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EXTERNAL TRANSMITTAL
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ORNL
CENTRAL FILES NUMBER

59-4-44

DATE: April 30, 1959

COPY NO. 116

SUBJECT: Quarterly Report of the Solution Materials Section for the Period
ending April 30, 1959

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ORNL CF 56-1-167	Period Ending January 31, 1956
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ORNL CF 56-10-13	Period Ending October 31, 1956
ORNL CF 57-1-144	Period Ending January 31, 1957
ORNL CF 57-4-55	Period Ending April 30, 1957
ORNL CF 57-7-121	Period Ending July 31, 1957
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ORNL CF 58-4-131	Period Ending April 30, 1958
ORNL CF 58-7-132	Period Ending July 31, 1958
ORNL CF 58-10-95	Period Ending October 31, 1958
ORNL CF 59-1-79	Period Ending January 31, 1959

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I. SUMMARY

Studies concerned with the deposition of salts from simulated fuel solutions under boiling conditions were continued. Deposition of salts did not occur when a heated Zircaloy-2 bypass section was mounted either vertically or horizontally, even when the flow rate was low and the heat flux was high. However, when the bypass was mounted about 10 degrees from the horizontal, deposition occurred readily provided the flow rate was low and the solution boiled.

Additional deposition tests were carried out in loop L-2-23 in which the core section was heated. These tests demonstrated that under conditions where deposition took place, increasing the acid concentration of the solution decreased the rate and extent of deposition but did not completely prevent it. Also, it appeared that deposition occurred more readily under boiling conditions when the solution temperature was 225°C than when it was either 250 or 280°C. By use of an apparatus combining a standard x-ray machine, a TV camera sensitive to x-rays and a closed-circuit TV receiver, it was possible to observe the deposition process. These observations clearly demonstrated the necessity of a heated metal surface above a stable gas phase to obtain massive salt deposition.

Several reagents were tested to determine their ability to dissolve stainless steel corrosion products. Of the reagents tested, Deoxidine-170 was the most effective. In a 36-hr loop run at 125°C a Deoxidine-170 solution completely removed the tightly adherent corrosion product scale from the surface of the loop. Zircaloy-2 and stainless steel were not significantly attacked by the reagent but titanium specimens corroded at a rate in excess of 600 mpy.

A simulated HRT fuel solution was stable with regard to uranium concentration when diluted to 23 ppm at 250°C; however, some copper was lost from solution. In other stability tests solutions containing about 6 g of uranium per liter and equivalent concentrations of copper sulfate and sulfuric acid were not completely stable at 320°C with either H₂O or D₂O as solvent.

Preliminary tests in a uranyl sulfate solution indicate that an 18-8 stainless steel alloyed with either small amounts of platinum or copper is more corrosion resistant at low flow rates than a conventional 18-8 stainless steel; however, the addition of either copper or platinum did not reduce the corrosion rate of 18-8 stainless steel at high flow rates.

A study was made to determine the susceptibility of off-specification type 347 stainless steel to intergranular attack by uranyl sulfate solutions. Sensitized specimens of several heats of the alloy which failed to pass the boiling 65% HNO₃ test in the sensitized condition were subjected to uranyl sulfate solutions at 100, 200, and 300°C. In no case was intergranular attack observed. On the other hand, sensitized specimens of the unstabilized type 310 stainless steel showed mild intergranular attack under the same exposure conditions.

Continued testing with a single heat of cast type 347 stainless steel has confirmed previously reported data to the effect that the cast alloy is more resistant to stress-corrosion cracking than is the wrought alloy. When cracking has been observed in the cast alloy, the cracks appear to be closely related to areas of surface cold work.

Six commercial grades of aluminum oxide suitable for use as check balls in valves in slurry service were corrosion tested in static slurry environments. At 100°C five of the six materials corroded at rates of less than 2 mpy; at 300°C only one material, "Alox," showed adequate corrosion resistance.

Corrosion tests with Uniloy 19-9DL showed that the alloy in the annealed and in the annealed-and-aged condition has corrosion resistance similar to that of type 347 stainless steel in simulated reactor fuel solutions and has less tendency to gall than the austenitic stainless steels. In view of its favorable mechanical properties, it should find use in various HRP applications.

II. INTRODUCTION

The data presented on the following pages represent the detailed results obtained during the quarter ending April 30, 1959, by the Solution Materials Section of the Reactor Experimental Engineering Division. A summary of the data has been given in the Homogenous Reactor Project Quarterly Progress Report for the period ending April 30, 1959.

This report is 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. LOOP CORROSION STUDIES (R. S. Greeley, S. E. Bolt, W. C. Ulrich, E. S. Snively, A. J. Shor, H. C. Savage, and J. C. Griess)

A. Deposition of Salts from Dilute Fuel Solutions on Heated Metal Surfaces

During the past quarter the investigation of the deposition of salts from boiling simulated reactor fuel solutions on hot metal surfaces was continued. Tests were carried out in a heated Zircaloy-2 bypass in 100A loop H and in a 5-gpm in-pile type pump loop in which the core section was externally heated. These tests are described below.

1. Heated Zircaloy-2 Bypass. Table I lists the general operating conditions that prevailed during runs H-124A, B, and C which were made during the last quarter and run H-124 which was described previously.⁽¹⁾ The general procedure for conducting the tests was also the same as was reported last quarter.⁽¹⁾ In all cases D_2O solutions containing 0.025 m UO_2SO_4 , 0.014 m D_2SO_4 , 0.011 m $CuSO_4$, and 200 ppm nickel as nickel sulfate were used. The purpose of these four runs was to investigate the effects of flow rate, bypass orientation and pressurization on salt deposition and heat transfer properties.

Run H-124A was conducted with the bypass in a vertical position with solution flow from the bottom to the top under three sets of conditions:

(1) The system was pressurized with oxygen and steam to 1300-1350 psia, and the main-stream temperature was 280°C. The dissolved oxygen concentration in the main-stream was about 2000 ppm. Power to the bypass heaters was supplied in 500-watt steps corresponding to 5600 Btu/hr·ft² until a maximum heat flux of 40,000 Btu/hr·ft² was reached. (2) Hydraulic pressurization of 1800 psia was utilized instead of oxygen overpressure so a low dissolved oxygen concentration of about 20 ppm in the circulating solution could be achieved, and the main-stream temperature was lowered to 250°C. Again power to the bypass heaters was

TABLE I. Summary of Tests with Uranyl Sulfate Solution in Heated Zircaloy-2 Pipe Section

Run Number	Bypass Position	Flow Direction	Pressure (psia)	Loop Temp. (°C)	Press. Temp. (°C)	Flow Rate (fps)	Max. Heat Flux Btu/hr·ft ²	Maximum Wall Temp. °C (calc.)	Maximum h Btu/hr·ft ² ·°F	Salt Deposition
H-124	Vertical	Top to Bottom	1150*	280	280	0.10-0.65	58,000	430	400	No
H-124A	Vertical	Bottom to Top	1300-1350*	280	280	0.10-0.80	40,000	351	460	No
			1800**	250	250	0.20-0.80	46,000	415	430	No
			1800**	280	280	0.20	39,500	372	360	No
H-124B	Horizontal		1115-1450*	280	283	0.10-0.20	39,000	391	300	No
			1800**	280	280	0.10-0.70	50,500	444	440	No
H-124C	Inclined 10 deg	Top to Bottom	200-250*	150	150	0.15-0.20	16,300	226	270	No***
			650*	200	205	0.15	16,000	298	200	Yes
		Bottom	1000-1050*	250	255	0.08-0.30	16,000	327	215	Yes
			840-1690*	280	285	0.15	15,700	362	340	Yes

* Steam +O₂.

** Hydraulic.

***Not conclusive; solution sample from the bypass showed increased uranium concentration, but a continuous loss from the loop solution was not observed.

increased incrementally until a maximum heat flux of 46,000 Btu/hr·ft² was reached. (3) The main-stream temperature was raised to 280°C, the pressure maintained at 1800 psia hydraulically, and the power to the bypass heaters was supplied stepwise until a maximum heat flux of 39,500 Btu/hr·ft² was reached.

No deposition occurred during any of these tests.

Run E-124B was made after the bypass was installed in a horizontal position and consisted of two parts. In the first part the system was pressurized with oxygen to 1115-1450 psia, and the main-stream temperature was 280°C. The pressurizer temperature was increased to 285°C. Bypass heater power was added in 500-watt increments until a maximum heat flux of 39,000 Btu/hr·ft² was obtained. In the second part hydraulic pressure of 1800 psia was applied, and the main-stream and pressurizer temperatures were maintained at 280°C. Power was supplied to the bypass heaters until a maximum heat flux of 50,500 Btu/hr·ft².

No deposition occurred during either of these tests.

Tests carried out with a glass mockup indicated why deposition would not be expected under these conditions. These tests showed that even with substantial gas injection all surfaces were wetted when the bypass was either horizontal or vertical; even at low flow rates the stream of fluid consisted of alternate slugs of liquid and gas, the diameters of which were equal to the diameter of the tube. Any salts that might momentarily deposit would be washed from the surface as the slug of liquid passed through the tube. This behavior was in contrast to that observed when the bypass was mounted 10 to 15 degrees from the horizontal. In this case two-phase flow in which the liquid flowed in

the lower part of the tube and gas in the region above was observed. Under these conditions heating of the bypass resulted in boiling and deposition of salts on the surface above the gas phase.

Run H-124C was made with the bypass inclined about 10 degrees from the horizontal. This was the orientation of the bypass during the original run, H-121,⁽²⁾ when deposition was first observed. The flow in the inclined bypass was from top to bottom, and the run was made in four parts with different conditions for each part. (1) The system was pressurized with oxygen and steam to 200-250 psia, and the main-stream temperature was maintained at 150°C. The bypass heater power was increased until a maximum heat flux of 16,300 Btu/hr·ft² was reached. Deposition was not conclusively observed; the solution sample from the bypass showed increased uranium concentration, but a continuous loss from the loop solution was not seen. (2) The total system pressure was adjusted to 650 psia steam and oxygen pressure, and the main-stream and pressurizer temperatures were held to 200 and 205°C, respectively. Power to the bypass heaters was added in 500-watt increments until a maximum heat flux of 16,000 Btu/hr·ft² was reached. Deposition, noted by a decrease in the concentration of the main-stream circulating solution, occurred in the heated Zircaloy-2 bypass. (3) The total system pressure was raised to 1000-1050 psia steam and oxygen pressure, and the main-stream and pressurizer temperatures were increased to 250 and 255°C, respectively. Power to the heating elements of the Zircaloy-2 bypass was raised incrementally until a maximum heat flux of 16,000 Btu/hr·ft² was reached. Deposition occurred. (4) The total system pressure was varied between 840 and 1690 psia steam and oxygen pressure, and the main-stream and pressurizer temperatures

were 280 and 285°C, respectively. Heat was added to the bypass until a maximum heat flux of 15,700 Btu/hr·ft² was obtained. Deposition occurred.

The effect of gas (oxygen) concentration in solution on boiling and salt deposition was investigated by comparing oxygen and hydraulic pressurization. Partial gas pressurization resulted in oxygen concentrations as high as 2000 ppm, while with hydraulic pressurization the oxygen concentration was held to about 20 ppm. The total system pressure was also varied as shown in Table I and as reported previously.⁽¹⁾

With hydraulic pressurization (about 20 ppm oxygen) and with the bypass mounted 10 to 15 degrees from the horizontal, deposition could be achieved only under conditions of maximum heat flux (58,000 Btu/hr·ft²) and minimum flow rate; even then only 20% of the salts was lost from solution and presumably deposited in the bypass.⁽¹⁾ With gas pressurization (about 2000 ppm oxygen) essentially all salts were lost from solution, even at a low heat flux (16,000 Btu/hr·ft²).

Boiling in the bypass was evidenced by the change in thermocouple readings along the length of the heated test section. For nonboiling conditions, the temperature rise of the solution as it went through the bypass was linear, or nearly so. As the heat flux was increased and boiling began, the thermocouple readings fluctuated and the temperature differences between thermocouples became erratic. The type of boiling, as indicated by the fluid film heat transfer coefficients shown in Table I, was not affected by the orientation of the bypass, the dissolved gas concentration (from 20 to 2000 ppm) or total system pressure. All values, including those previously reported for run H-123,⁽¹⁾

between 200 and 400 Btu/hr·ft², values indicative of film-type boiling. Considering the fact that the experiments were not designed to obtain a high degree of reproducibility from run to run, it is concluded that there is no real difference in the numbers and that the type of boiling observed was the same in all cases.

2. Heated Core Section, Loop L-2-23. Additional out-of-pile solution stability tests have been made using loop L-2-23 with an externally heated titanium core. This core was described previously.⁽³⁾ A second series of tests was also performed with a stainless steel core with an improved heater permitting higher heat fluxes and more complete core temperature measurements.

The purpose of these runs was to continue the investigations made previously both in-⁽⁴⁾ and out-of-pile⁽¹⁾ on the stability of uranyl sulfate solutions in contact with heated metal surfaces. Tests were made to investigate the effects of bulk solution temperatures, total pressure, solution composition, heat flux, and flow rate.

(a) Titanium Core.--Previous runs in this system were made with bulk solution temperatures of 250 or 280°C.⁽⁵⁾ The present runs at 225°C represent a continuation of the investigation of the effect of solution temperature and the effect of free acid concentration on the deposition process. Table II presents the test conditions and the results of the runs performed this quarter. The extent of deposition at any time was determined by chemical analysis of an aliquot of the circulating solution.

TABLE II. Summary of Operating Conditions,

Loop L-2-23, Titanium Core

Loop temperature, 225°C
 Pressurizer temperature, 227°C
 Core flow rate, 0.3 fps
 Core heat, 8,000 Btu/hr·ft²

Run Number	UO ₂ SO ₄ Conc. (m)	D ₂ SO ₄ Conc. (m)	CuSO ₄ Conc. (m)	O ₂ psi	Total Press. (psia)	Deposition Half-Time (hr)	% U Deposited after 60 hr
15	0.025	0.014	0.011	165	550	7	96
15A	0.025	0.014	0.011	146	518	8	96
18	0.025	0.025	0.011	147	558	18	65
19	0.025	0.050	0.011	200	594	18	68

As noted in Table II, loss of uranium from solution was observed in all cases. It appeared that the deposition process was initiated more readily at 225°C than at 250 or 280°C. It was also observed that the rate and extent of deposition was influenced by the sulfuric acid concentration. At the lowest acid concentration, 0.014 m, the time to lose half of the salts from solution was about 8 hr. The uranium concentration was reduced from 6 g per liter to about 0.2 g per liter after 90 hr operation. With 0.025 m D₂SO₄ in the solution, the half-time was about 18 hr. The concentration of uranium reached a value of about 2.4 g per liter after 90 hr operation. The rate and extent of loss of salts from a solution containing 0.050 m D₂SO₄ was about the same as with

0.025 m D_2SO_4 solution. Increasing the acid concentration from 0.014 m to 0.025 m, after deposition had occurred, had no apparent effect in recovering the deposited salts.

The salts lost from solution could be rapidly recovered by any one of the following procedures: (1) removal of core heat, (2) increase in total system pressure with increased steam pressure, or (3) increase in solution flow rate.

At the conclusion of the above tests, the titanium core was sectioned for examination of the interior surfaces. Corrosion attack was found on the upper section of the core where deposition of salts had presumably occurred. Figure 1 is a photograph of this surface. The interface between liquid and vapor is clearly visible; attack on the surface below the liquid level was negligible. The location and type of attack was similar to the severe attack found on the surface of the heated Zircaloy-2 bypass section exposed under comparable conditions. (1)

(b) Stainless Steel Core.--After the titanium core had been removed for examination, the loop was equipped with a stainless steel core. Calrod-type heating elements were cast in aluminum around the outside of the core and thermocouples were spotted on top, bottom, and sides of the core surface. With this arrangement, higher and more uniform heat fluxes were obtained and more complete temperature measurements were possible than with the titanium core.

Preliminary tests of the new stainless steel core were made with water to determine heat input to the core and to compare the temperature distribution on the outside of the core surface with and without heat. With no

Fig. 1. A Photograph of the Inside of the Titanium Core
Showing the Attack on the Upper Surface

heat on the core the six thermocouples on the core agreed with each other and read solution temperature. When heat was applied to the core, but with loop pressure and flow rate such that boiling did not occur, the thermocouples on top, midside and bottom of the core indicated a uniform temperature above solution temperature over the entire core surface area. However when the heat was increased and the loop pressure and flow rate were such that boiling in the core occurred, the thermocouples on the top of the core gave the highest temperature reading, and the bottom thermocouples gave the lowest outside wall temperature. Runs with uranyl sulfate solution showed similar behavior of the thermocouples and deposition of salts occurred under the same conditions as in the titanium core.

In order to deposit salts on the heated core surface, it was necessary to maintain a flow rate of about 0.3 fps or less and provide very little or no steam overpressure. This was true for heat fluxes through the core wall of 8,000 to 25,000 Btu/hr·ft². Recovery of the salts, after deposition had occurred, could be accomplished by increasing the flow rate to 0.4 to 0.6 fps. The exact flow rate required to recover the salts was dependent on the core heat flux; the higher heat required a higher flow for recovery.

(c) X-Ray Observations of the Core.--Direct observation of boiling, vapor-phase formation, and salt deposition in the core was made with a standard 300 KVA x-ray machine in conjunction with a television camera sensitive to x-rays. The camera was connected to a closed-circuit television receiver. A 1.3 m UO₂SO₄ solution, containing 500 ppm CrO₃ for corrosion inhibition, was used to magnify the contrast between vapor, liquid, and deposited salts in the core.

The initiation and formation of a stable vapor phase in the top section of the core was clearly observable. About an hour was required to form a stable vapor space which continued to increase in volume over a period of several hours until it occupied one third to one half the core volume. The liquid-vapor interface was considerably turbulent initially, but this turbulence decreased until it was barely (if at all) observable when the vapor space reached its maximum volume. After a stable vapor pocket had formed, a darkening was observed on the upper surface of the core which finally covered an area representing one fourth to one third of the core surface. Thus a more or less stable three-phase system, liquid, vapor and deposited salts, was observed. Figure 2 is a photograph of the screen of the television receiver taken with the camera focused on the core and the loop under the following conditions: solution temperature, 267°C ; flow rate, 0.3 fps; core heat flux, $8,000 \text{ Btu/hr}\cdot\text{ft}^2$; oxygen concentration, about 500 ppm; and no steam overpressure.

Some of the deposited salts were recovered when the solution flow rate was increased from 0.3 to 0.4 fps. The vapor space persisted, but the liquid-vapor interface became turbulent. At least some of the salts returned to the circulating solution as drops falling through the vapor space and by small rivulets running down the side of the core. Increasing the flow to 0.6 fps resulted in a rapid decrease in the volume of the vapor phase so that in about 5 min the core was completely filled with liquid. Rapid dissolution of the deposited material occurred, although the deposit appeared to persist somewhat longer than the vapor phase.

Fig. 2. X-Radiograph of L-2-23 Core
Showing Deposit on Upper Surface
Separated from Liquid by Vapor Blanket

The salts deposited on the upper core surface could also be returned to the solution and the vapor space gradually removed by removing heat from the core wall. Some dripping of the deposited material was also noted under these conditions.

Tests were also made in which salts were deposited from the solution by boiling in the core at a solution temperature slightly above the second-liquid-phase temperature for the $1.3 \text{ } m \text{ } \text{UO}_2\text{SO}_4$ solution (285°C). A definite increase in density was observed in the liquid in the bottom section of the core. That this darkening was an additional liquid phase was confirmed by momentarily stopping the flow and observing the settling of the dense phase. A distinct interface between the light- and heavy-phase liquids was observed. At this point four phases, composed of light and heavy liquid, vapor and deposited salts were clearly visible on the television viewing screen. After observing the heavy-liquid phase the pump was started at 20 cps (corresponding to 0.2 fps through the core). The temperature of the solution was then gradually lowered below the second-liquid-phase temperature and the disappearance of the dense solution in the bottom of the core was observed. It was interesting to note that even after the solution temperature was lowered below 285°C , 5 to 10 min were required at the low flow rate to eliminate the concentration gradient from the core.

The over-all loop corrosion rate (type 347 stainless steel) during these tests with $1.3 \text{ } m$ uranyl sulfate at temperatures in the range of $260\text{-}295^\circ\text{C}$ was 2.5 mpy. Thus the addition of 500 ppm of CrO_3 appeared to effectively inhibit corrosion. Based on previous corrosion tests in the 100A pump loops, the

corrosion rate of type 347 stainless steel would be expected to be between 30 and 50 mpy under these conditions.

The above observations were made with a 1.3 m UO_2SO_4 solution in the loop. Subsequent experiments with a solution containing only 0.04 m UO_2SO_4 , 0.025 m H_2SO_4 , and 0.025 m CuSO_4 indicated that adequate contrast between the gas and liquid phase was obtained even with the dilute solution. With the exception of the formation of a second-liquid phase, there were no detectable differences in behavior between the two solutions when heat was applied to the core.

Using the dilute solution, most of the salt was allowed to deposit in the upper part of the heated core at a flux of about 12,000 Btu/hr·ft². The core heat flux was then increased to 20,000 Btu/hr·ft² so that a maximum temperature of 472°C was reached on the top outside surface of the core wall in the heated section; other thermocouples indicated temperature on the outside of the core in excess of 400°C, the limit of the recorder. The purpose of heating the core wall excessively was to determine if the heat would result in decomposition of the deposit with subsequent return of acid to the solution. Analysis of samples of solution indicated that no decomposition of the deposited salts occurred.

The removal of core heat following the above test permitted the wall temperatures to drop to that of the solution temperature of 280°C. In about 15 min all noticeable deposit had disappeared from the upper core surface without any noticeable return of the uranium to the bulk solution as drops of liquid as had been observed with the 1.3 m UO_2SO_4 . During this period the gas phase persisted.

3. Discussion. The results obtained during the past quarter support the hypothesis presented previously concerning the mechanism by which salts are lost from simulated reactor fuel solutions when passed through heated sections of pipe. It was postulated that when a solution boiled (or outgassed) as it passed through a pipe heated around its circumference, deposition or crystallization of salts would occur on the upper surface if a stable gas pocket formed; i.e., if two-phase flow occurred. It was presumed that the boiling of the solution would produce a spray of small droplets which would evaporate as they struck the hot, dry metal wall above the gas phase. That such a vapor pocket and deposit of salt does occur was conclusively proved by use of the x-ray equipment discussed earlier. Furthermore experiments with a glass mockup showed such a behavior is observable even at atmospheric pressure.

Experiments carried out in the heated Zircaloy-2 bypass and reported earlier⁽¹⁾ showed that the presence of dissolved gas is not necessary for deposition to occur, although it is easier to produce deposition when the solution contains a substantial quantity of dissolved gas. With hydraulic pressurization (or presumably with steam pressurization) and minimum oxygen concentration (about 20 ppm) extreme conditions were required to produce deposition; with a flow rate of 0.1 fps and 58,000 Btu/hr·ft² only 20% of the salts could be deposited. Under similar conditions of flow and solution composition except for about 500 ppm dissolved oxygen, as much as 90% of the salts could be deposited at heat fluxes as low as 8,000 Btu/hr·ft². The presence of a dissolved gas (oxygen in these studies) probably facilitates the formation of a stable gas pocket, and thereby deposition, by virtue of

the fact that as the solution boils in the heated section gas is stripped from solution and forms a noncondensable gas pocket. In the above sense boiling is considered to be the evolution of gas bubbles from the solution. Thus in a system containing gas, deposition is possible under subcooled boiling conditions, whereas without gas such is not the case. Once a reasonably stable gas pocket has formed, the passage of gas bubbles through the gas-liquid interface produces a spray of droplets which is the means of transporting salt to the upper surface.

In light of the above discussion it is obvious that orientation of the bypass is important in that it determines whether or not a stable gas pocket will exist. Experiments with the glass mockup showed that with either horizontal or vertical mounting of the glass tube a stable gas pocket did not form, but that all surfaces were frequently wetted with large quantities of solution. That the same behavior occurred in the Zircaloy-2 bypass mounted either horizontally or vertically was evidenced by the fact that no detectable amount of salt was lost from solution even when vigorous boiling occurred in the bypass. Stable two-phase flow and a means of getting small quantities of the solution to the heated metal surface above the gas phase are essential to obtain massive deposition of the salts.

Flow rate of the solution in the heated section is also an important variable in the deposition process. With high flow rates turbulence at the solution-vapor interface can be sufficiently great so that quantities of solution too large to be evaporated rapidly come in contact with the upper surface and dissolve any previously deposited material. Moreover, at high

flow rates many gas bubbles formed at the metal-solution interface could possibly be carried out of the heated section before they attained sufficient size to collect in the top of the tube and form a stable gas phase.

The effect of acid concentration on the deposition process has not been thoroughly investigated, but the data indicate that increasing the acid concentration decreases the rate and extent of deposition but does not prevent it. Also, what happens to the acid during the deposition process seems to depend on the particular system. In the Zircaloy-2 bypass the acid concentration of the solution did not change until essentially all the salt had been deposited, at which time some loss of acid was experienced. In tests with the in-pile loop the acid was lost from solution at the same rate and to the same extent as other salts. The reason for this difference in behavior is not known.

During run 17 (and earlier runs) of the HRT, uranium and copper were lost from solution in much the same manner as was observed in the above-described experiments.⁽¹⁾ The loss was a function of power but was independent of the temperature of the solution. This general behavior pattern suggested that the mechanism of loss might be the same in the two cases. As a result a program of reactor operation is planned to determine if such is the case. If such a mechanism is responsible for the loss of copper and uranium from the HRT fuel solution, increasing the total pressure on the system and reducing the partial pressure of gas (added oxygen or radiolytic) should reduce the likelihood of this type of loss. It should be pointed out that two major differences exist between the HRT experiences and

those encountered out-of-pile. When uranium and copper were lost during operation of the HRT, a net production of acid resulted. Out-of-pile, acid either disappeared from solution or remained unchanged as the salts deposited. This difference in behavior may be due to a radiation-induced decomposition of the salts or it may be due to the presence of hydrogen gas in the core of the reactor. This latter point will be investigated out-of-pile. The other difference is that deposition of measurable amounts of salts has been achieved out-of-pile only on surfaces separated from the solution by a stable gas blanket. It is difficult to see how such a steady separation of metal and solution could exist in the essentially spherical geometry of the HRT core. The results of the planned tests in the HRT should be helpful in deciding whether boiling deposition is a factor contributing to the loss of uranium and copper from the HRT solution.

B. Scale Dissolution and Peptization

Possible partial plugging of the HRT heat exchangers by deposition of corrosion products could create an urgent need for a means to remove the corrosion scale without damage to other components in the reactor system. Localized corrosion due to oxygen depletion under loose corrosion product deposits or in a plugged tube could lead to rapid penetration of the stainless steel. It is likely that plugging would be caused by fairly large flakes of corrosion products which might crack loose from the piping walls due to differential expansion during thermal cycling. Thus it was expected that a reagent which would either dissolve the scale or break up the flakes and peptize them would be effective in cleaning the tubes.

Both dynamic and static tests were made on several reagents which appeared promising in ability to remove scale. These reagents included Deoxidine-170 (inhibited phosphoric acid), Versenol-120 buffered by ammonium acetate, nitric acid mixed with hydrogen peroxide, and oxalic acid.

1. Inhibited Phosphoric Acid Solution. Two tests, one of 5 hr and one of 36 hr duration, were made with Deoxidine-170, a proprietary descaling solution consisting of about 8 M H_3PO_4 , a corrosion inhibitor, and a detergent. Conditions of the tests were based on recommendations by members of the Chemical Technology Division.⁽⁶⁾ Loop M was used for both tests of the solution since the loop surface contained a considerable quantity of scale deposited during previous corrosion tests with simulated HRT fuel solutions. An array of stainless steel coupons was exposed during each run. The array used in the 5-hr run consisted of five new coupons and five which had been covered with scale by an exposure to a solution of 0.025 m UO_2SO_4 , 0.04 m $MgSO_4$, 0.04 m D_2SO_4 , 0.02 m $CuSO_4$ at 225°C for 400 hr. The new coupons and those with scale occupied alternate positions in the tapered-coupon holder so that each kind was exposed to the solution in the velocity range of 10 to 70 fps. Initially the loop was charged with 20 liters of Deoxidine-170 and 100 psi of oxygen, then heated to 100°C. The solution caused overloading of the 100A pump, and it was necessary to raise the loop temperature to 125°C before the pump could be operated continuously. The run was continued for 5 hr.

The new coupons were practically unaffected by the descaling solution and retained their original luster; weight losses averaged only

0.055 mg/cm². The filmed coupons, however, were also visibly unaffected except for one at the upstream end of the coupon holder which lost most of its scale. The reason for the failure of the solution to defilm the coupons was apparent from solution samples taken during the run. The original Deoxidine-170 solution contained 1.1 grams per liter of iron. The iron concentration first decreased, then increased rapidly during the remainder of the 5-hr run. It appeared that the solution began dissolving scale only after circulating for 3 hr, and full effectiveness was not achieved during the short test.

Therefore a longer test was made. In this test, conducted for 36 hr at 125°C, Deoxidine-170 gave very satisfactory results as a descaling agent. Essentially all scale was removed from the interior loop surface and from the type 347 stainless steel pin specimens prefilmed by exposure for 100 hr at 250°C to 0.17 M UO₂SO₄. Metal loss amounted to only about 0.3 mg/cm². The average amount of scale originally on the pins was 2.2 mg/cm². Additional prefilmed type 347 stainless steel specimens, consisting of strips clamped together with filmed sides joined to form a crevice, were exposed to the Deoxidine-170 in the loop pressurizer. Examination of these specimens after the run showed that all scale in the crevice had been removed, leaving a clean surface with no indication of crevice attack by the phosphoric acid. An array of prefilmed type 321 stainless steel coupons was completely descaled by the solution, and no significant corrosion of the coupons was observed at any solution velocity from 8 to 48 fps. Prefilmed and new Zircaloy-2 pins

showed a slight weight gain which indicated negligible corrosion. Titanium specimens, however, both new and prefilmed, suffered an average weight loss of 31 mg/cm^2 , which corresponds to a corrosion rate of 660 mpy. The one new Stellite 98 M2 pin included in the run also showed a relatively high weight loss of 21 mg/cm^2 .

Deoxidine-170 effectively removed the scale from all surfaces by actually dissolving the scale, as was evidenced by the lack of solids in the solution samples taken during the run and the absence of loose scale in the loop at the end of the run. The complete removal of scale which had been deposited on several platinum pins in a run with uranyl sulfate solution indicated that the presence of stainless steel base metal was not necessary for scale dissolution.

2. Versenol-120 - Ammonium Acetate Solution. The use of a mixture of 20% Versenol-120 and 25% ammonium acetate as a descaling solution was suggested by O. Menis and was subsequently tested under dynamic conditions in Loop F and in static laboratory tests. Versenol-120 is the trisodium salt of N-hydroxyethylethylenediaminetriacetic acid, an effective complexing agent for ferric ions in alkaline solutions. The ammonium acetate buffer maintained the pH of the test solution at about 9.0.

Two runs were made with the Versenol solution in loop F. In each case the temperature was maintained at 125°C , and the loop was pressurized with 100 psi of helium.

In the first run a coupon holder containing both prefilmed and new type 347 stainless coupons was exposed to the descaling solution. One side

of the coupon holder was packed tightly with corrosion-product scale which had been collected from other test loops. During the 80-hr run, both line and hydroclone samples were taken for analysis; all contained solid matter which was in a finely divided state. After 16 hr the loop was shut down for inspection of the coupon holder, and it was noted that the oxide plug was still intact. The holder was returned to the loop and exposed for an additional 64 hr.

Examination of the specimens at the conclusion of the run showed the five new coupons to be practically unaffected by the descaling treatment; the average weight loss was only 0.036 mg/cm^2 for the 80-hr period. A large portion of the film on the scaled coupons was removed by the treatment as indicated by an average weight loss of 1.0 mg/cm^2 . The bulk-scale plug in the coupon holder was still intact after the additional treatment except for a small portion at each end of the holder.

Iron concentration was determined on the supernatant of centrifuged samples and again on samples which were shaken to insure suspension of all solids. These determinations revealed that much of the iron removed by the solution was dissolved; for example, at the termination of the run, dissolved iron was 6.0 g per liter, while total iron amounted to 9.7 g per liter. A total of 225 g of Fe_2O_3 was removed from the loop.

The Versenol-120-ammonium acetate solution was tested again in loop F for a period of 41 hr. Only two coupons were placed in the holder, and the remaining space was packed with corrosion-product scale as before. On termination of the run the coupons were found to be practically unaffected.

The average weight loss was 0.06 mg/cm^2 . Although the drained solution contained a considerable quantity of iron, the oxide plug in the coupon holder was still intact.

3. Nitric Acid - Hydrogen Peroxide Solution. A mixture of 10% HNO_3 and 3% H_2O_2 has been successfully used to remove iron-bearing scales from the walls of high-temperature autoclaves. Laboratory tests showed that the solution was also effective in breaking up flakes of scale under static conditions even though the scale was not completely dissolved. It was learned later that the flakes used in these tests were high in uranium content which could account for their instability in the reagent.

The solution was tested in loop K at 100°C with a helium over-pressure of 100 psi. To determine the plug-removing ability of the mixture, a $1/4$ in. ID $1\frac{1}{4}$ -in. long tubing holder was packed with oxide and placed in one of the parallel bypasses of the loop so that it completely blocked the flow. The pressure differential across the packed holder was estimated to be 40 psi with the pump on. In addition, an array of pins consisting of titanium, Zircaloy-2, and type 347 stainless steel specimens was included in the test.

In order to avoid excessive decomposition of peroxide the pump was allowed to run only occasionally for periods of 15 min or until the loop temperature rise due to pump operation reached 50°C . This procedure was repeated hourly through part of the run. After 20 hr of operation the plugged holder was inspected and the scale was found to be intact. Solution

was then put back in the loop and hydrogen peroxide was added to replace that which had decomposed. Procedure for the remaining 67 hr of the run was varied somewhat. In order to facilitate removal of the scale plug, the loop was pressurized to 1000 psi with nitrogen for 15 min. The pressure was then suddenly lowered to 50 psi. This procedure was repeated every 4 hr; however, the treatment did not appear to be particularly effective since most of the samples taken from the loop contained little or no solid matter. Analyses of the samples showed that about 75% of the hydrogen peroxide decomposed during the first 20 hr of the run. The additional peroxide restored the concentration to about the 3% level, and it remained nearly constant thereafter.

No weight losses were observed for the Zircaloy-2 or type 347 stainless steel pins; however, two Ti-45A pins lost 0.7 and 0.9 mg/cm², respectively, and two Ti-6% Al, 4% V pins lost 2.4 and 1.7 mg/cm². The test was unsuccessful in removing the scale plug from the tube specimen holder.

Another test was made of the solution in loop K; however, only the packed holder was placed in the loop, and no corrosion specimens were included. The loop was filled with the 10% HNO₃-3% H₂O₂ solution and pressurized to 50 psi with nitrogen. Periodically during the run the loop pressure was increased to 1500 psi with nitrogen, after which the bypass containing the packed holder was heated to 110°C for a few minutes followed by reduction of loop pressure to 50 psi. The remainder of the loop was maintained at 50°C. The purpose of the periodic pressurization and heating of the bypass was to force the peroxide solution into voids in the oxide bed

and to form gas (oxygen) by thermal decomposition of the peroxide. It was hoped that release of the loop pressure might cause the expanding gas to remove mechanically some of the packed oxide. These efforts were unsuccessful and were discontinued after 45 hr of operation.

4. Oxalic Acid Solution. A 0.05% oxalic acid solution, pH 2.3, was tested in loop K at 40°C to determine its scale-dispersing ability as well as its corrosive action toward various materials used in the HRT. The loop was operated for 72 hr with a nitrogen overpressure of 100 psi. The iron concentration in solution reached 12 ppm at the termination of the run, and the oxalate concentration and pH were nearly constant throughout the test. No significant quantity of scale was removed from the loop and no significant weight losses were observed for pin specimens of 55A Titanium, type 347 stainless steel, Zircaloy-2, or Stellite 3; however, a Stellite 98M2 pin lost 0.6 mg/cm².

5. Conclusions. Deoxidine-170 appeared to be superior to any of the other reagents tested as descaling agents. Although Versenol-120 buffered with ammonium acetate removed a large quantity of scale from a 100A loop, much of the scale was not in solution, and instability of the reagent could result in the formation of undesirable side products.

None of the reagents tested appears promising for removal of a tightly packed plug from a heat-exchanger tube. The obstruction in the tube would prevent ready access of fresh reagent to the oxide, and dissolution would be very slow with even the best of the solutions tested. On the other hand, Deoxidine-170, because of its ability to dissolve thin, tightly

adherent scales, may be useful for decontaminating reactor systems, thereby reducing the shielding necessary for remote maintenance.

C. Stability of Fuel Solutions

1. Fuel Dilution. If the hole in the HRT core tank were patched, it is possible that the patch would not be completely leakproof. Should the fuel leak into the blanket (water), a dilution of the fuel solution would occur. If the dilution caused hydrolytic precipitation of a uranium-containing compound on the core tank, a local hot spot would result. To determine the stability of very dilute fuel solutions the following experiment was run in Loop N.

The loop was charged with 12 liters of distilled water, heated to 250°C, and pressurized with oxygen to give a concentration of 600 to 800 ppm. After the loop had been at temperature for 72 hr, 20 ml of a 0.04 m UO_2SO_4 -0.025 m H_2SO_4 -0.02 m CuSO_4 -0.005 m NiSO_4 solution was added by means of an injection pump. Samples of the circulating solution were then taken at intervals of 15 min for 2 hr and less frequently for an additional 48-hr period. This procedure was repeated for successive additions of 40, 80, and 500 ml of the simulated fuel solution. Results plotted in Fig. 3 show that calculated and determined uranium concentrations agreed within experimental error below uranium concentrations of 100 ppm. However, a considerable, unexplained discrepancy was encountered for the 500-ml addition; the observed uranium concentration was significantly less than the calculated concentration. Copper was the least stable species in solution; less than 80% of the added copper was present in solution at all

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Fig. 3. Calculated and Observed Uranium Concentration Versus Time.

concentrations. Nickel concentration data were erratic, but in general fair agreement between observed and calculated values was obtained.

Stability of the lower uranium concentrations may be accounted for by the relatively high acid content of the solution due to production of Cr(VI). Assuming that Cr(VI) is produced by the reaction

one equivalent of acid is produced for each gram-atom of chromium oxidized. In oxygenated solutions this reaction is difficult to avoid completely in a stainless steel loop. For example, when the 20-ml fuel solution addition was made, 40 ppm of Cr(VI) had been produced; this concentration corresponds to the production of 0.0008 equivalents of hydrogen ions per liter, which is roughly the normality of the uranium added. The excess acid would be expected to have a stabilizing influence on the dilute solution. Since Cr(VI) would not form under reactor conditions, this run is being repeated in a titanium loop to avoid the formation of Cr(VI) and hydrogen ions during the run.

2. Stability and Corrosiveness of Simulated Fuel Solutions.

The hydrolytic stability and corrosiveness of simulated light- and heavy-water fuel solutions were determined in 100A loops. Concentration of components in the two solutions were essentially the same on a volume basis and were expected to show the relative effects of the two solvents on corrosion rates of various alloys. In each case pin-type specimens of various alloys and an array of type 347 stainless steel coupons were exposed to the

solution at 250°C for 200 hr; the corrosion specimens were then removed and the solution was circulated at 320°C for an additional period to determine its chemical stability.

(a) D₂O Solutions.--The composition of the heavy-water solution was 0.025 m UO₂SO₄, 0.025 m D₂SO₄, 0.025 m CuSO₄, and 0.005 m NiSO₄. As shown in Fig. 4, concentrations of the solution components remained constant within experimental error during the 250°C part of the test; however, both uranium and copper were lost from solution at 320°C. The losses were presumably due to hydrolytic precipitation as indicated by an increase in acid concentration.

Table III is a list of the corrosion rates for the various materials exposed to the solution at 250° C. Corrosion rates of pin specimens showed no abnormalities, but the critical velocity of type 347 stainless steel coupons was 32 fps, a value much higher than that usually observed for similar solutions containing 0.025 m acid.⁽⁷⁾ The corrosion rates of the coupons at low velocities, 11 to 30 fps, were between 7.8 and 14.8 mpy, or approximately the same as those observed for the pin specimens at 17 fps. Cr(VI) reached a concentration of 45 ppm during the run, and the addition of chromates to loop solutions has been shown to raise the critical velocity of type 347 coupons; however, chromates also decrease the low-velocity corrosion rate and increase the high-velocity corrosion rate, neither of which was observed in this test.⁽⁸⁾ In addition, the rate of buildup of Cr(VI) was not abnormally high.

Fig. 4. Concentration Versus Time of Uranium and Copper in Simulated Fuel Solutions.

TABLE III. Corrosion Rates of Various Alloys Exposed to Light and Heavy Water Fuel Solutions for 200 Hours at 250°C and a Solution Velocity of 17 fps

D₂O Solution: 0.025 m UO₂SO₄, 0.025 m D₂SO₄, 0.025 m CuSO₄, 0.005 m NiSO₄

H₂O Solution: 0.03 m UO₂SO₄, 0.03 m H₂SO₄, 0.025 m CuSO₄, 0.005 m NiSO₄

Alloy	Corrosion Rate (mpy)	
	D ₂ O	H ₂ O
Ti-55A	0.0	0.0
347, cast	10.6	12.5
347, wrought	9.6	12.0
347, wrought	8.8	13.6
347, wrought	9.7	12.9
309SCb	10.2	12.0
309SCb	9.7	12.7
CD4MCu	9.5	10.7
Incoloy 804	13.1	12.5
Zircaloy-2	0.7*	1.4*

* Calculated from weight gain.

(b) H₂O.--The solution used in the light-water test was 0.03 m UO₂SO₄, 0.03 m H₂SO₄, 0.025 m CuSO₄, and 0.005 m NiSO₄. This solution was also stable at 250°C but differed from the D₂O solution in that only uranium was lost at 320°C while copper was apparently stable as shown in Fig. 4.

Corrosion rates of pin-type and coupon specimens exposed during the run at 250°C were found to be slightly higher than those observed for the D₂O run. In spite of the higher corrosion rates, the critical velocity of type 347 stainless steel coupons was 47 fps in the H₂O solution. The reason for the high critical velocities observed in both the D₂O and H₂O

runs is unknown. A direct comparison of corrosion rates in the two solutions is complicated by the fact that the tests were made in different loops. Corrosion rates observed in the LOOA loops have been shown to be affected markedly by the loop history.⁽⁹⁾ For example, corrosion rates in a new, film-free loop are generally lower than those measured in equipment which contains a quantity of scale on the pipe walls. Neither of these tests was made in new loops, but the loop used for the H₂O test had previously been used to evaluate a phosphoric acid descaling solution which contained a corrosion inhibitor, and it is possible that the removal of scale or the deposition of inhibitor on the loop walls could have influenced corrosion rates observed in the subsequent test in spite of thorough rinsing with distilled water.

D. Corrosion Tests with Various Alloys

Recent work reported in the literature^(10,11) has shown that the introduction of small amounts of impurities into a metal or alloy will, in certain cases, increase the corrosion resistance of the metal. One prominent example is the inclusion of a few tenths of a per cent of platinum in stainless steel. The platinum acts as a cathodic site with low hydrogen overvoltage, thereby allowing the anodic sites to polarize into passive-potential regions as a result of the increased anodic current. If the anodic sites do not achieve passivity, e.g., if chloride is present or the temperature is too high, then the platinum-containing material will corrode at a much greater rate than the same material containing no platinum.

It has been postulated that, in a dynamic system, a critical velocity exists because, at the higher velocities, sufficient concentrations of corrosion products at the metal surface cannot be achieved to precipitate a protective barrier.⁽¹²⁾ Thus a greater film-free corrosion rate would correspond to a higher critical velocity, and on this basis one would expect the platinum alloys to have higher critical velocities than the austenitic stainless steels containing no platinum.

To determine the corrosion resistance of alloys containing small amounts of intentionally added impurities, small heats of type 304 stainless steel containing either platinum or copper were made by the HRP Metallurgy Section, and the alloys were tested for 200 hr in a 0.04 m UO_2SO_4 - 0.025 m D_2SO_4 - 0.02 m $CuSO_4$ solution in heavy water at 250°C. Table IV is a list of results for pin-type specimens machined from either the cast or wrought material at solution velocities of 17 and 68 fps. Corrosion rates of the pins at low velocities showed that the 0.5% platinum and the 1.2% copper alloys offered some improvement over type 304 stainless steel but not to an outstanding degree. Poor performance of the 0.1% (cast) platinum pin was expected, as tests have shown that the cast materials are generally less corrosion-resistant than the wrought. At 68 fps all stainless alloys corroded at about the same rate. More experiments will be carried out on the platinum and copper alloys to determine their critical velocity and other corrosion characteristics in simulated fuel solutions.

TABLE IV. Average Corrosion Rates of Various Alloys During a 200-hr
Exposure to a 0.04 m UO_2SO_4 , -0.025 m D_2SO_4 , -0.02 m CuSO_4
Solution in D_2O at 250°C

Alloy	Corrosion Rate (mpy)	
	17 fps	68 fps
Ti-45A	0.1	1.2
304 stainless steel (wrought)	35.0	97.0
304 stainless steel (wrought)	36.0	99.0
304 + 0.1% Pt (cast)	40.0	102.0
304 + 0.5% Pt (wrought)	15.0	88.0
304 + 0.5% Pt (wrought)	15.0	96.0
304 + 1.2% Cu (wrought)	23.0	91.0
304 + 1.2% Cu (wrought)	22.0	94.0
347 stainless steel (wrought)	62.0	107.0
347 stainless steel (cast)	74.0	125.0
347 stainless steel (cast)	72.0	104.0
Incoloy 804	66.0	145.0

Incoloy 804 (25 Fe, 29 Cr, 44 Ni, 1 Mn, 0.4 Cu), tested at the same time as the other alloys, has been found in static tests to be less resistant to corrosion by uranyl sulfate solutions than type 347 stainless steel.⁽¹³⁾ In the present tests the same was found, although the difference between Incoloy 804 and wrought type 347 stainless steel was not great.

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

A. Intergranular Corrosion of Type 347 Stainless Steel

A test program has been completed for which the objective was to determine whether any correlation existed between the intergranular corrosion behavior of type 347 stainless steel in boiling 65% HNO_3 and its behavior in uranyl sulfate solutions. The boiling nitric acid test,⁽¹⁴⁾ an ASTM test designed specifically to measure the sensitivity of the austenitic stainless steels to intergranular corrosion attack, is employed as an acceptance test for type 347 stainless steel used in the HRT and associated programs. Hundreds of nitric acid tests have been performed with many heats and different forms of the alloy.

The criterion for HRP acceptance of type 347 stainless steel is that the average penetration rate of the sensitized steel in boiling 65% HNO_3 , determined from the observed weight loss, for usually five 48-hr periods shall not exceed a value of 0.002 in. (2 mils) per month.⁽¹⁵⁾ The sensitizing treatment, as stated in the HRP specification, consists of heating specimens for 1 hr in air at 1250°F followed by air cooling. The

sensitizing treatment used for specimens in the present investigation consisted of heating for 1 hr at a slightly lower temperature, 1200°F.

From the many acceptance tests that were run, specimens from a number of type 347 stainless steel heats that exhibited average penetration rates ranging between 1.3 and 39.2 mils/mo were selected. In addition, an unstabilized grade, type 310 stainless steel, was included for comparative purposes. A summary of the corrosion rates of the sensitized test materials in the boiling nitric acid solution is given in Table V. The severity of intergranular attack was proportional to the magnitude of the observed penetration rates. For example, the alloy that corroded at a rate of 1.3 mils/mo did not show intergranular attack, whereas the type 347 stainless steel that corroded at an average rate of 39.2 mils/mo exhibited intergranular penetration in excess of 10 mils; intense pitting was present also.

One of the test environments was a solution containing 0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , and 0.005 m $CuSO_4$. Tests were run in this oxygenated solution at temperatures of 100, 200, and 300°C. A few tests were run also in a similar but oxygen-deficient solution at 300°C to simulate conditions that would exist in a crevice. The second environment, selected because of its increased corrosivity, was oxygenated 1.33 m UO_2SO_4 solution at 100 and 250°C. The major portion of the tests was run with two heats of type 347 stainless steel, Lot Nos. 13 and 24 in Table V, which corroded at average penetration rates of 1.3 and 39.2 mils/mo, respectively, in the boiling 65% HNO_3 test. These two materials will hereinafter be designated as the control and the off-spec materials.

TABLE V. Results of Boiling 65% HNO_3 Test on Sensitized*
Stainless Steel Test Materials

48-Hr Periods	Penetration Rate (mils/mo per 48-hr period)**					
	310 SS (Lot 2)	347 SS (Lot 13)	347 SS (Lot 24)	347 SS (487/c)	347 SS (No. 34)	(No. 431/A)
1st	1.7	1.1	5.8	12.3	2.2	1.3
	1.8	1.0	6.2	11.3	2.5	
2nd	59.0	1.1	25.5	6.6	3.8	1.7
	57.8	0.8	28.5	6.3	3.9	
3rd	72.2	1.2	48.1	5.1	8.2	4.4
	76.5	1.1	55.4	5.0	8.4	
4th		1.7	52.7	3.8		7.7
		1.4	58.7	3.8		
5th		1.8	51.5	3.6		9.0
		1.6	60.0	3.7		
Average	44.3	1.4	36.7	6.3	4.7	5.0
	45.4	1.2	41.8	6.0	4.8	

* Heated 1 hr at 1200°F followed by air cooling.

** Where two numbers are given, duplicate specimens were exposed.

1. Dilute Fuel Solution Tests. Sensitized specimens of the control and off-spec type 347 stainless steel test materials were exposed for 5000 hr at atmospheric boiling in the dilute solution. The average defilmed corrosion rate for each material was less than 0.1 mpy. Metallographic examination of specimens from the two heats at the completion of the tests, disclosed no intergranular penetration. A sensitized specimen of another heat of type 347 stainless steel in the form of a 1/4-in. sched-80 pipe (No. 487/c in Table V) exhibited a higher corrosion rate, 0.4 mpy, in a similar environment, after 5000 hr; the rate increased slowly with increased exposure time. However, metallographic examination of the inner and outer walls of the specimen showed nothing other than a fairly severe surface roughening.

Annealed and sensitized specimens of type 310 stainless steel (1/2-in.-dia tubing) were exposed also for 5000 hr at atmospheric boiling in the dilute solution. The observed defilmed corrosion rates were less than 0.1 mpy. The annealed material was not subject to intergranular attack, but the sensitized specimens showed intergranular penetration extending to a depth of approximately 3 mils (Fig. 5).

At 200°C in the oxygenated dilute solution, neither the control nor the off-spec type 347 stainless steel specimens in the sensitized condition were attacked intergranularly after 5000 hr. The average defilmed corrosion rates, which decreased with increased exposure time, were 0.1 mpy for the control material and 0.2 mpy for the off-spec material. Figure 6 presents a graph of defilmed weight losses as a function of the exposure

a. Outer Wall Surface

b. Inner Wall Surface

Fig. 5. The Intergranular Penetration of Sensitized 1/2-in.-dia
Type 310 Stainless Steel Tubing After 5000 hr in Boiling,
Aerated $0.04 \text{ } m \text{ } \text{UO}_2\text{SO}_4$ - $0.02 \text{ } m \text{ } \text{H}_2\text{SO}_4$ - $0.005 \text{ } m \text{ } \text{CuSO}_4$
Solution. Etched in Glyceria-regia.
Magnification 250X.

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Fig. 6. Corrosion of Type 347 Stainless Steel by Oxygenated 0.04 m UO_2SO_4 -0.02m H_2SO_4 -0.005m CuSO_4 Solution at 200°C.

time for the two materials. Also included are data for annealed control specimens. The latter curve fell approximately midway between the curves for the sensitized control and off-spec specimens. Each point on the curves represents the average defilmed weight loss for duplicate specimens. The shape of the curves is typical for the behavior of type 347 stainless steel exposed under static conditions in a simulated reactor fuel solution.

Annealed and sensitized specimens of type 310 stainless steel were exposed also at 200°C for 5000 hr in the oxygenated dilute solution; average corrosion rates were 0.1 and 0.2 mpy, respectively. Metallographic examination of the annealed specimens after test showed uniform metal removal. The sensitized tube-type specimens exhibited marked evidence of intergranular attack similar to that shown in Fig. 5 except that the intensity of the attack was more severe. The maximum penetration was 6 mils.

At 300°C, the average corrosion rate for both sensitized control and off-spec type 347 stainless steel specimens was 0.3 mpy after 2000 hr in the oxygenated reactor fuel solution. Figure 7 shows the observed weight losses as a function of exposure time for the two types of materials and also for annealed control specimens. The average corrosion rate for the latter specimens was 0.2 mpy. All observed corrosion rates decreased with increased exposure time. Metallographic examination of the specimens showed no signs of intergranular attack. The sensitized off-spec specimens were slightly pitted with pits not exceeding 1 mil in depth. Other off-spec type 347 stainless steel specimens listed in Table V were exposed for periods up to 5000 hr in the 300°C environment. Subsequent examination failed to disclose any signs of intergranular corrosion.

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Fig. 7. Corrosion of Type 347 Stainless Steel by Oxygenated 0.04 m UO_2SO_4 - 0.02 m H_2SO_4 - 0.005 m CuSO_4 Solution at 300°C.

Annealed specimens of type 310 stainless steel corroded at an average rate of 0.2 mpy during 5000 hr at 300°C in the oxygenated fuel solution. Sensitized specimens corroded at an average rate of less than 0.1 mpy during the same period. The latter specimens exhibited a superficial grain boundary attack which was considerably less intense than that experienced in the 100 and 200°C tests. The maximum depth of penetration in the 300°C test was 0.5 mil. The annealed specimens exhibited no sensitivity to intergranular corrosion.

2. 1.33 m UO₂SO₄ Tests. Boiling tests with aerated 1.33 m UO₂SO₄ solution were conducted for 5000 hr with sensitized control and off-spec type 347 stainless steel specimens. In both cases, the average corrosion rates were less than 0.1 mpy. Metallographic examination of the off-spec specimens showed a very superficial grain boundary attack, not exceeding 0.5 mil in depth. The attack was not of sufficient intensity to be classed as intergranular corrosion. The sensitized control specimens underwent uniform attack. Sensitized specimens of type 310 stainless steel corroded at a rate slightly under 0.1 mpy during 5000 hr in the boiling uranyl sulfate environment. Pronounced grain boundary attack was disclosed by metallographic examination upon completion of the test. The depth of penetration was approximately 4 mils. Numerous incidences of grain dropping were observed also.

Twenty-five hundred-hour tests were run with sensitized type 347 stainless steel control and off-spec specimens at 250°C in oxygenated 1.33 m UO₂SO₄ solution. The average 2500 hr corrosion rate for both types

of material was 1.3 mpy; the average 50-hr rate for the two materials was 55 ± 5.0 mpy. Specimens were sectioned and examined for signs of intergranular sensitivity; the results appear in Fig. 8. The sensitized control specimen exhibited a shallow pitting attack (0.5 mil or less in depth); the sensitized off-spec specimen underwent relatively uniform attack. The large, dark-colored area in the photomicrograph of the latter specimen is an unidentified inclusion. Neither specimen was subject to intergranular attack. Other sensitized specimens of type 347 stainless steel that exhibited penetration rates in excess of 2.0 mils/mo in the boiling nitric acid test (Table V) were exposed for similar periods in the uranyl sulfate solution at 250°C. None of the specimens tested were attacked intergranularly.

3. Oxygen-Deficient Core Solution Tests. The concluding phase of the intergranular corrosion studies involved tests with the sensitized control and off-spec type 347 stainless steel test materials at 300°C in an oxygen-deficient 0.04 m UO_2SO_4 solution containing 0.02 m H_2SO_4 and 0.005 m $CuSO_4$. In a stainless steel system without oxygen, uranyl sulfate solutions undergo reduction to uranium oxide (either UO_2 or U_3O_8) with the formation of free sulfuric acid. Consequently the resulting environment is quite corrosive to stainless steel until corrosion consumes the acid. This is the type of environment that would exist in a crevice that did not have ready access to oxygen. Tests were run to determine if such an environment were capable of producing intergranular corrosion attack on the control and off-spec type 347 stainless steel.

a. Control Material

b. Off-spec Material

Fig. 8. Surface Attack on Sensitized Type 347 Stainless Steel
After 2500 hr at 250°C in Oxygenated 1.33 m UO_2SO_4 Solution.

Etched in Glycercia-regia.

Magnification 250X.

Specimens of the above two materials were sensitized and exposed in newly machined autoclaves containing the simulated core solution and exposed for two separate periods of continuous operation, 200 and 1000 hr. No excess oxygen was introduced into the autoclaves. Reduction of uranium during the tests was essentially complete; final dissolved uranium concentrations in all cases were less than 0.01 gm/liter as compared with an initial concentration of 10.6 gm/liter. The 200-hr defilmed corrosion rates for the sensitized control and off-spec specimens were 3.3 and 1.6 mpy, respectively; the 1000-hr rates were 3.0 and 1.3 mpy, respectively. It should be pointed out that these rates would have been higher had not the corrosion of the specimens and autoclaves consumed most of the acid.

Metallographic examination of the exposed specimens revealed surface roughening and shallow pitting. The pits were 1 mil or less in depth. No signs of intergranular corrosion attack were found. The surface condition of the 1000-hr specimens is shown in Fig. 9.

A complete summary of observed corrosion rates and the incidence of intergranular penetration for the sensitized test materials in all environments tested is given in Table VI. The following conclusions were suggested by the data:

- (1) There is no relationship between the intergranular corrosion behavior of sensitized type 347 stainless steel in the boiling 65% HNO_3 test and its behavior in aqueous uranyl sulfate solutions at temperatures up to 300°C. Steels subject to intergranular penetration and exhibiting corrosion rates as high as 39.2 mils/mo in the boiling nitric acid test did not undergo intergranular attack in the uranyl sulfate environments.

a. Sensitized Control Specimen

b. Sensitized Off-Spec Specimen

Fig. 9. Surface Attack on Type 347 Stainless Steel Specimens

Exposed 1000 hr at 300°C in Oxygen-Deficient

$0.04 \text{ m } \text{UO}_2\text{SO}_4 - 0.02 \text{ m } \text{H}_2\text{SO}_4 - 0.005 \text{ m } \text{CuSO}_4$

Solution. Etched in Glyceria-regia.

Magnification 250X.

TABLE VI. Intergranular Corrosion Behavior of Sensitized^(a)
Stainless Steels in Uranyl Sulfate Solutions

Material Type	Medium	Temp. (°C)	Total Time (hr)	Corrosion Rate (mpy)	Intergranular Penetration
347 SS (control) ^(c)	Fuel solution ^(b)	100	5000	<0.1	None observed
347 SS (off-spec) ^(d)			5000	<0.1	None observed
310 SS (e)			5000	<0.1	Present; 3 mils deep
347 SS (control)	Fuel solution	200	5000	0.1	None observed
347 SS (off-spec)			5000	0.2	None observed
310 SS			5000	0.2	Present; 6 mils deep
347 SS (control)	Fuel solution	300	2000	0.3	None observed
347 SS (off-spec)			2000	0.3	None observed
310 SS			5000	<0.1	Superficial attack
347 SS (control)	Fuel solution (O ₂ deficient)	300	200	3.3	None observed
347 SS (control)			1000	3.0	None observed
347 SS (off-spec)			200	1.6	None observed
347 SS (off-spec)			1000	1.3	None observed
347 SS (control)	1.33 m UO ₂ SO ₄	100	5000	<0.1	None observed
347 SS (off-spec)			5000	<0.1	None observed
310 SS			5000	<0.1	Present; 4 mils deep
347 SS (control)	1.33 m UO ₂ SO ₄	250	2500	1.3	None observed
347 SS (off-spec)			2500	1.3	None observed

(a) Heated 1 hr in air at 1250°F.

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

(c) Penetration rate (sensitized) in boiling 65% HNO₃, 1.3 mils/mo.

(d) Penetration rate (sensitized) in boiling 65% HNO₃, 39.2 mils/mo.

(e) Penetration rate (sensitized) in boiling 65% HNO₃, 44.9 mils/mo.

(2) Sensitized, unstabilized type 310 stainless steel which was highly subject to intergranular corrosion in the boiling nitric acid test was also subject to intergranular attack in uranyl sulfate solutions at 100°C and above. Presumably a similar behavior would be exhibited by other grades of unstabilized austenitic stainless steels, exclusive of the extra-low carbon types.

B. Stress-Corrosion Cracking of Cast Type 347 Stainless Steel

Preliminary tests with a single heat of cast type 347 stainless steel showed it to possess unusually good resistance to stress-corrosion cracking in boiling 42% MgCl_2 solution and in high-temperature chloride-containing water.^(16,17) Only one instance of cracking occurred in a number of tests.

During the past quarter, additional tests have been run with the same heat of cast type 347 stainless steel in the above-mentioned environments. Numerous tests have been started also with different heats of the same alloy as well as with heats of other cast austenitic stainless steels. The results of these tests will be reported at a future date.

A summary of the results obtained thus far with the cast type 347 stainless steel in chloride-containing water at 300°C is given in Table VII. The simple-beam type specimens were machined from a 3-in.-dia centrifugally cast pipe. In a total of 12 specimens, only the one case of cracking (referred to above) was found after exposure periods ranging up to 2000 hr. Since this single crack was disclosed only by metallographic examination, the possibility does exist that other specimens may exhibit cracks upon

metallographic examination at the completion of the tests. It should be noted that wrought type 347 stainless steel stress specimens exposed in the same environment are subject to cracking in periods of 500 hr or less.

TABLE VII. Stress-Corrosion Cracking Behavior of Cast
Type 347 Stainless Steel* in
Chloride-Containing Water
at 300°C

Chloride Conc (ppm)	Initial Solution pH	Applied Stress (psi)	Total Time (hr)	Remarks
0	6.5	20,000	1800	No cracks
0	6.5	20,000	2000	No cracks
100	2.8	30,000	2000	No cracks
100	6.5	20,000	1500	One shallow crack
100	6.5	20,000	1600	No cracks
100	10.5	30,000	2000	No cracks

* Simple-beam, mechanically abraded specimens.

The results of the boiling magnesium chloride tests are summarized in Table VIII. U-bends and simple-beam specimens were used. The specimens were machined from 3-in.-dia centrifugally cast pipe; some specimens were used as machined and others were polished. An interesting fact

TABLE VIII. Stress-Corrosion Cracking Behavior of Cast
Type 347 Stainless Steel in Boiling 42% MgCl₂
Solution at 154°C

Specimen Type	Surface Condition	Applied Stress (psi)	Surface Cold Work	Total Time (hr)	Remarks
Simple beam	Abraded	20,000	None	30	No cracks at 90X
Simple beam	Machined	15,000	*	50	Cracks in stamped identification numbers (both specimens)
Simple beam	Machined	30,000	*	50	No cracks at 90X
Simple beam	Machined	30,000	Yes	5	Cracks (both specimens)
U-bend	Machined	>40,000	Severe	1	Cracks (both specimens)
U-bend**	Machined	<40,000	Severe	2	Cracks (both specimens)
Simple beam	Electropolished	15,000	None	50	Cracks in stamped identification numbers only (both specimens)
Simple beam	Electropolished	30,000	None	50	No cracks at 90X

* Submitted for metallographic examination--results not yet available.

** Annealed 1 hr at 1950°F after bending.

was disclosed by metallographic examination of the specimens. The sensitivity to cracking appeared to be associated directly with areas of cold work. No evidence of a cold-worked structure was found on the mechanically polished simple-beam specimens stressed at 20,000 psi; these specimens did not crack in 30 hr, the time of the test. Similarly, electropolished specimens showed no surface cold work except in areas around stamped identification numbers. A highly deformed crystal structure was observed in these areas and cracks formed. No cracking occurred on any other portion of the specimens. Machined specimens, particularly the U-bends, had severely cold-worked surface structures; the specimens were highly subject to cracking for the most part during short periods of exposure. In the case of the U-bends, the cold-work effect in the areas of maximum stress extended to a depth of approximately 15 mils below the surface. Additional tests will be run to examine the effect of cold working in greater detail.

C. Corrosion of Sintered Aluminum Oxide by Thoria Slurry

Six commercial grades of aluminum oxide were exposed to oxygenated thorium oxide (LO-37-1400) slurry at 100 and 300°C for evaluation of corrosion resistance. The materials are under consideration for use as check balls in valves for slurry service. The slurry used for the tests contained 3 kg ThO_2 /kg H_2O . Specimens were completely covered by the slurry during operation of the static tests.

Observed corrosion rates for 100- to 1000-hr periods are included in Table IX. The rates were calculated from weight change determined by drying and weighing the scrubbed specimens repeatedly until a relatively

constant weight loss was obtained. Five of the six alumina specimens exhibited acceptable corrosion resistance at 100°C; the 1000-hr corrosion rates were 1.2 mpy or less. The sixth material, designated as P-3142 and produced by the Diamonite Corporation, corroded at a rate of 7 mpy during a 1000-hr test. In all cases, the corrosion rates remained constant or decreased with increased exposure time.

TABLE IX. Corrosion of Sintered Aluminum Oxide in
Oxygenated Thoria Slurry* at 100 and 300°C

Supplier	Trade Name	% Al_2O_3	Corrosion Rate (mpy)			
			100°C		300°C	
			500 hr	1000 hr	100 hr	300 hr
American Lava Corporation	AlSiMag 614	95	1.1	0.7	16	13
Centralab Corporation	4-948	85	1.9	1.2	5	7
Diamonite Corporation	P-3142	94.7	12	7	20, 30	23, 23
Frenchtown Corporation	95% Body	95	0.5	0.3	10	10
Thermal Refractory Company	Alox	99.6	0.2	0.2	0.5, 0.5	0.5, 2.0
Norton Company	LA-687	99	1.0	0.6	5, 20	10, 20

* 300 g ThO_2 /100 ml of H_2O .

Only one of the six aluminas, a material designated as Alox and produced by the Thermal Refractory Company, showed promising corrosion resistance at 300°C; duplicate specimens showed corrosion rates of 0.5 and 2 mpy after 100- and after 300-hr exposure periods. The 300-hr rates for the other five materials varied from 7 to 23 mpy.

In both the 100 and 300°C tests, there was no direct relation between the purity of the aluminum oxides and their observed corrosion behavior. Although the material designated as Alox, which exhibited the best over-all corrosion resistance, was the highest-purity product tested (99.6%), there was no apparent correlation between purity and corrosion rate for the other materials.

D. Corrosion of Uniloy 19-9DL Stainless Steel

Uniloy 19-9DL is an austenitic stainless steel that has been modified by the addition of small amounts of molybdenum, tungsten, titanium, and niobium. The resulting crystal structure consists of an austenitic matrix with approximately 5% ferrite. The nominal chemical composition of the alloy in weight per cent is as follows: 0.28-0.35 C, 18-20 Cr, 8-11 Ni, 0.75-1.50 Mn, 1.00-1.75 Mo, 1.00-1.75 W, 0.10-0.35 Ti, 0.25-0.60 Nb + Ta, and balance iron. The mechanical properties of the alloy in the annealed and in the annealed-and-aged condition are compared with those for annealed type 347 stainless steel in Table X. The annealed yield strength of the alloy shows a 50% improvement over that for type 347 stainless steel.

Type 19-9DL stainless steel has been used successfully as a bolt material and as valve trim at elevated temperatures in oil refineries and

in steam generation plants. Because of its favorable mechanical properties, the material was considered as one of potential interest for bolting applications in the Homogenous Reactor Program.

TABLE X. Comparison of Mechanical Properties of
Types 19-9DL and 347 Stainless Steels

Material	Condition	Tensile Strength (psi)	Yield Strength (psi)	Hardness (Rockwell)
347 SS	Annealed	90,000	40,000	B75-80
19-9DL	Annealed	108,000	61,000	B92
	Annealed - aged at 1200°F	130,500	88,500	C23

Extensive corrosion testing with the alloy in a number of different heat-treated conditions was carried out in a simulated reactor fuel solution containing 0.04 m UO_2SO_4 , 0.02 m H_2SO_4 , and 0.005 m $CuSO_4$ and in boiling 5% HNO_3 solution. The corrosion resistance of as-received material (condition unknown) was very erratic in the reactor fuel solution at temperatures of 100 and 300°C. At the lower temperature, severe corrosion was encountered; attack rates during 50- and 100-hr exposures ranged from 180 to 240 mpy. At 300°C, however, 1000-hr exposure periods produced corrosion rates not greater than 2 mpy. The behavior of the as-received material was poor

also in 5% HNO_3 at atmospheric boiling; 300-hr corrosion rates varied from 30 to 40 mpy.

It was found that the corrosion resistance of the as-received material could be improved markedly by the use of either of two heat treatments, (1) annealing for 1 hr at 1800°F or (2) age-hardening for 50 hr at 1350°F. Both heat treatments resulted in average 1000-hr corrosion rates not in excess of 0.5 mpy in simulated reactor fuel solution at 100 and 300°C and in the boiling 5% HNO_3 solution.

Annealed specimens from a second heat of 19-9DL stainless steel were heated at 1200°F for periods of 0.5, 1, 2, 3, 5, 10, 20, 30, and 48 hr and subsequently exposed at atmospheric boiling for periods between 1000 and 1100 hr in a 0.04 m UO_2SO_4 -0.02 m H_2SO_4 -0.005 m CuSO_4 solution. Observed corrosion rates were 0.3 mpy or less as compared with less than 0.1 mpy for the annealed material, thereby indicating no significant effect of the 1200°F heat treatment on the corrosion behavior of the alloy.

The stress-corrosion cracking behavior of the alloy was examined in a number of environments, with and without chloride ions present. The results are summarized in Table XI. No cracking occurred in chloride-free deionized water during 2000-hr exposure periods at 300°C. In the chloride-free reactor fuel solution at 300°C, the annealed specimen was found to have a very small crack in a region deformed by stamping of identification numbers. No cracks were found elsewhere on the specimen. The annealed-and-aged specimen remained crack-free during a 200-hr exposure in a similar environment.

TABLE XI. Stress-Corrosion Cracking Behavior of
Type 19-9DL Stainless Steel

Environment	Specimen Type	Specimen Condition	Temp. (°C)	Total Time (hr)	Remarks
Deionized H ₂ O	Simple beam ^(a)	Annealed ^(b)	300	2000	No cracks
	Simple beam ^(a)	Annealed and aged ^(c)	300	2000	No cracks
Reactor fuel solution ^(d)	U-bend	Annealed	300	2000	Small crack in stamped number
	U-bend	Annealed and aged	300	2000	No cracks
Reactor fuel solution ^(d) + 50 ppm chloride	Simple beam ^(e)	Annealed	100	250	Cracks
	Simple beam ^(a)	Annealed and aged	100	300	No cracks
	Simple beam ^(a)	Annealed and aged	100	300	No cracks
42% MgCl ₂	U-bend	Solution-quenched ^(f)	154	3	Cracks

(a) Stressed at 32,000 psi.

(b) All annealing conducted for 1 hr at 1800°F.

(c) All aging conducted for 1 hr at 1200°F.

(d) 0.04 m UO₂SO₄-0.025 m H₂SO₄-0.01 m CuSO₄.

(e) Stressed at 50,000 psi.

(f) Heated 1 hr at 2100°F.

Two annealed-and-aged simple-beam specimens, stressed at 32,000 psi, were resistant to cracking for a period of 300 hr in the boiling reactor fuel solution containing 50 ppm of chloride. The test was terminated after 300 hr because of unusually severe pitting and subsurface attack on the specimens. An annealed simple-beam specimen, stressed at 50,000 psi, cracked during a 100-hr exposure in the chloride-containing environment. A U-bend specimen exposed in boiling (154°C) 42% MgCl_2 solution cracked during a 3-hr period, a behavior analogous to that for type 347 stainless steel.

Final experiments were concerned with an evaluation of the anti-galling characteristics of the 19-9DL stainless steel. Five 3/8-16 cap screws were exposed at 300°C, three in oxygenated 0.04 m UO_2SO_4 -0.025 m H_2SO_4 -0.01 m CuSO_4 solution, and two in deionized water. The cap screws were in both an annealed condition and an annealed-and-aged condition; the screws were initially stressed to approximately 20 ft-lb. During the tests, the cap screws were dismantled and restressed frequently. No tendencies toward galling were observed during 1500-hr test periods. Under the same conditions, a similar cap screw fabricated from type 304 stainless steel galled in less than 500 hr in the deionized water environment.

In conclusion, it appears that in a properly heat-treated condition, annealed or annealed-and-aged, the satisfactory corrosion resistance of Uniloy 19-9DL stainless steel and its superior mechanical properties in these heat-treated conditions (as compared to those for type 347 stainless steel) would make the alloy suitable for a number of applications within

the Homogenous Reactor Program. Actually, its general corrosion behavior in the above conditions compares favorably with that of type 347 stainless steel in similar reactor-related environments. Its susceptibility to stress-corrosion cracking, however, in chloride-containing reactor fuel solution appears to be analogous to that of type 347 stainless steel. Preliminary tests indicate also that the alloy possesses good anti-galling properties.

V. REFERENCES

1. J. C. Griess et al., Quar. Rep. Solution Materials Section, Jan. 31, 1959, ORNL CF-59-1-79, pp 12-15.
2. J. C. Griess et al., Quar. Rep. Solution Materials Section, Oct. 31, 1958, ORNL CF-58-10-95, pp 8-14.
3. J. C. Griess et al., HRP Quar. Prog. Rep., Jan. 31, 1959, ORNL-2696, p 84 and Fig. 11.3 on p 99.
4. G. H. Jenks et al., HRP Quar. Prog. Rep., Jan. 31, 1959, ORNL-2696, pp 133-143.
5. Reference 1, pp 16-20.
6. D. E. Ferguson, private communication.
7. J. C. Griess et al., Quar. Rep. Solution Corrosion Group, April 30, 1958, ORNL CF-58-4-131, p 9.
8. J. C. Griess et al., HRP Quar. Prog. Rep. April 30, 1955, ORNL-1895, p 91.
9. J. C. Griess et al., Quar. Rep. Solution Corrosion Group April 30, 1957, ORNL CF-57-4-55, p. 19.
10. N. D. Tomashoff, "Methods for Increasing the Corrosion Resistance of Metal Alloys," Corrosion 14, 229t-236t (1958).
11. Chemical and Engineering News 37, No. 15, p 26 (1959).
12. J. C. Griess et al., HRP Dynamic Solution Corrosion Studies: Quar. Ending July 31, 1956, ORNL CF-56-7-52, p 24.
13. Reference 1, p 48.
14. Boiling Nitric Acid Test for Corrosion-Resisting Steels, ASTM Designation: A 262-55T, ASTM Standards, Part I, Ferrous Metals, 1955, pp 1108-1112.
15. Modified Type 347 Austenitic Stainless Steel Material, HRP Specification No. 200a, Mar. 21, 1957, p 3.
16. J. C. Griess et al., HRP Quar. Prog. Rep. Oct. 31, 1958, ORNL-2654, pp 120-121.
17. Reference 3, pp 90-91.

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