium, copper, and nickel sulfate salts and a residue of concentrated sulfuric acid which attacked the upper Zircaloy-2 pipe wall.

(b) Vertically Mounted Bypass Tests.--In order to confirm these hypotheses, a second Zircaloy-2 bypass was constructed in which thermowells were placed so that the thermocouples would read more nearly the wall temperature under the heated section. The new bypass is illustrated in Fig. 1. A calibrated metering

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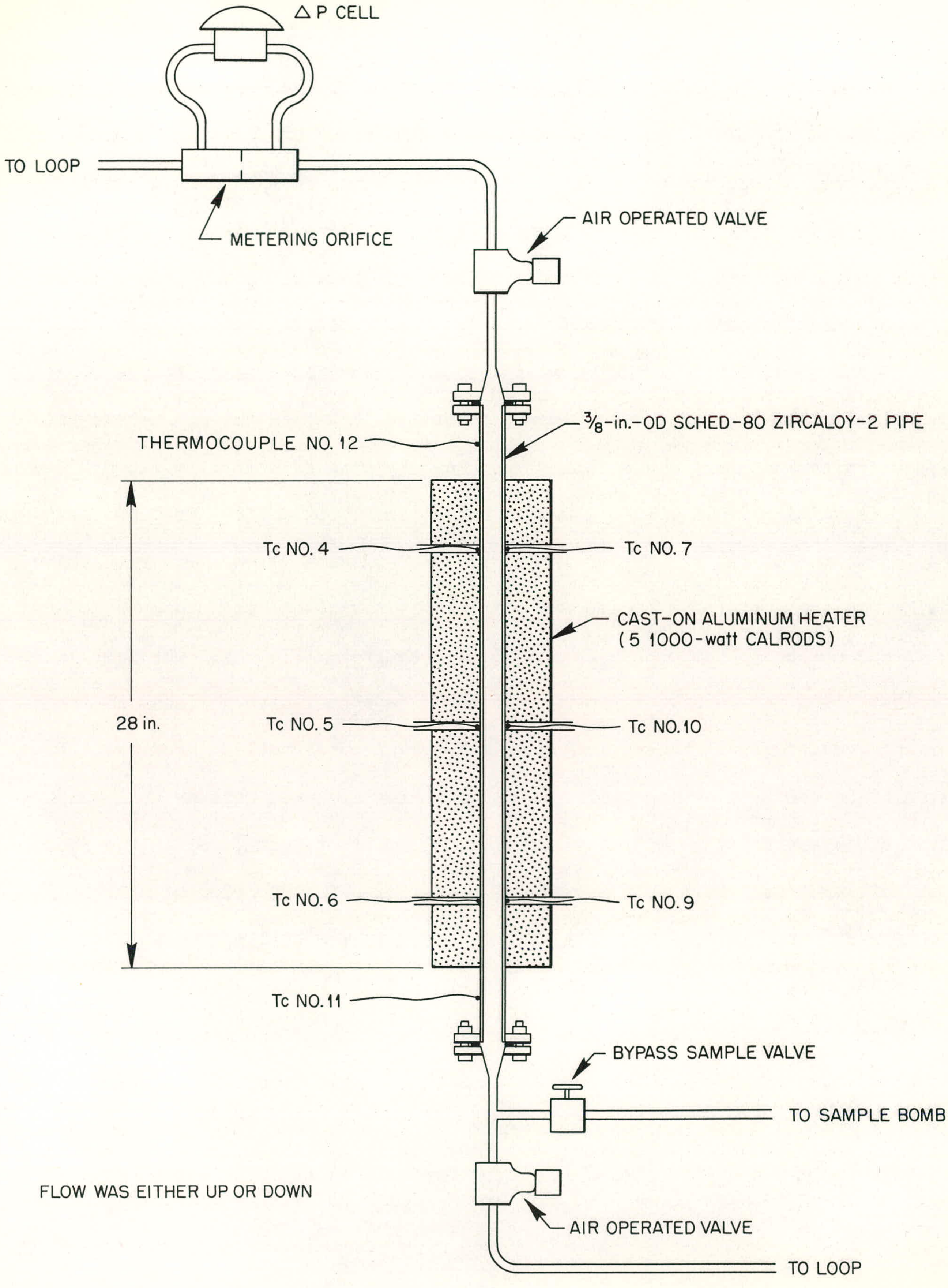

Fig. 1. Zircaloy-2 Bypass as Installed Vertically on 100A Loop H.

orifice connected to a differential-pressure-measuring cell was installed upstream of the heated Zircaloy-2 bypass to determine flow rates at operating temperature and pressure. Also, the orientation of the bypass was changed from a nearly horizontal to a vertical position with the solution entering at the top. The glass mockup indicated that in the vertical position the pipe walls would be wet continuously with incoming solution.

For the initial tests the main loop and pressurizer temperatures were controlled at 280°C, and a total loop pressure of 1150 psia was maintained with oxygen pressurization. The solution used was the same as before, viz., 0.025 m UO_2SO_4 containing 0.015 m D_2SO_4, 0.01 m $CuSO_4$, and 0.004 m $NiSO_4$ in D_2O. Heat was applied to the Zircaloy-2 bypass in steps. The solution temperature rise through the heated section of the bypass was obtained by taking the difference between inlet and outlet thermocouples 12 and 11, respectively (Fig. 1). The temperature gradient along the length of pipe was found to be approximately linear for nonboiling conditions but became nonlinear and erratic when boiling occurred. By calculating the inside pipe-wall temperatures from measured outside wall temperatures and comparing them with the solution saturation temperature, it was found that boiling should have occurred at low heat fluxes in the order of about 7500 Btu/ft^2·hr. Most of the data were obtained in the boiling region. As boiling became more vigorous, the flow rate decreased and became erratic, probably by interruption of the flow by the large amounts of vapor and gas produced. When the flow rate decreased to the lowest value deemed safe (about 0.12 gpm; 0.2 fps), the pump frequency was increased upon each increase in heat flux in order to maintain the minimum flow rate through the bypass. In this way a heat flux of

58,700 Btu/ft^2·hr was attained. The maximum inside Zircaloy-2 pipe-wall temperature was 430°C under these conditions.

No deposition of uranium occurred despite the vigorous boiling and despite the fact that the maximum wall temperature was as much as 100°C above the second-liquid-phase temperature. This was strong evidence for the hypothesis that so long as the pipe walls were wet continuously (or even intermittently) with incoming solution, deposition would be prevented.

The tests were repeated several times with slight modifications: (1) System pressure was increased from 1150 to 1400 psia with oxygen and operated as above. (2) The system was changed to hydraulic pressurization and operated at 1450 psia. The gas content of the solution was maintained at about 20 ppm oxygen. (3) System pressure was increased to 1800 psia hydraulically but otherwise operated as in item 2 above. (4) The system was hydraulically pressurized to 1150 psia, but oxygen was added directly to the loop through a thermal valve to give a concentration of about 1000 ppm. (5) The main-stream temperature was lowered to 250°C, and the system was hydraulically pressurized to 1800 psia. Oxygen was maintained at 20 ppm. (6) The direction of flow through the bypass was reversed; i.e., made to go up from bottom to top. The system was pressurized with oxygen to 1300 psia, and the main-stream temperature was 280°C. (7) With flow from bottom to top as in item 6, the system was hydraulically pressurized to 1800 psia, and the main-stream temperature was 250°C. Oxygen was maintained at 20 ppm.

No deposition occurred during any of these tests. Heat input data were measured carefully under each condition to obtain heat transfer data. These data will be the subject of a separate report.[7]

2. Loop L-2-23 Tests

In addition to the above tests, in-pile loop L-2-23 was operated out-of-pile at the Y-12 in-pile loop mockup facility for the purpose of studying uranium deposition on heated metal surfaces. The preliminary results obtained to date have been reported elsewhere[4] in some detail. Briefly, deposition of uranium, copper, and nickel sulfates occurred from a solution containing 0.025 *m* UO_2SO_4, 0.015 *m* D_2SO_4, 0.011 *m* $CuSO_4$, and 0.004 *m* $NiSO_4$ in D_2O being circulated through the core region at 0.3 fps (pump on 20 cps) at main-stream temperatures of 225, 250, and 280°C when the temperature of the core wall was increased to produce local boiling by the application of 8,000 to 10,500 $Btu/ft^2 \cdot hr$. Figure 2 is an X-radiograph of the loop core section (containing corrosion specimens) taken after deposition had occurred (upper photograph) and after the deposit had been caused to dissolve (lower photograph) by removal of heat from the core section. As shown, the deposit of salt is only on the upper part of the core wall under the heated area where a vapor pocket would be expected to form when boiling occurred. The deposit on the core wall could also be dissolved by increasing the solution flow rate or by increasing the loop pressure to prevent boiling.

Since the addition of sulfuric acid to the HRT appeared to decrease the loss of uranium from solution,[8] several tests were carried out with solutions containing various concentrations of sulfuric acid. At a loop temperature of 280°C and a pressurizer temperature of 283 to 286°C with 8,000 $Btu/hr \cdot ft^2$ applied to the core, a 0.04 *m* UO_2SO_4 + 0.0067 *m* $CuSO_4$ solution lost uranium and copper when the sulfuric acid concentration was 0.006 *m*, but deposition did not occur when the acid concentration was 0.010 or 0.025 *m*. However, deposition did occur in the latter case when the heat flux was increased to 20,000 $Btu/hr \cdot ft^2$

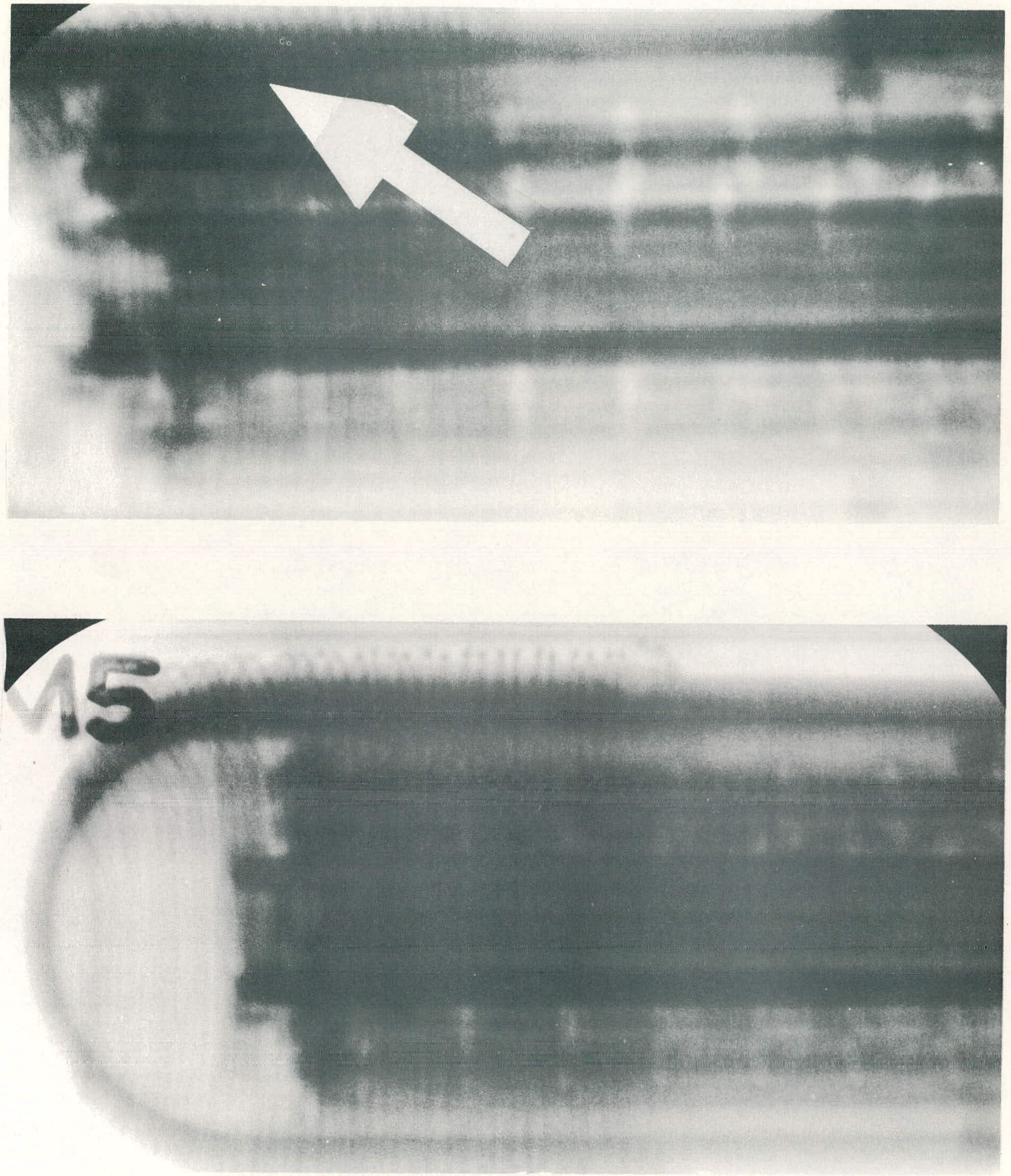

Fig. 2. X-Radiograph of L-2-23 Core Showing Salt Deposition (top, arrow), and Operation Without Deposition (bottom)

and the pressurizer temperature decreased to 279°C. Similarly, deposition of uranium, copper, and nickel occurred from a 0.025 *m* UO_2SO_4-0.011 *m* $CuSO_4$-0.004 *m* $NiSO_4$ solution at a loop temperature of 280 and pressurizer temperature of 280°C with 8,000 $Btu/hr{\cdot}ft^2$, when the acid concentration was 0.015 *m* but not with 0.025 *m* D_2SO_4. On the other hand deposition did occur from 0.025 *m* UO_2SO_4-0.011 *m* $CuSO_4$-0.004 *m* $NiSO_4$ solution at a loop and pressurizer temperature of 225°C with 8,000 $Btu/hr{\cdot}ft^2$ when the acid concentration was 0.015, 0.025, and 0.05 *m*.

However, there were indications that the rate and extent of deposition were decreased at the higher acid concentrations. The reason for the different effect of the acid at 225°C than at 280°C is not clear.

Figure 3 is a plot of concentration of several ions <u>versus</u> time in one of the L-2-23 tests. The "half-times" (time for the concentration to decrease to one-half its original value) for uranium, copper, nickel, and sulfate were almost identical (about 28 hr), showing that the salts were depositing together. The loss of acid from the main circulating solution was significant, since deposition in the HRT resulted in an increase in acid concentration.[8] Acid was lost in L-2-23 at a slower rate than the other ions, having a half-time of about 35 hr. This behavior was observed in 100A Loop H[9] and perhaps indicates that the uranium, copper, and nickel were deposited partially as bisulfate salts. In this case the kinetics of the disassociation of the bisulfate ion and the relative solubilities of the sulfate and bisulfate salts may have caused the delay in the loss of acid.

After 90 hr of circulation with the core heater on and deposition occurring, the core heat was removed. Within 12 hr, concentrations in the main-stream had returned to their original values. Actually concentrations were slightly

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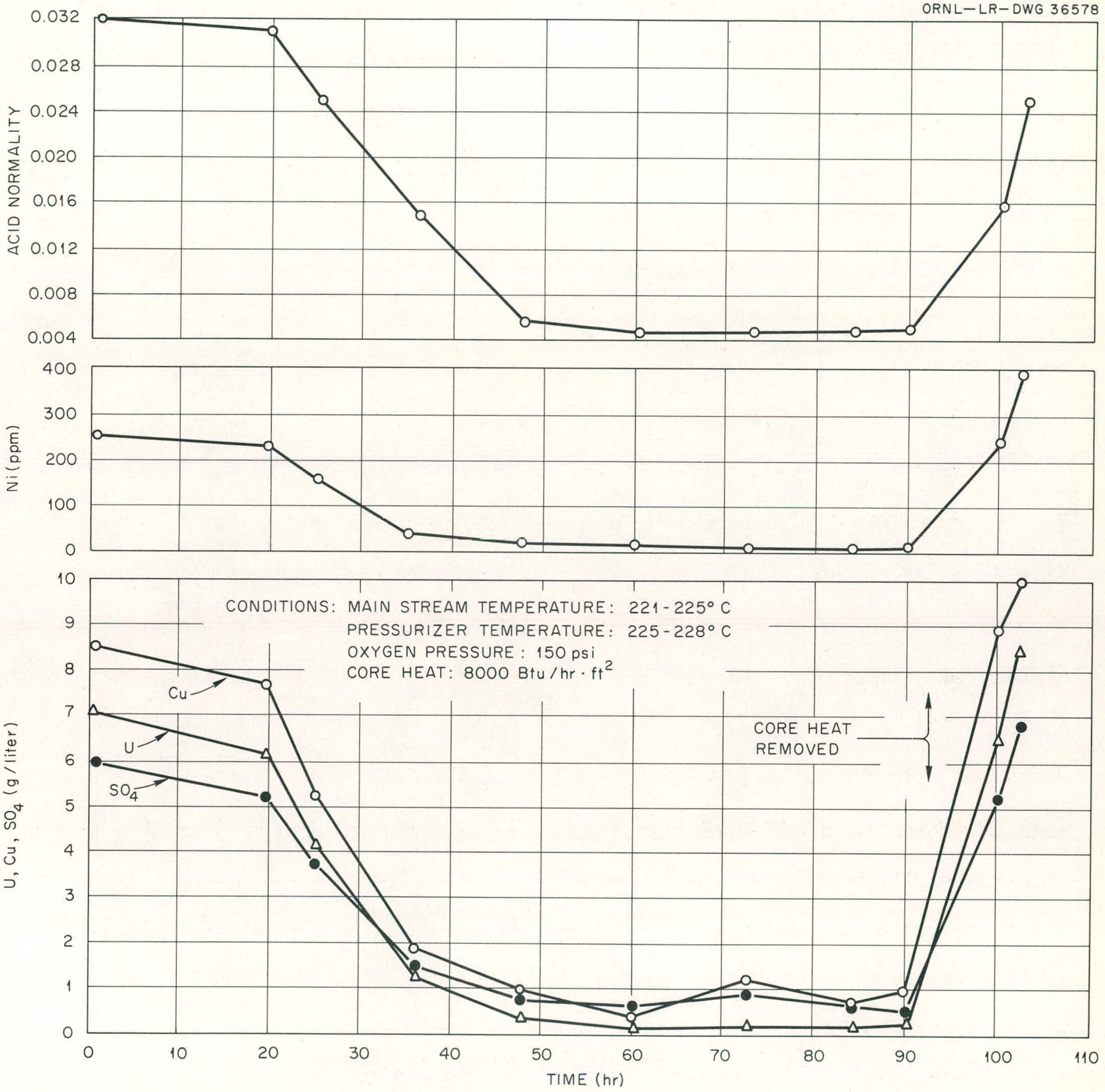

Fig. 3. Changes in Concentration of Various Ions with Time in Loop L-2-23 (Operated out-of-pile).

higher than the original, since makeup solution of the original solution had been added to replace dilute solution samples taken when deposition was occurring.

Curves similar to Fig. 3 were obtained under a variety of conditions. All curves were qualitatively similar, but the half-time and the final equilibrium values of concentrations in the main circulating stream appeared to be specific for each condition.

Therefore, the following conclusions were drawn from all of the above tests:

(1) Deposition of uranium, copper, and nickel occurred as acid-containing sulfate salts on a hot, dry pipe wall.

(2) Boiling of the solution was necessary but not sufficient to cause deposition. The formation of a vapor space or gas pocket was necessary in addition in order to give a hot, dry surface on which evaporation could occur. Therefore heat flux, solution flow rate, surface temperature, and surface geometry or orientation were important variables which affected boiling and the formation of a vapor space.

(3) The tendency for deposition was decreased by the addition of sulfuric acid to the solution or by maintaining low concentrations of noncondensable gases in solution.

(4) The deposited salts were readily soluble in the solution whenever boiling ceased.

B. Effect of Hydroclone Inlet Geometry on Effectiveness of Separating Solids

It was observed during run F-70 that a hydroclone attached to F loop during a test of the HRT core-pressure-vessel flange and transition joint mockup collected only about 14% of the oxide formed by corrosion during the run.[10] It was felt, however, that the low effectiveness of the hydroclone may have been due to the inlet line geometry. During run F-70, the inlet line to the hydroclone was attached to the main loop piping as shown in Fig. 4; and the possibility existed that a significant portion of the solids circulating in the main-stream may have been swept past the opening leading to the hydroclone. Therefore the system was redesigned as shown in Fig. 5 to permit attaching the inlet line at the bottom of the pressurizer, allowing solids to "fall" into the line leading to the hydroclone. The venturi shown in Fig. 5 was installed to establish the proper pressure drop across the hydroclone. In both installations the flow rate through the hydroclone was 0.6 gpm under 46 ft of head. Under these conditions the 0.4-in. hydroclone should have removed essentially all particles having a mean diameter of 0.8 micron or greater after a maximum of 50 hr.[11]

The three initial runs in the present series were made with the hydroclone attached in the "normal" manner. Run F-71 was made to check out the system and establish the sampling schedule for the hydroclone underflow pot. Three samples taken consecutively each day appeared to remove solids completely from the underflow pot.

In run F-72 the four type 347 stainless steel pins and three of the titanium pins used in run F-71 were replaced with seven type 410 stainless steel pins in the expectation that the pins would corrode heavily and put a large amount of corrosion products into circulation. Actually corrosion of the type 410 stainless steel pins was not so severe as expected. Therefore the run can be considered to have been a second check-out of the system. The solids collected in the hydroclone underflow pot were removed and weighed. Table II is a list of

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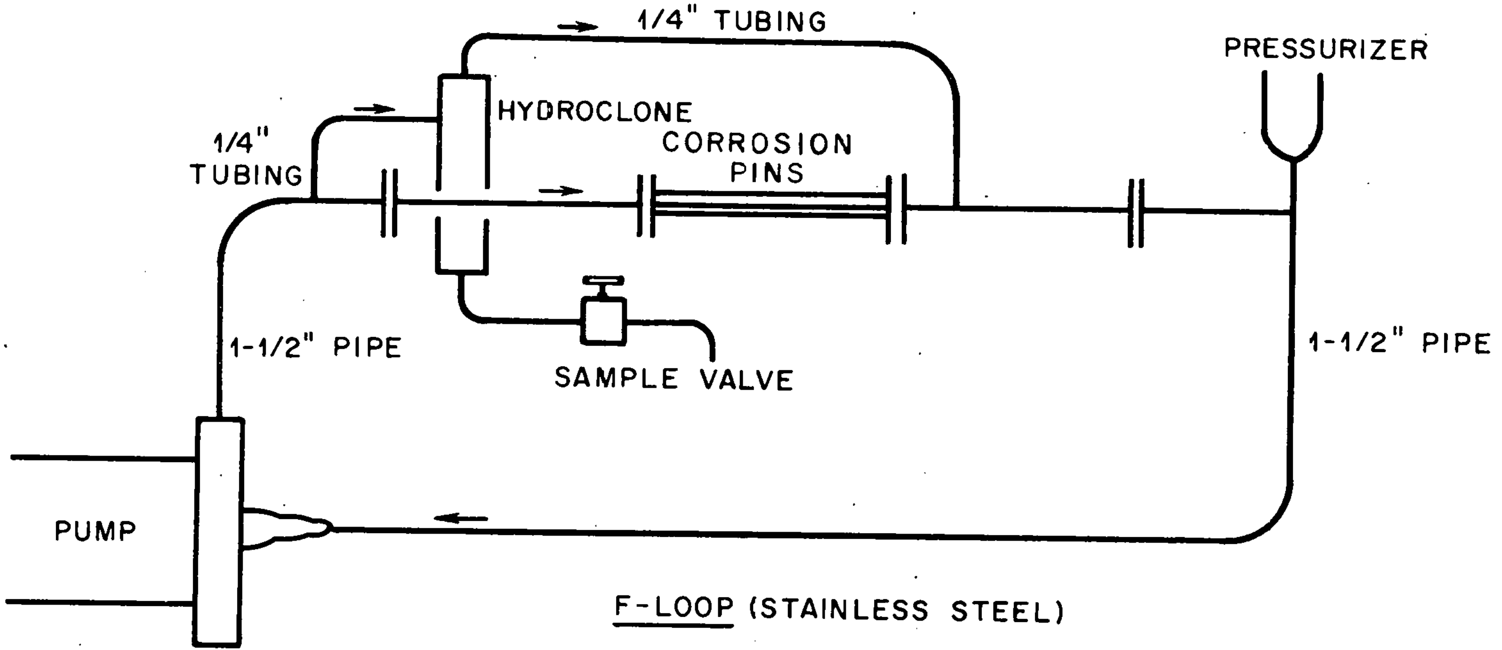

Fig. 4. Hydroclone Mounted in "Normal" Position

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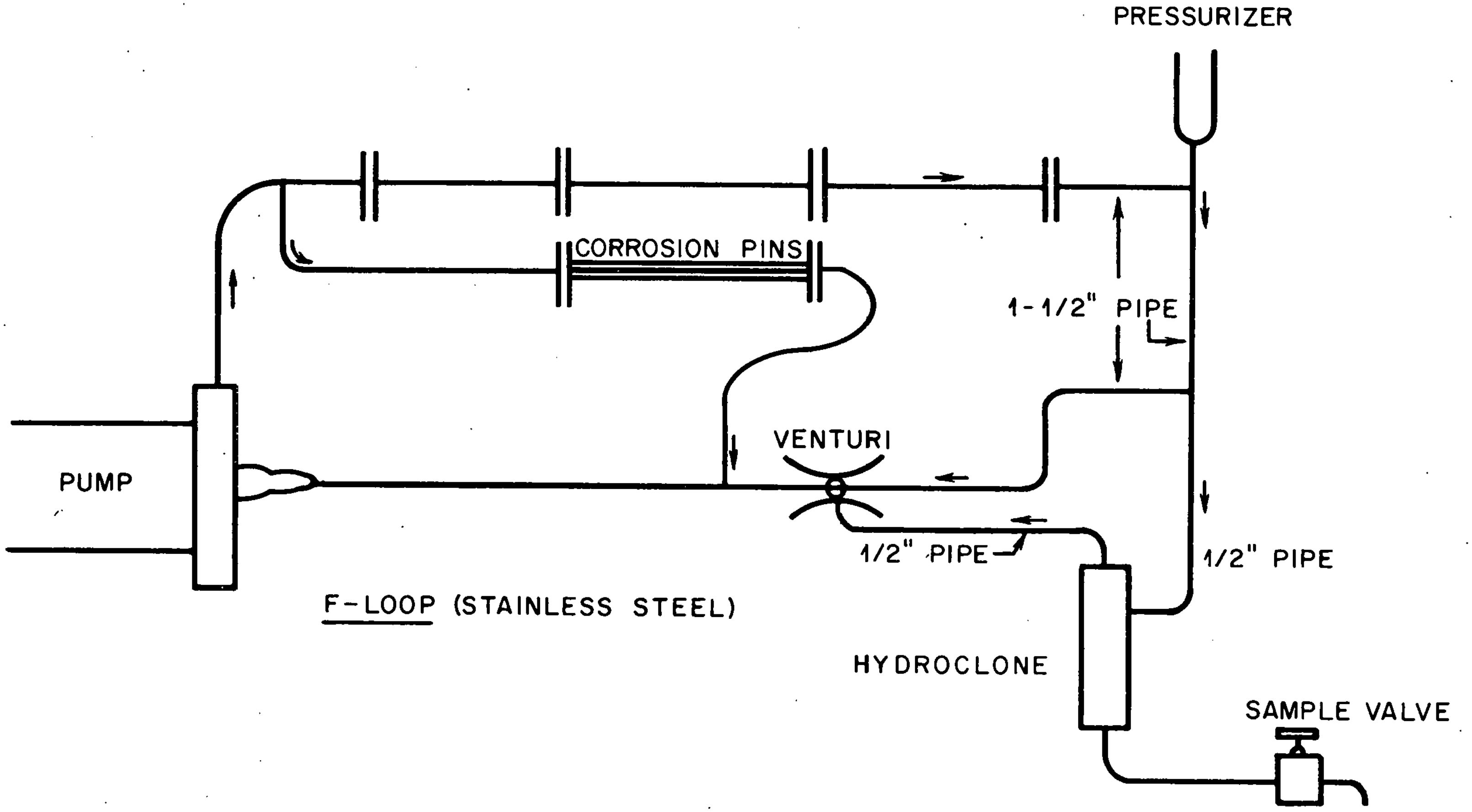

Fig. 5. Hydroclone Mounted in "Fallout" Position

the amount of oxide produced in each run, both from corrosion of the pins and from corrosion of the loop, and of the total amount of oxide collected in the underflow pot. Not included in the table is an unknown amount of scale cracked off the loop walls and thrown into circulation during startup by differential thermal expansion of the metal and oxide. Actually, the best estimate of the amount of scale so cracked loose would be from the amount of scale collected in the underflow pot, since the scale cracked off would presumably have a fairly large particle size which should be efficiently removed by the hydroclone. If we neglect the amount of scale cracked loose, the hydroclone collected 7.7% of the solid corrosion products formed during the run. The quantity of stainless steel corroded during the run was obtained from the nickel concentration and volume of solution and from the weight loss of specimens which did not contain nickel. If we assume that half the scale collected was from scale cracked loose (0.34 g), the effectiveness is lowered to 7.4%.

In run F-73 the type 410 stainless steel pins were replaced with seven carbon steel pins. The carbon steel pins corroded heavily; 27.5 g of steel was dissolved. As can be seen in Table II, 9% of the scale formed was collected, neglecting scale cracked off the loop. Therefore the hydroclone mounted in the "normal" manner was only about 7 to 9% effective in removing solids whether a little or a relatively large amount of solids was produced.

Runs F-74 and 75 were made with the hydroclone attached in the "fallout" position as shown in Fig. 5. No steel corrosion pins were included in run F-74. Surprisingly, the hydroclone appeared to be 42% effective in removing solids. However, very likely most of the scale collected was actually produced in run F-73 and was cracked loose on startup of F-74, since the run had to be started twice when the pump drew high amperage 18 hr after the original startup. The two samples before pump trouble and three samples shortly after the second startup contributed 1.72 g of the 3.12 g total.

Table II. Amounts of Scale Formed and Collected in Runs F-71 through 75

Run No.	Scale Formed by Corrosion			Scale Collected in Hydroclone (g)	Per Cent of Corrosion Products in Underflow Pot
	Loop (g)*	Pins (g)*	Total (g)*		
F-71	6.42	1.24	7.66	Not weighed	-
F-72	7.15	1.72	8.87	0.68	7.7
F-73	4.30	39.29	43.59	3.93	9.0
F-74	7.43	0.0	7.43	3.12	42
F-75	4.77	36.37	41.14	2.24	5.5

* As Fe_2O_3.

Run F-75 was made with ten carbon steel pins in order to produce a large amount of oxide in the system. The hydroclone was only 5.5% effective (neglecting scale cracked off the loop walls).

Therefore no clear-cut advantage of mounting the hydroclone in the "fallout" position was indicated. On the other hand, the advantage of cracking the scale off the loop walls by thermal cycling was evident, as observed in run F-70.[12]

During all five runs, samples of solution from the main circulating stream were generally quite clear without visible suspended solids after the first 50 hr or so of the run. Therefore it appeared that with either hydroclone mounting most of the solids which got into circulation were removed by the hydroclone, but that the major fraction of the solids formed by corrosion did not remain in the circulating stream.

Two platinum pins were exposed in runs F-73 and -75, and in each run the pins gained weight by deposition of oxide. Table III gives the weight and compositions of the tenacious scale deposited. If the average scale weight is taken to be 1.6 mg/cm^2 in F-73 and 0.8 mg/cm^2 in F-75, the amount deposited over the whole loop would have been about 36 g in F-73 and 18 g in F-75. The platinum pins were also weighed as-removed from the loop after F-75. The weight loss upon scrubbing off the loose, "fine" scale averaged 0.52 mg/cm^2, giving a total of 12 g of loose scale on the entire loop. Taken together, the loose and tenacious scale accounted for 48 g of oxide in F-73 and 30 g in F-75. Therefore, very roughly, the total amount of oxide produced by corrosion during each run was accounted for, either by collection in the underflow pot, or by deposition on the loop walls.

Table III. Analysis of Scale Collected on Platinum
Pins During Runs F-73 and -75

Run No.	Scale Weight (mg/cm^2)	Composition (Weight %)				
		Fe	Cr	Ni	U	Cu
F-73	1.8	54	2.3	0.4	5.7	< 1
	1.4	36	1.3	0.5	4.3	< 1
F-75	0.78*	61	0.5	0.4	4.3	1.6

* Scale on two pins was combined.

The weight of the tenacious scale on the platinum pins illustrates that a major fraction of the oxide formed by corrosion of steel deposits on all metal surfaces and does not circulate long, if at all. The loose scale may arise from particles too small for the hydroclone to separate effectively and from scale that cracks off the loop walls and settles out when the pump is stopped and the loop cooled at the end of the run. It is possible that the oxide formed by corrosion is distributed from the corroding area to the rest of the system as colloidal particles.

The amount of uranium found in the scale on the platinum pins, about 4%, is higher than the usually observed 1%, although even higher percentages have occasionally been found.[13]

The low percentage of chromium in the scale in relation to its percentage in the steel is due partially to the solubility of chromium(VI) in the solution used, and perhaps partially to the fact that when stainless steel corrodes the chromium is oxidized immediately to the trivalent state whence it can hydrolyze to the oxide in situ. Iron, on the other hand, is oxidized in two steps to the trivalent state and so has more of a chance to be swept into the solution before hydrolysis to the oxide.

All of the oxide collected in the hydroclone was given as a wet residue to the Chemical Technology Division for further characterization. We would like to acknowledge the assistance of R. A. McNees and his group in determining the weight of oxide collected in all of the runs and of P. A. Haas for the loan of the hydroclone.

C. Instability of Uranyl Sulfate-Lithium Sulfate and Uranyl Sulfate-Magnesium Sulfate Solutions

Several in-pile experiments have shown the value of adding lithium sulfate to uranyl sulfate solutions to decrease radiation-induced corrosion of Zircaloy-2.[14] However, slightly different uranium and copper concentrations from those used in the in-pile experiments would be required for use in the HRT, which made it advisable to determine the stability of solutions more nearly simulating the HRT core and blanket concentrations. In one test the solution was 0.025 m UO_2SO_4 containing 0.13 m Li_2SO_4, 0.063 m D_2SO_4, and 0.02 m $CuSO_4$ in D_2O, corresponding to the core solution, and in another test the solution was 0.01 m UO_2SO_4 containing 0.045 m Li_2SO_4, 0.027 m D_2SO_4, and 0.005 m $CuSO_4$ in D_2O, corresponding to the blanket solution. Both solutions were circulated initially at 300°C in stainless steel loops.

Figures 6 and 7 illustrate the change in concentration of several ions with time in the runs with simulated core (run J-97) and blanket (run K-25) solution, respectively. Both solutions were unstable; the more concentrated solution lost 80% of its copper and 10 to 20% of its uranium; the more dilute solution lost 90% of its copper and 60% of its uranium. As the uranium and/or copper came out of solution, the acid concentration increased in proportion, indicating that the loss was due to a hydrolytic process and not to crystallization of salts as described in Sec. III-A of this report. The lithium concentration was relatively stable during both tests except for an initial 20% decrease at the start of J-97. The modified Marshall ratios calculated for the final solutions at 300°C were 0.32 and 0.30 for the core and blanket solutions, respectively. These values are considerably lower than observed previously for solutions containing less lithium sulfate and sulfuric acid.[15]

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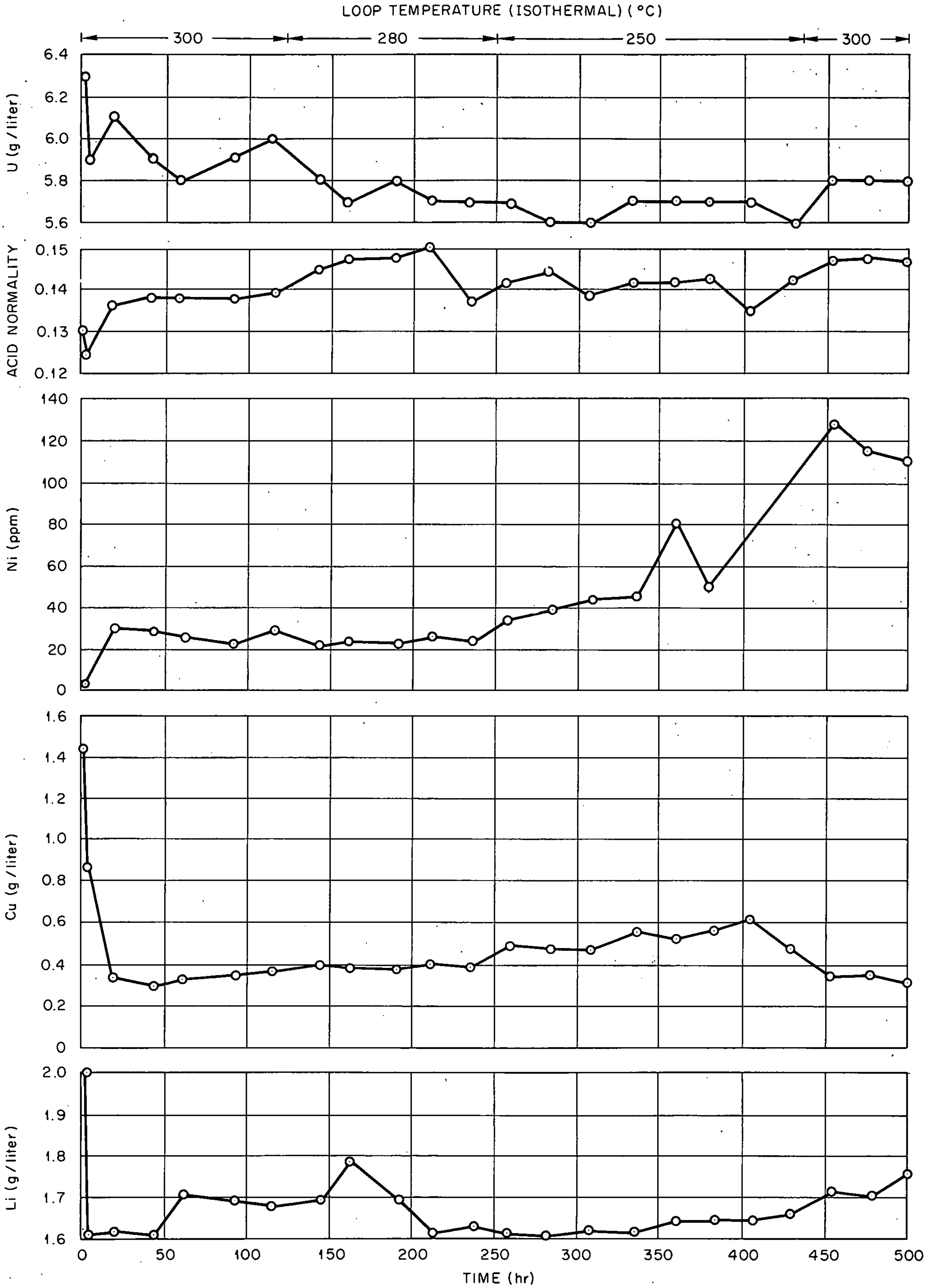

Fig. 6. Concentration of Several Ions vs Time in Run J-97.

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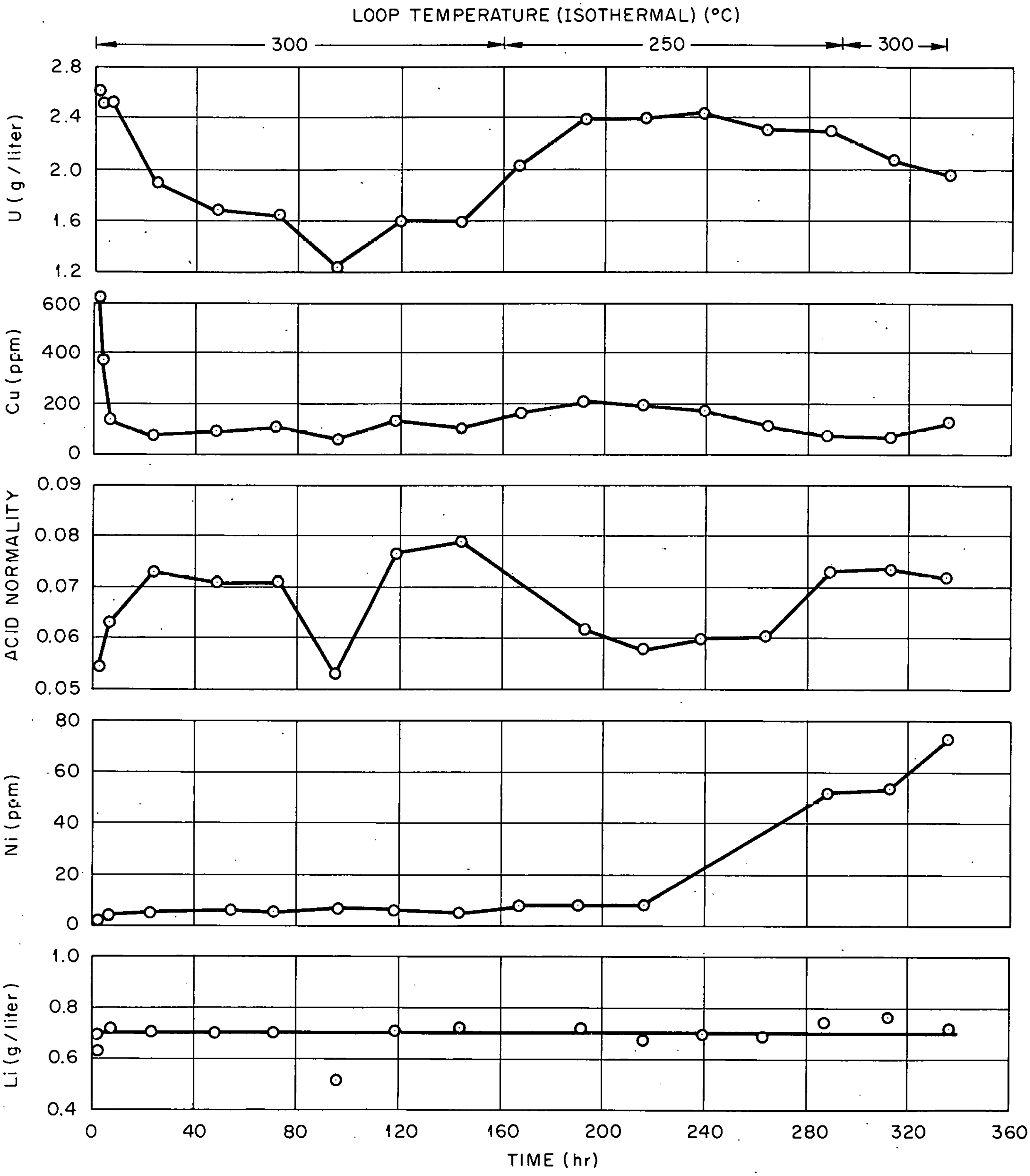

Fig. 7. Concentration of Several Ions vs Time in Run K-25.

As indicated in Figures 6 and 7, the temperature was lowered during each run in order to determine to what extent solubilities increased. In J-97, the copper concentration increased from 0.35 to 0.4 g per liter upon lowering the temperature from 300 to 280°C and then increased to 0.5 g per liter on going to 250°C. Upon raising the temperature to 300°C, the copper concentration again dropped back to 0.35 g per liter. The uranium concentration appeared to decrease on going to 280 and 250°C. The acid concentration also was erratic. In run K-25 the temperature was lowered to 250°C, and 80% of the uranium reappeared in solution. The copper concentration increased from 0.1 to 0.2 g per liter at the same time.

Since magnesium sulfate is generally more soluble in these solutions than lithium sulfate,[15] a test similar to J-97 was made with a solution containing 0.04 *m* UO_2SO_4, 0.2 *m* $MgSO_4$, 0.1 *m* D_2SO_4, and 0.01 *m* $CuSO_4$. Figure 8 is a plot of the concentration of several ions versus time for this test, run A-127. As can be seen, this solution also was unstable at 300°C. No other temperatures were investigated. The behavior of the solution was different from that of the lithium-containing solutions in that magnesium was the main unstable species and the acid concentration decreased rather than increased, as in the previous tests. No uranium was lost from solution, but about 20% of the copper precipitated. The loss of both magnesium and acid suggested that some magnesium bisulfate was precipitated, although the amount of acid lost was only about one-half that of the magnesium lost. The modified Marshall ratio of the final solution at 300°C was 0.36, again lower than previously observed with magnesium-containing solutions.[15]

The results of the above three tests showed that a 0.025 or 0.04 *m* UO_2SO_4 solution containing a high sulfate concentration as lithium or magnesium sulfate

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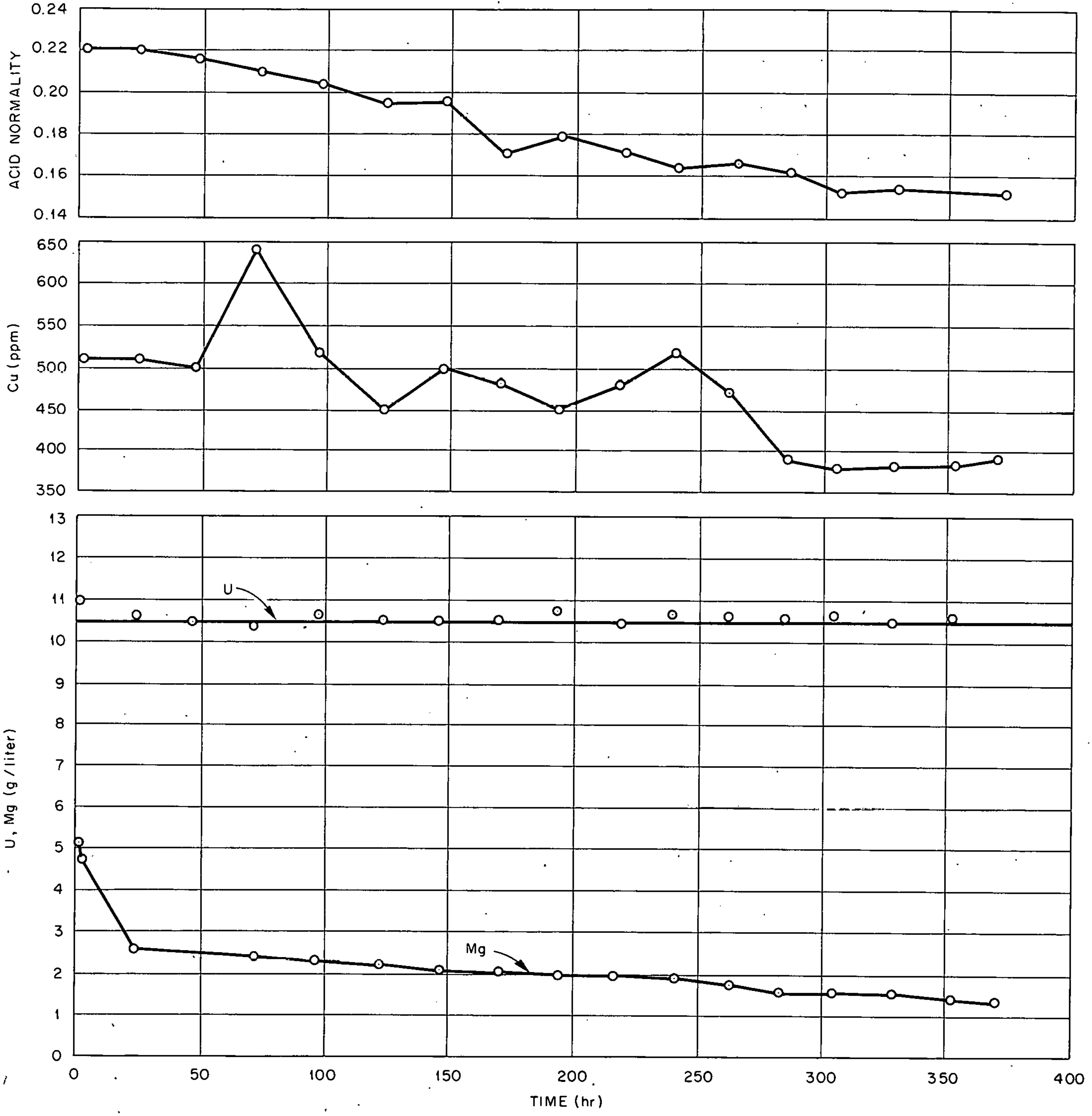

Fig. 8. Concentration of Several Ions vs Time at 300° C in Run A-127.

and enough copper sulfate for HRT use would not be stable unless excessive amounts of sulfuric acid were incorporated in the solution.

D. Corrosiveness of Uranyl Sulfate-Lithium Sulfate Solutions

During the tests described in Sec. III-C above, it was realized that the addition of sulfuric acid would stabilize the solutions but would also increase their corrosiveness, particularly in crevices. In order to determine quantitatively the effect of acid on corrosion, two tests were made with 0.04 *m* UO_2SO_4 containing H_2SO_4, 0.2 *m* Li_2SO_4, and 0.01 *m* $CuSO_4$. Both tests were carried out in a stainless steel loop at 225°C, the temperature at which corrosion is usually most serious in these systems. In the first run the sulfuric acid concentration was 0.1 *m*, and in the second it was 0.2 *m*.

The first run with 0.1 *m* H_2SO_4 was made for 469 hr, after which the specimens were removed from the loop, scrubbed, weighed, and then returned to the loop for an additional 200-hr exposure. In this way it was possible to determine that up to about 20 fps the type 347 stainless steel lost roughly 14 mg/cm^2 and then filmed over and practically stopped corroding. Above the critical velocity the corrosion rate was constant at 35 to 45 mpy.

The second run with 0.2 *m* H_2SO_4 was scheduled for 200 hr, but a type 347 stainless steel ring gasket corroded drastically at a crevice between it and a type 347 stainless steel sample barrel, causing a leak within 143 hr. Therefore it was demonstrated that the addition of relatively large concentrations of acid to these solutions can lead to severe crevice attack.

The corrosion of the type 347 stainless steel specimens in the latter run did not show the expected increase in attack, however. The critical velocity was actually higher, about 35 fps, and weight losses below the critical velocity were only about 0.6 mg/cm^2. Corrosion rates above the critical velocity were erratic, 20 to 100 mpy. The reason for the higher critical velocity and small low velocity weight loss may have been that three cast type 347 stainless steel specimens dissolved completely, introducing 12.4 g of steel corrosion products into the solution. The type 347 stainless steel clamping bands used to clamp the specimen holder together were also severely corroded in the crevice between the specimen holder and the sample barrel. It has been shown on numerous occasions previously that a large quantity of corrosion products in solution will inhibit corrosion of fresh steel surfaces.[16] The reason for the dissolution of the cast specimens is not known. However, visual inspection of identical unexposed specimens revealed the presence of surface cracks or imperfections. Since the solution was shown to attack crevice areas, the imperfections may have served as crevices which then led to drastic attack.

A third run was made to investigate crevice corrosion. A solution similar to that used in the first run was used, 0.04 m UO_2SO_4 containing 0.1 m H_2SO_4, 0.2 m Li_2SO_4, and 0.01 m $CuSO_4$, and the temperature of circulation was 200°C. Type 347 stainless steel specimens 3/8 in. x 3 in. x 1/16 in. were bolted together in pairs to form a crevice and four such pairs were suspended in the loop pressurizer where the flow rate past the specimens was about 0.03 fps. It was anticipated that the very low flow rate would enhance crevice attack, since a similar static test had shown extensive corrosion of this type.[17] However, at the end of 200 hr no crevice attack or accelerated corrosion was evident. Therefore it appeared that even a very slight flow past the specimens was enough to prevent the crevice attack that was observed in the static tests.

E. Inhibition of Stress-Corrosion Cracking with Fluoride and Phosphate

Studies on the effect of fluoride and phosphate ions on the stress-corrosion cracking behavior of type 347 stainless steel exposed to oxygen- and chloride-containing water at 200°C were continued. It was shown previously that water containing 10 to 15 ppm oxygen and 50 ppm chloride as potassium chloride would produce many cracks within 200 hr in type 347 stainless steel specimens stressed beyond their yield point; however, the addition of either 190 ppm fluoride as potassium fluoride or 60 ppm phosphate as trisodium phosphate to the water decreased the frequency of cracking to a very low value.[18] Recently a 1000-hr loop run was made to determine the combined effect of fluoride and phosphate ions. The water contained about 50 ppm chloride as potassium chloride, 14 ppm oxygen, 190 ppm fluoride as potassium fluoride, and 60 ppm phosphate as trisodium phosphate, and was circulated at 200°C. Seven type 347 stainless steel specimens were exposed totally immersed at a flow rate of about 3 fps. Six of the specimens were stressed beyond their yield strengths and one was mounted unstressed as a control. Two of the stressed specimens were mounted singly, two were coupled together, and two were coupled to carbon steel specimens in order to study galvanic and couple effects. The unstressed control specimen was also coupled to a carbon steel specimen.

At the end of 1000 hr the specimens were examined metallographically; one small crack was found. Peculiarly enough, this single crack occurred on the unstressed control specimen. However, the crack was at the end of the specimen where the stamped identification numbers produced large local stresses.

The combination of fluoride and phosphate was not completely effective in preventing stress-corrosion cracking. Statistically, the difference in cracking frequency between the solution containing phosphate and that containing phosphate and fluoride was not significant. Since phosphate is already present in HRT boiler water, there would appear to be no benefit in adding fluoride ions to it.

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

A. Stress-Corrosion Cracking

1. Boiling Uranyl Sulfate Solution - Effect of Preformed Films

Tests have been continued to determine the effectiveness of preformed films on type 347 stainless steel in preventing stress-corrosion cracking of the alloy in a boiling, simulated reactor fuel solution containing 0.04 *m* UO_2SO_4, 0.02 *m* H_2SO_4, 0.005 *m* $CuSO_4$, and 50 ppm of chloride as potassium chloride. The prefilming was conducted in a similar solution containing no chloride ions. Studies emphasizing effectiveness of the film against cracking as a function of the prefilming temperature have been conducted during the past quarter. Preliminary results of the investigation have been reported.[19] Prefilming was accomplished by exposing stressed specimens for periods of 100 hr in the above chloride-free, oxygenated fuel solution at 25°C intervals over the temperature range from 100 to 300°C. The test specimens consisted of elastically stressed U-bends prepared from strips sheared from annealed 0.025-in.-thick type 347 stainless steel. A total of nine such specimens was generally used for each prefilming temperature. Previous studies had shown that approximately 50% of similar untreated specimens (29 out of 60) of the same heat of type 347 stainless steel developed cracks during the first 500 hr of exposure in boiling, aerated 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ solution containing 50 ppm of chloride.[20]

Table IV summarizes the results of the stress-corrosion cracking tests with the U-bend specimens prefilmed at the different temperatures. In all tests except one, the specimens were stressed prior to the filming treatment. One set of 6 specimens, pretreated at 300°C, was stressed after the 100-hr prefilming treatment. Of the 78 specimens that were prefilmed after stressing, not a single case of cracking was observed during exposure periods of 500 to 3500 hr. Similarly, no cracks were found in the 6 specimens that were prefilmed before stressing during a 500-hr period. The latter results indicated that the preformed film was of sufficient ductility to withstand rupturing during the bending operation. When cracking occurs in tests with untreated specimens, it invariably takes place during the first 500 hr.

Since the use of a prefilming treatment at temperatures between 100 and 300°C was completely successful in preventing cracking of the 0.025-in.-thick type 347 stainless steel, a few experiments of a similar nature were made with a different heat of the alloy. Untreated, elastically stressed U-bend specimens of this alloy, prepared from annealed 1/16-in.-thick sheet, cracked 100% of the time in the boiling, chloride-containing, simulated fuel solution.[21] All 9 specimens cracked during the first 200 hr of test. For the present tests, a prefilming temperature of 100°C was selected. Twelve of the 1/16-in.-thick specimens were prefilmed for 100 hr in the boiling, chloride-free, 0.04 m UO_2SO_4-0.02 m H_2SO_4-0.005 m $CuSO_4$ solution. Half of the 12 specimens were prefilmed after stressing, and the remaining specimens were prefilmed before the stressing operation. All specimens were placed in the above boiling solution containing 50 ppm of chloride. After 1500 hr of exposure, the following results were obtained: (1) one of the specimens that were prefilmed after stressing was cracked; cracking occurred during the interval between 500 and 1000 hr of test, and (2) three of the specimens that were prefilmed before stressing cracked during the exposure interval between 200 and 500 hr. The high percentage of failures on the latter specimens may have been due to rupturing of the preformed film during stressing.

Table IV. Effect of Prefilming Temperature(a) on Stress-Corrosion Cracking Behavior of Type 347 Stainless Steel in Boiling, Chloride-Containing Synthetic Fuel Solution(b)

Prefilming Temperature (°C)	Number of Specimens	Total Test Time (hr)	Observations
100	6	3500	No cracking
125	9	2500	No cracking
150	9	2500	No cracking
175	9	2500	No cracking
200	9	2500	No cracking
225	9	2500	No cracking
250	9	2000	No cracking
275	9	1500	No cracking
300	9	500	No cracking
300(c)	6	500	No cracking

(a) Prefilming treatments conducted for 100 hr in chloride-free 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ solution.

(b) 0.04 *m* UO_2SO_4-0.02 *m* H_2SO_4-0.005 *m* $CuSO_4$ solution containing 50 ppm of chloride.

(c) Specimens prefilmed prior to stressing.

The experimental data definitely show that preformed films effectively reduce the susceptibility of type 347 stainless steel to stress-corrosion cracking in a boiling, chloride-containing, simulated homogeneous reactor fuel solution. Prefilming before stressing afforded complete protection on specimens from a heat of the alloy that in the absence of the preformed film exhibited a 50% susceptibility to cracking; approximately 85% protection was realized on a heat of the alloy that was 100% subject to cracking in the absence of a preformed film. The reason for the difference in degree of susceptibility to cracking in untreated specimens of the above two heats of type 347 stainless steel has not been resolved.

2. Chloride-Containing Water

(a) Cast Type 347 Stainless Steel.--Previous tests with cast type 347 stainless steel showed it to possess excellent resistance to stress-corrosion cracking in a number of chloride-containing environments.[22] In one test a stressed, simple-beam specimen of the cast alloy was exposed for 100 hr in boiling (154°C) 42% $MgCl_2$ solution. Although substantial subsurface attack was subsequently disclosed by metallographic examination, no cracks were found. The environment generally produces cracking in wrought type 347 stainless steel in a stressed condition in 5 hr or less. Recently the test was repeated with duplicate stressed simple-beam specimens from the same heat of the cast alloy. After 5 hr, both specimens showed numerous shallow cracks. Why these specimens cracked and the first one run under identical conditions did not crack is unknown. One possible explanation may be that the latter two specimens were severely cold-worked on the surface to a depth of a mil or two, whereas little cold-work was apparent on the surface of the first specimen.

In an additional test, duplicate strips of cast type 347 stainless steel, machined from the same heat of the alloy, were cold-formed into standard U-bend specimens and exposed to the boiling magnesium chloride solution. Both specimens developed many small cracks in less than 5 hr. Metallographic examination of the cracked specimens showed that severe cold-work and a definite change in microstructure resulted from the bending operation. The microstructure of the metal can be seen in Fig. 9, which shows the cold-worked material and apparent grain boundaries as well as one large pit and numerous cracks (see Fig. 10 for microstructure of the same alloy stressed in the elastic range).

Further tests with the same heat of the cast type 347 stainless steel were made with simple-beam stress specimens exposed at 300°C in water saturated with air at room temperature containing 100 ppm of chloride. Initial solution pH values of 2.8, 6.5, and 10.5 were obtained by the use of either hydrochloric acid or sodium hydroxide. Unstressed control specimens of the alloy were also exposed in pH 6 chloride-free water at 300°C. A single case of cracking, if such, occurred in the pH 6.5 environment after 1500 hr. The crack or defect was only detected during metallographic examination at the end of the test. The affected area is shown in Fig. 10. It is possible that the defect may have been the result of an imperfection in the casting which opened up during the stressing operation. No other defected areas were found on the specimen. The crack or defect was approximately 4 mils in depth. Since repeated metallographic polishing and etching failed to reveal any indication of a grain boundary in the immediate vicinity of the affected area, it was concluded that the defect was restricted to a single, very large crystal in the alloy. Grain boundaries were disclosed by the etching procedure in the remaining portion of the specimen.

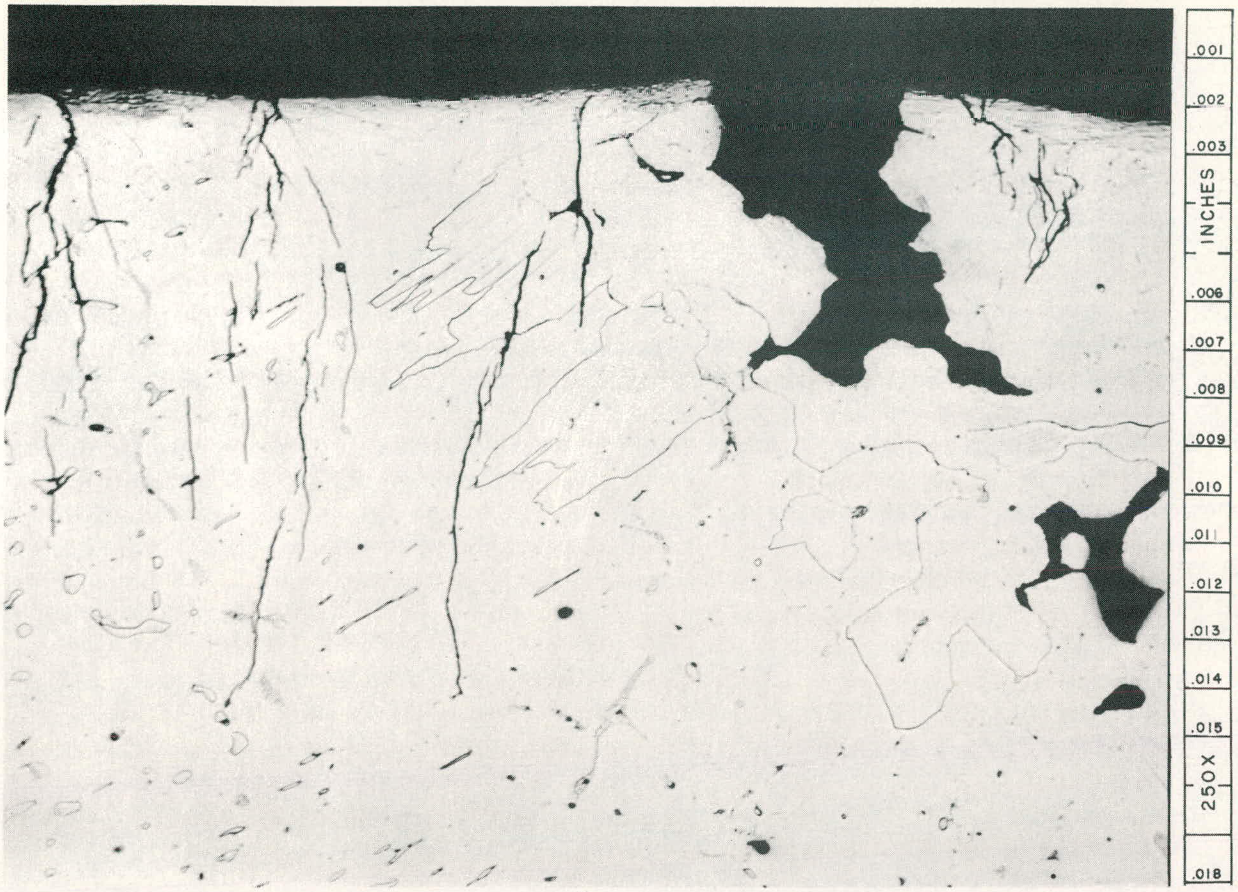

Fig. 9. The Microstructure of Cast Type 347 Stainless Steel from a U-Bend Stress Specimen after Testing in Boiling 42% Magnesium Chloride Solution

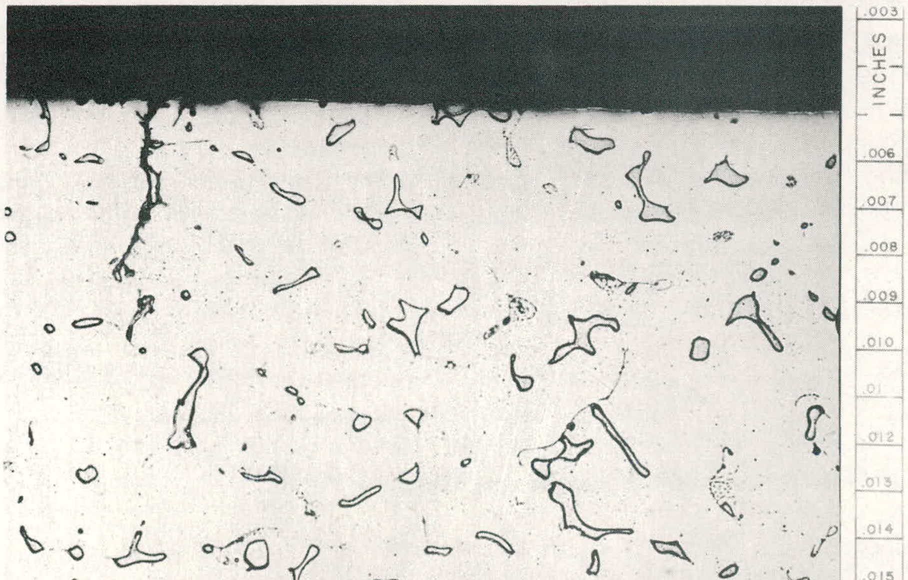

Fig. 10. Defect or Crack Found in Stressed Cast Type 347 Stainless Steel after 1500 hr at 300°C in Chloride-Containing Water

A summary of the stress-corrosion cracking tests with the cast type 347 stainless steel specimens in high-temperature, chloride-containing water is shown in Table V. The general corrosion resistance of the alloy, as determined from the present tests, appeared to be at least comparable to the corrosion resistance of the wrought alloy observed in other similar tests. Corrosion rates were 0.5 mpy or less for the specimens listed in Table V; the rates decreased with increased exposure time. The cast material was more resistant to the formation of heavy scales and edge pitting than is commonly found on wrought specimens in the same environments.

Table V. Stress-Corrosion Cracking Behavior of Cast Type 347 Stainless Steel in Oxygenated[(a)] Water at 300°C

Chloride Content (ppm)	Initial Solution pH	Total Time (hr)	Specimen Appearance
0(b)	6.0	2000	No significant attack.
100	2.8	1000	Few shallow pits; no cracks.
100	6.5	1500	One very shallow crack disclosed by metallographic examination. Moderate pitting.
100	6.5	1600	Moderate pitting; no cracks.
100	10.5	1000	Many shallow pits; no cracks.

(a) Air-saturated at room temperature.

(b) Unstressed control specimens.

The results to date indicate that cast type 347 stainless steel is more resistant to chloride-induced stress-corrosion cracking than is the wrought alloy but that it is not immune to cracking. Future work will be concerned with determining the effect of surface layers of cold-worked material on the cast alloy and with determining the behavior of different types of cast austenitic stainless steel.

(b) CD4MCu Stainless Steel.--Stress-corrosion cracking tests with both cast and wrought forms of CD4MCu stainless steel are being continued; preliminary results have been reported.[23] Since the alloy, developed as a high-strength casting alloy, is not commercially available in wrought form, small heats were rolled by the Metallurgy Division at ORNL. The environments for the present tests consisted of oxygenated water at 300°C containing 100 ppm of chloride at initial pH values of 2.8 and 10.5. The initial pH values were obtained with the use of either hydrochloric acid or sodium hydroxide.

The cast material was tested in the form of simple-beam stress specimens, whereas elastically stressed U-bend specimens were prepared from the wrought material. Unstressed control specimens of the wrought form of the alloy were tested also in chloride-free, pH 6 oxygenated, distilled water at 300°C. A summary of the test results is given in Table VI.

Figure 11 shows the one incidence of transgranular cracking observed on one of the stressed wrought specimens after 500 hr in pH 2.8 chloride-containing water. None of the other stressed specimens exhibited signs of cracks after accumulated exposure times of 300 to 1000 hr thus far. The appearance of the specimens was characterized by thin, light tan-colored films; the intensity of the corrosion attack was very mild. The tests will be continued.

Table VI. Stress-Corrosion Cracking Behavior of CD4MCu Stainless Steel in Oxygenated[(a)] Water at 300°C

Chloride Content (ppm)	Alloy Form	Initial Solution pH	Total Time (hr)	Specimen Appearance
0[(b)]	Wrought	6.0	1000	No significant attack
100	Wrought	2.8	1000	Crack in one specimen after 500 hr; light general corrosion
100	Cast	2.8	300	No cracks; light general corrosion
100	Wrought	10.5	1000	No cracks; light general corrosion
100	Cast	10.5	300	No cracks; light general corrosion

(a) Air-saturated at room temperature.

(b) Unstressed control specimens.

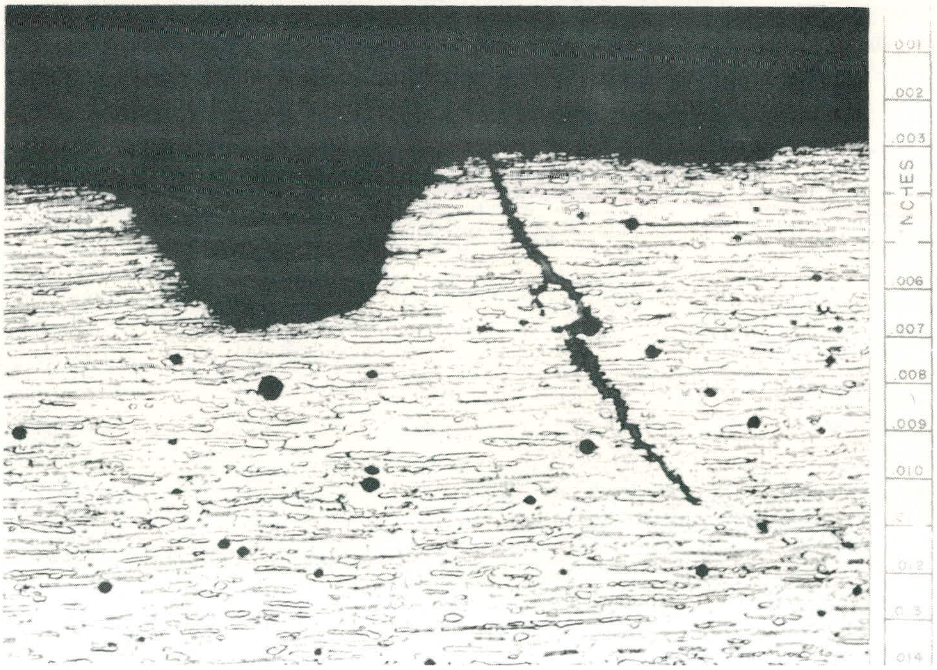

Fig. 11. Crack in Wrought CD4MCu Stainless Steel after 1000 hr at 300°C in Chloride-Containing Water

B. Corrosion of Titanium by Oxygen-Free Uranyl Sulfate Solution

Tests were run at 250°C to determine the corrosion resistance of titanium-75A in oxygen-free heavy water solutions containing uranyl sulfate and deuterium sulfate and to determine the chemical stability of the solutions under such conditions. Four solutions ranging in composition from 0.02 to 0.1 *m* UO_2SO_4 were used with deuterium sulfate concentrations of 0.02 and 0.10 *m*. The titanium test material was 0.010-in.-thick strip in an as-received condition. In order to obtain a high ratio of surface area to solution volume, strips of the titanium were rolled into coils, each with a surface area of approximately 28 square centimeters. Three of the coiled specimens were placed in each of four quartz tubes with 5-ml volumes of the test solutions. The ratio of surface area to solution volume was 17 cm^2/ml. Oxygen removal was accomplished by bubbling helium through the solutions. While still under a helium atmosphere, the solutions were frozen. The tubes were then evacuated, sealed, placed in stainless steel autoclaves partially filled with water, and heated for 100 hr at 250°C.

All specimens upon removal from test showed weight gains ranging from 0.1 to 0.3 mg/cm^2. The condition of the specimens was similar to that usually observed on titanium exposed to oxygenated uranyl sulfate solutions at elevated temperatures. Thin, uniform, golden-tan films predominated; in a few cases, vivid blue and purple interference colors were observed. There were no indications of deposits on the surfaces that probably would have been seen in the case of any solution instability.

An estimate of corrosion rates on the specimens was made from the observed weight gains assuming that (1) the corrosion film consisted of titanium dioxide and (2) all oxide film that formed during the exposure remained on the surface of the specimens. The corrosion rates ranged between 0.4 and 1.2 mpy. There was no significant difference in the corrosivity of the respective test solutions.

The initial and final solution compositions and the average corrosion rates are shown in Table VII. Although the solution analyses showed slightly lower uranium and sulfate concentrations in the final solutions than in the original solutions, there was no visible evidence that the solutions had undergone any reduction. The fact that both sulfate and uranium were lost from solution indicates that reduction and hydrolytic precipitation to oxides of uranium did not occur. It is possible that part of the difference between reported initial and final concentrations may have been due to the fact that analyses of the original solutions were performed on relatively large aliquots of solution (20 ml), whereas all final determinations were made on a 5-ml solution volume from each test.

Table VII. Corrosion Rates and Solution Compositions
for Tests with Titanium-75A in Degassed
Uranyl Sulfate Solutions at 250°C
(Test Time: 100 hr)

Test Solution	Composition	pH	U (mg/ml)	SO_4 (mg/ml)	$\frac{SO_4}{U}$	Excess Acid (*m*)	Average Corrosion Rate (mpy)(a)
0.04 *m* UO_2SO_4 0.02 *m* D_2SO_4	Initial	1.4	10.8	6.5	1.511	0.021	0.7 ± 0.2
	Final	1.3	8.5	5.4	1.574	0.020	
0.04 *m* UO_2SO_4 0.1 *m* D_2SO_4	Initial	0.8	11.1	14.2	3.149	0.099	0.6 ± 0.3
	Final	0.8	9.2	13.9	3.751	0.115	
0.2 *m* UO_2SO_4 0.02 *m* D_2SO_4	Initial	1.3	51.3	23.4	1.135	0.022	1.0 ± 0.2
	Final	1.1	48.6	21.4	1.092	0.018	
1.0 *m* UO_2SO_4 0.02 *m* D_2SO_4	Initial	1.0	251	106	1.046	0.024	0.7 ± 0.2
	Final	1.0	248	100	1.000	ND(b)	

(a) Determined from average weight gains observed on three specimens per test.
(b) No excess acid detected.

The preceding tests indicate that titanium and oxygen-free uranyl sulfate solutions are relatively stable for limited periods of time under certain conditions. However, the results should not be construed to mean that the tests could have been run indefinitely without evidence of chemical instability. A possible indication of solution instability appeared in a test in which a large mass of titanium-55A turnings was sealed in a titanium autoclave with air-saturated 0.04 *m* UO_2SO_4-0.025 *m* H_2SO_4-0.005 *m* $CuSO_4$ solution and run without opening for 1000 hr at 300°C.[24] Chemical analysis of the final solution showed reductions of approximately 15 and 25% in uranium and copper concentrations, respectively. More recently it was reported that nearly complete reduction of an oxygen-free 0.17 *m* UO_2SO_4 solution occurred during a 1000-hr run at 315°C in a titanium thermal loop.[25]

C. Corrosion of Zircaloy-2 in the Second-Liquid Phase of a 1.33 *m* UO_2SO_4 Solution at 300°C

In a reactor fuel solution, the possibility exists that the temperature of the solution could get hot enough to cause separation of a second-liquid phase containing very high concentrations of uranium and appreciable concentrations of copper. Since this possibility exists, tests were conducted to determine the out-of-pile corrosion behavior of Zircaloy-2 in the heavy phase of such a separated solution as a function of copper concentration in the original solution. The test solutions were 1.33 *m* UO_2SO_4 containing 0, 0.01, 0.04, and 0.1 *m* $CuSO_4$. The solutions and pin-type specimens were placed in quartz liners contained in stainless steel autoclaves and pressurized with approximately 150 psi of oxygen. The tests were run at 300°C. At various intervals during a 980-hr test, solutions and specimens were examined. New solution was used for each run. The fact that a second-liquid phase existed at 300°C was apparent from the high density of the solution in the bottom of each container at the end of the test.

Nothing of significance occurred on the Zircaloy-2 specimens immersed in the second phase. The specimens acquired dark-colored films with numerous small striations of white oxide deposits. All specimens exhibited weight gains not exceeding 0.3 mg/cm^2. Analyses of the reconstituted solution after the second run, which was of 400 hr duration, showed the zirconium content to be less than 5 ppm in all tests.

Thus it must be assumed from the above tests that the corrosivity of second-liquid-phase uranyl sulfate solution is of negligible consequence on Zircaloy-2 and that copper concentrations up to 0.1 *m* as copper sulfate in the room-temperature solution have no effect on the observed corrosion behavior of the alloy in the second phase at 300°C.

D. Miscellaneous Corrosion Tests

The corrosion behavior of two materials of possible interest to the Homogeneous Reactor Project was examined in several reactor-related environments. Test results for Incoloy 804 and Electrolyzed stainless steel are presented as follows:

1. Incoloy 804

A new nickel-base alloy developed by the International Nickel Company, Incoloy 804, was subjected to corrosion testing in an oxygenated, simulated reactor fuel solution. The composition of the alloy was 29% Cr, 25% Ni, 1% Mn, 0.4% Cu, 0.06% C and balance iron; the hardness of the test material was 90 Rockwell B.

Corrosion tests were run for 1000 hr at 100, 200, and 300°C in a 0.04 *m* UO_2SO_4-0.025 *m* H_2SO_4-0.01 *m* $CuSO_4$ solution. The average defilmed rates of attack for duplicate specimens were <0.1, 1.3, and 3.8 mpy, respectively, at 100, 200, and 300°C. At 100°C, specimens retained their original metallic appearance whereas those exposed at 200 and 300°C exhibited thin, lustrous-black films and were subject to shallow pitting. It was not possible by cathodic defilming to completely remove the corrosion film on the 200°C specimen. Film removal on the 300°C specimen was accomplished with no difficulty, however. The observed corrosion rate of 1.3 mpy at 200°C was relatively constant with accumulated exposure time and the rate at 300°C, 3.8 mpy, decreased slightly with increased exposure time.

Although the corrosion resistance of Incoloy 804 was found to be tolerable, its general behavior at elevated temperatures was inferior to that of type 347 stainless steel. Unless the alloy possesses mechanical properties or resistance to stress-corrosion cracking superior to the 18-8 stainless steel, its use in homogeneous reactor systems cannot be recommended.

2. Electrolyzed Stainless Steel

"Electrolyzing," a proprietary process developed by the Electrolyzing Corporation of Chicago, Illinois, is used to coat metallic parts with a chromium-rich layer for wear and corrosion protection. The hardness of the applied coating varies from 70 to 72 Rockwell C. Since materials with such surface hardness would be useful in many homogeneous reactor applications, a number of corrosion tests were performed with coated specimens.

The initial tests were made in oxygenated 0.04 m UO_2SO_4-0.02 m H_2SO_4-0.005 m $CuSO_4$ solution at 100 and 300°C with Electrolyzed type 347 stainless steel coupons. The Electrolyzed layer was approximately 0.2 to 0.3 mil thick as shown in Fig. 12. The deposited layer was completely resistant to the above solution during a 1000-hr run in the boiling solution (100°C); no weight change was observed, and there was no change in the physical appearance of the specimen.

A 1000-hr run was made at 300°C also. During this period, the specimen acquired a dark red-brown film; the corrosion rate was approximately 1 mpy, increasing slightly with increased exposure time. Metallographic examination upon completion of the test failed to disclose any signs of the Electrolyzed layer, and it was concluded that the coating was removed by contact with the oxygenated, high-temperature environment.

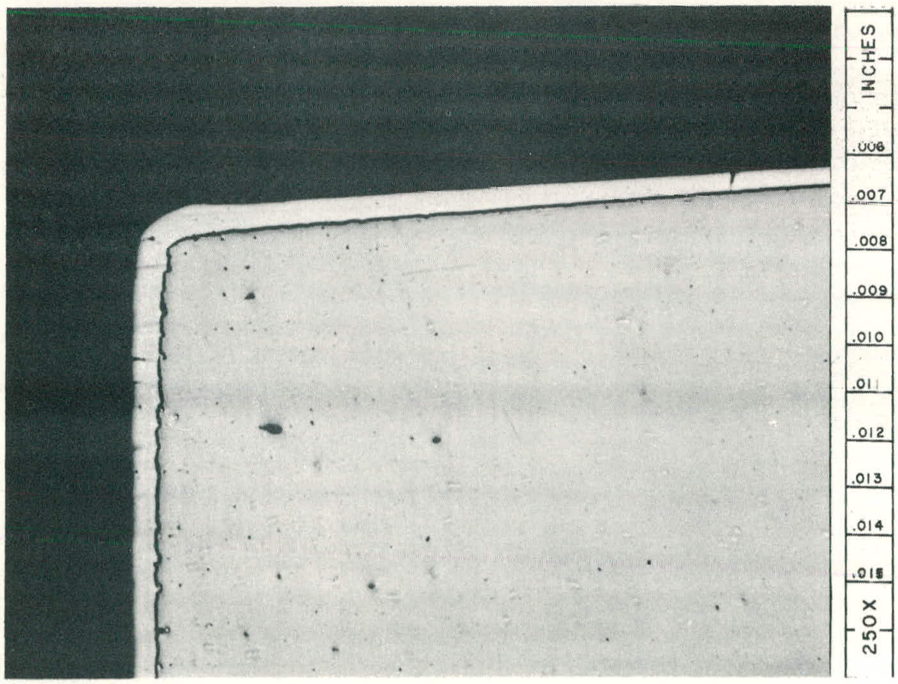

Fig. 12. Electrolyzed Coating on Unexposed Type 347
Stainless Steel Coupon
(Coating Thickness ~0.3 mil)

The behavior of the Electrolyzed layer was examined also in oxygenated deionized water at 300°C contained in a titanium autoclave. A cylindrical pin of type 304 stainless steel with a coating thickness slightly under 0.2 mil was used for the test. During a 300-hr test, the specimen and water were examined frequently; fresh water was used each time the specimen was examined. In the initial runs, the water was bright yellow in color, indicating the presence of hexavalent chromium. The dissolved chromium content reached a maximum value of 430 ppm after 100 hr of exposure.

A heavy, black film formed on the specimen during the 300-hr exposure; upon completion of the test, the black film was easily removed by scrubbing, disclosing a lustrous, golden-brown surface. The specimen was examined metallographically; no trace of the Electrolyzed layer was found.

In other tests, a 3/8-16 Electrolyzed type 304 stainless steel cap screw of the type used for bolting the thermal barrier in centrifugal pumps was stressed at approximately 11,000 psi and exposed at atmospheric boiling (100°C) in 0.04 m UO_2SO_4-0.025 m H_2SO_4-0.01 m $CuSO_4$ solution containing 50 ppm of chloride as potassium chloride. After the 1000-hr test, an apparent crack was found in the head of the bolt which had corroded at a rate of 7 mpy. Since metallographic examination of various areas on the cap screw revealed that little or none of the original Electrolyzed layer was present after the exposure, the observed "crack" on the head could not be attributed to stress-corrosion cracking of the Electrolyzed layer itself. Grinding to determine the depth of the "crack" disclosed massive areas of subsurface attack as shown in Fig. 13 rather than a conventional stress-corrosion crack. Except for partial removal of the layer, no other localized attack was found on the cap screw.

In conclusion, it was found at 300°C in both oxygenated, deionized water and simulated HRT reactor fuel solution and also chloride-containing fuel solution at 100°C that the Electrolyzed layer was gradually removed. Thus its use in high-temperature oxygenated aqueous solutions could not be considered. The corrosion resistance of the Electrolyzed layer was excellent in boiling, chloride-free simulated reactor fuel solution, however, and presumably it could be used for hard-facing applications at this temperature or below.

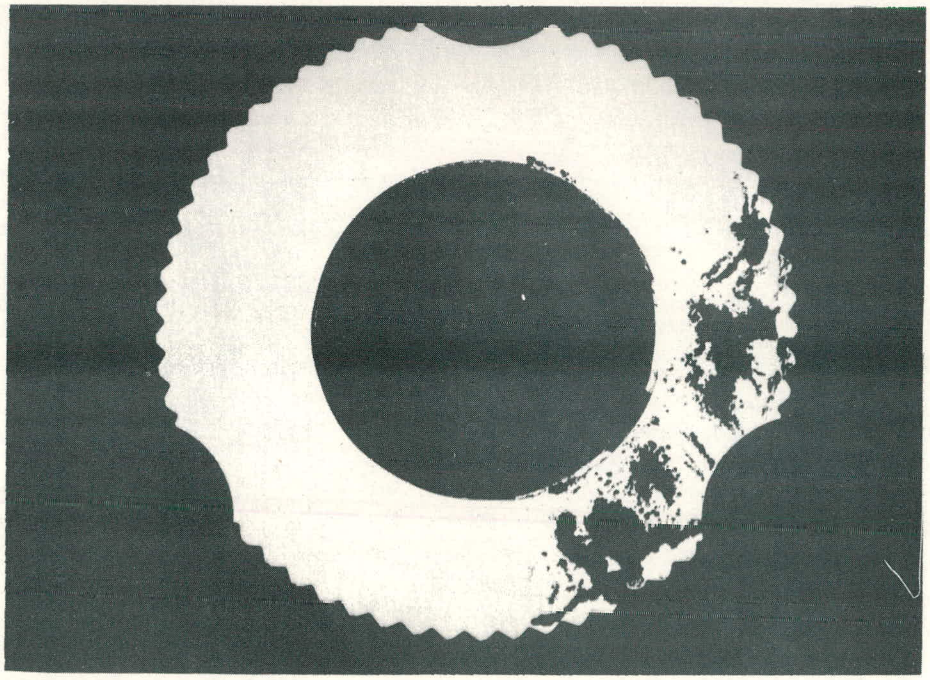

Fig. 13. Subsurface Attack in Electrolyzed Type 304 Stainless Steel Cap Screw after 1000 hr in Boiling, Chloride-Containing Simulated HRT Fuel Solution

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