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Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation Post Office Box X
Oak Ridge, TennesseeORNL
CENTRAL FILES NUMBER

CF- 58-8-28

DATE: August 5, 1958

SUBJECT: HRP-CPP: Dissolution of Zirconium and
Stainless Steel Corrosion Product Oxides

TO: F. L. Culler

FROM: J. W. Snider, P. A. Haas

COPY NO. 34

ABSTRACT

Dissolution methods were developed to permit representative sampling of the slurry of corrosion and fission products collected by the HRT chemical processing plant. The procedure selected for HRT-CPP application was to use 15 ml of 10.8 M H_2SO_4 per gram of solids with agitation by boiling in a tantalum lined dissolver.

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1.0 SUMMARY

A dissolution method was developed to permit representative sampling of the slurry of corrosion and fission products collected by the Homogeneous Reactor Test chemical processing plant. The requirements were essentially complete solution of the solids using procedures and equipment capable of the remote, leak-free, and maintenance-free operation required in a radiochemical plant. Laboratory studies were followed by plant scale tests of sulfuric acid and phosphoric acid as dissolvents. The procedure selected was dissolution with 15.0 ml of 10.8 M H_2SO_4 per gram of solids in a tantalum-lined dissolver. Agitation was provided by boiling throughout two cycles of 4 hours at 4 M H_2SO_4 and 4 hours at 10.8 M H_2SO_4 . Over 99.5% of the synthetic corrosion-fission product solids were dissolved without difficulty by this procedure.

2.0 INTRODUCTION

Studies were made to test and develop alternate dissolution procedures for complete dissolution of HRT corrosion product oxides in equipment which fulfills radiochemical plant requirements. To determine the effectiveness of the hydroclone in the HRT-CPP, the solids removed must be dissolved in order to obtain a representative sample. Chemical Development Section A studies determined a procedure for dissolution of the simulated corrosion products with sulfuric acid. Unit Operations studies were made to test this procedure on a scale comparable to the HRT-CPP operation. The studies included production and dissolution of simulated corrosion products.

The equipment used for dissolution was a prototype of the HRT-CPP dissolver operated as required to fulfill the remote operation requirements of a radiochemical plant. The other requirements were to dissolve more than 99% of the corrosion oxides in an operating cycle of less than 24 hours. The dissolution cycle was tested and operational procedures set up for the HRT Chemical Plant. An alternate phosphoric acid dissolution procedure was tested to a preliminary degree (see appendix).

Boiling 10.8 M H_2SO_4 effectively converts corrosion product oxides to sulfate salts which have a limited solubility at this acid concentration. To completely convert large oxide particles to sulfate salts, the treatment with 10.8 M H_2SO_4 must be alternated with periods of low acid concentration (4 M H_2SO_4) to wash sulfate salts from the particle surfaces. Two such cycles were found effective for the particle sizes expected for HRT corrosion products.

3.0 RESULTS

Essentially complete dissolution of the simulated corrosion oxides was achieved by two cycle operation. The procedure consisted of adding 15 ml of 10.8 M H_2SO_4 per gram of synthetic corrosion product solids (see appendix) and refluxing for four hours. The solution was then diluted to 4 M H_2SO_4 and refluxed for four more hours followed by reconcentration to 10.8 M H_2SO_4 . The complete dissolution procedure consisted of two of the above cycles.

3.1 Agitation Requirements

The dissolution rate is a function of the agitation which was obtained from boiling convection. The dissolver was designed to simulate radio-chemical plant requirements, and mechanical agitation was not acceptable. The initial design with a completely steam jacketed dissolver did not give adequate agitation without excessive boilup rates which exceeded the capacity of the condenser and condensate return system. The excessive boilup was probably partially due to revaporization of condensate running down the dissolver walls. The dissolver heating jacket was segmented to restrict the heating surface to the bottom of the dissolver and, thereby increase the amount of agitation from a given boilup rate. Agitation by boiling was adequate after this change was made.

For the HRT-CPP tantalum lined dissolver, this partitioning of the steam jacket was obtained by welding in a carbon steel divider (Figure 1) For the Unit Operation's glass lined dissolver, a thicker spacer was welded to the jacket with an "O" ring seal to the glass lined body.

Unequal expansion of the tantalum liner and the stainless steel body of the HRT-CPP dissolver resulted in a 15-20 mil air gap and an overall heat-transfer coefficient of about 5 Btu/hr-ft²°F. (1) This gap was filled with mercury to give an acceptable overall heat transfer coefficient of 75 Btu/hr-ft²°F.

3.2 Concentration Control

The maximum dissolution rate occurs in 10.8 M H_2SO_4 and decreases rapidly above this concentration. Volume measurements of the accuracy required to determine concentrations are difficult. Measurement of the boiling temperature of H_2SO_4 solution was found to be the best means of

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FIGURE 1 HRT-CPP DISSOLVER AS ALTERED

acid concentration control. The 10.8 M H_2SO_4 concentration was obtained by adjustment to give a boiling point between 155°C and 157°C. This can very easily be duplicated in remotely controlled operations. The 4.0 M H_2SO_4 concentration was obtained by adjusting to a boiling temperature of 110°C.

After addition of dilution water to the 10.8 M H_2SO_4 , an air sparge was required to give a controlled mixing during heating to the boiling temperature. The water and acid have a tendency to stratify into two layers. The bottom concentrated layer has a higher boiling point than the less concentrated top layer. Originally the mixing of these two layers was by natural convection. The bottom layer was found to approach its boiling point before much mixing occurred. Once this mixing began, it accelerated itself yielding a super-heated solution which would boil over in a flash type evaporation. This effect was not altered by segmenting of the dissolver heating jacket to restrict the heating surface to the bottom portion. A small air sparge during the heating from 100°C to 110°C completely eliminated the sudden mixing and flash boiling.

3.4 Dissolver Product

Dissolution tests demonstrated from 99.1 to 99.6 per cent dissolution in the Unit Operations glass-lined dissolver (Table 1) and 99.6 to 99.9 per cent in the HRT-Cpp dissolver (Table 2), using the selected procedures (see Sec. 4.0). One instead of two cycle gave 99.5 per cent dissolution while 130% and 150% of the normal solids-acid ratio gave 99.0 and 91.7 per cent dissolution respectively. The composition of the undissolved solids had approximately the Fe-Cr-Zr ratios of the synthetic corrosion product feed (Table 3).

Material balances were calculated from dissolver product analyses and the average charge solids compositions (Table 4). Sampling and analyses of the feed solids are probably inaccurate; the uranium material balances are much better than those for the Fe, Cr, and Zr.

3.5 Corrosion Results

Use of a tantalum lined dissolver was selected for the HRT-CPP on the basis of corrosion tests by the REED division. (3) Glass lined equipment was rejected on the basis of fragility and unknown radiation damage effects, and zirconium alloys and tantalum were the only metals showing corrosion rates of less than 20 mpy in 10.8 M H_2SO_4 (Table 5).

Table 1. Unit Operations Dissolver Test Results

Conditions: Two Cycles as Described in Sec. 4.0

Run No.	Wt of Solids, (g)	Per Cent Dissolution ^a
1	400	99.1
2	400	99.6
3	400	99.5
4 ^b	400	99.0
5	400	99.6
6	400	---- ^c

^a Percent dissolution values are from weight of undissolved solids.

^b 11.25 ml of acid per gram of solids.

^c Foaming test (not analyzed for percent dissolution).

Table 2. HRT-CPP Dissolver Test Results ^a

Run No.	Solids Charged (g)	Number of Cycles	Excess Acid (%)	Dissolution ^b (%)
CP-1	365	2	830	99.7
CP-2	368	2	820	99.9
CP-3	365	2	830	99.6
CP-4	368	1	820	99.5
CP-5	534	2	550	91.7

^a Data from CF-57-7-113(2).

^b Percent dissolution values are from weight of undissolved solids.

Table 3. Unit Operations: Composition of Undissolved Solids

Run No.	Wt of Solids Remaining (mg)	Composition of Solids Remaining		
		Fe (%)	Cr (%)	Zr (%)
Feed	-----	28.	9.	35.
1	3,810	19.7	9.8	25.5
2	1,816	9.9	17.0	7.7
3	1,940	25.6	10.0	8.2
4	4,450	18.4	8.1	21.6
5	1,450	12.3	14.0	10.3

Table 4. Material Balances

Run ^a No.	U (%)	Zr (%)	Cr (%)	Fe (%)	H ₂ SO ₄ (%)
1	99.6	93.4	118.0	149.0	
2	93.7	68.2	82.1	98.3	
3	96.7	95.4	110.1	128.0	
4	110.0	85.0	110.0	108.0	
5	104.2	119.1	123.0	144.6	
CP-1	110	64	115	101	97
CP-2	120	81	87	104	100
CP-3	99	82	85	130	111
CP-4	120	86	97	107	95
CP-5	99	96	97	133	98

^a Data for CP-1 to CP-5 from CF-57-7-113⁽²⁾.

Table 5. Corrosion Rates in Sulfuric Acid Solutions

Material	4 M H ₂ SO ₄ at 109°C		Boiling 10.8 M H ₂ SO ₄		Oxygenated Boiling 10.8 M H ₂ SO ₄	
	Exposure Time (hr)	Average Corrosion Rate (mpy)	Exposure Time (hr)	Average Corrosion Rate (mpy)	Exposure Time (hr)	Average Corrosion Rate (mpy)
Carpenter-20 CB	524	32	4.5	39,000	22.5	22,000
Illium R	437	15	65	1,000	25	1,100
Hastelloy B	437	3.2	463	70	256	24
Lead	436	1	463	37	256	110
Tantalum	443	0	463	0.1	255	0.2
Zircaloy-2	437	0	463	11	255	5.5
Zirconium	437	0	463	6.2	256	7.5

When a liquid metal was suggested for improving the heat transfer between the tantalum dissolver liner and the stainless steel body, corrosion studies were made for these metals in contact with mercury and Cerrolow 117. Results (4) showed no detectable attack on the tantalum and less than 10 mpy at 260°C on the stainless steel.

Use of a stainless steel dissolver head was found to be practical from a corrosion standpoint and eliminated the fabrication and seal problems which persistently appeared during use of tantalum lined heads. During Unit Operations tests, corrosion of Carpenter 20 specimens located just below the vapor outlet were 26-51 mpy. This was believed to be due to foaming and/or entrainment during the 10.8 M H_2SO_4 reflux period. A gold plated conductivity probe indicated 0-10 mho^{-1} during the 4 M H_2SO_4 reflux as compared to 200-250 mho^{-1} during reflux of the concentrated acid; these values indicate foaming or entrainment. Use of cooling H_2O in the upper part of the segmented jacket of the HRT-CPP dissolver was expected to eliminate foaming and entrainment. The observed corrosion rate for 126 hours of H_2SO_4 reflux was less than 0.1 mpy for a Carpenter 20 specimen suspended below the dissolver head. (1)

4.0 SELECTED PROCEDURE

4.1 Description of Cycle

The selected procedure consisted of adding 15 ml of 10.8 M H_2SO_4 per gram of solids and refluxing for two cycles totaling about 20 hours. After four hours of refluxing at the 10.8 M H_2SO_4 concentration, the solution is diluted to 4 M H_2SO_4 and refluxed for four hours more. The solution is concentrated to 10.8 M H_2SO_4 by evaporation. The complete dissolution procedure consisted of two of the above cycles. With the segmented jacket, glass lined dissolver, the heating steam is 25-40 psig during the 4 M H_2SO_4 reflux and 100-150 psig during the 10.8 M H_2SO_4 reflux.

4.2 Method of Control

The acid concentration is adjusted from boiling point temperature measurements. The 10.8 M H_2SO_4 concentration is obtained by adjusting acid concentration until the boiling point is between 155°C and 157°C. The 4 M H_2SO_4 concentration is obtained by adjusting acid concentration to give a boiling point of 110°C.

During the concentration step, the heating steam pressure is increased from 25-40 psig to 100-150 psig over a two hour period.

4.3 Dilution Procedure

Air sparge agitation is used to insure mixing after addition of the volume of water required to dilute the 10.8 MH_2SO_4 to 4 MH_2SO_4 . The water is added at any convenient rate, then air sparge at a low rate (~ 100 cc/min) is used during the heatup from 100°C until refluxing begins.

5.0 REFERENCES

- (1) "Homogeneous Reactor Project -- Quarterly Progress Report for Period Ending July 31, 1957." ORNL-2379, pp. 24-26.
- (2) W. L. Albrecht. "HRT-CPP Results of Solids Dissolution Tests." ORNL CF-57-7-113, July 30, 1957.
- (3) J. C. Griess. Unnumbered memo to A. M. Rom titled, "Corrosion in Sulfuric Acid Solutions." September 4, 1956.
- (4) L. R. Trotter. "Corrosion Studies on Tantalum and Type 347 Stainless Steel in Contact with Cerrolow and Mercury." ORNL CF-57-8-66, August 14, 1957.

6.0 APPENDIX

6.1 Dissolver Construction

Three dissolvers, all approximately 6 in. in diameter by 4 feet long, were used for dissolution tests. All three were fabricated with hemispherical bottoms, heated walls and bottoms, a thermowell, a reflux condenser, and an inlet dip leg and vent in a flanged cap.

The phosphoric acid dissolutions and the initial sulfuric acid dissolutions were in a dissolver fabricated by fusing a cap to a 4 ft long section of 6 in. in diameter Pyrex pipe. Heating was by radiant panels. This heating method

and the condenser geometry were not representative of the expected pilot plant conditions. Therefore, studies in the glass pipe unit were discontinued after arrival of the HRT-CPP dissolvers.

Units of identical geometry except that one was glass lined while the other two were lined with tantalum were used for all other Unit Operations and HRT-CPP dissolver studies. The dip leg of the Unit Operations tantalum lined unit was installed excessively long and punched a hole in the tantalum liner when the top flange was tightened down. Therefore, the Unit Operations studies were made in a glass lined unit and check dissolutions were made in the tantalum lined HRT-CPP dissolver.

The dissolver bodies were 6 in. schedule 40 IPS stainless steel pipe with a pipe cap and a nozzle for a split flange to give total inside lengths of 48-1/2 inches (Figure 1). The steam jackets were initially full length and were fabricated of 8 in. schedule 40 IPS pipe and caps. Alterations were made (see Sec. 3.1) to give segmented steam jackets and thus localize the heat transfer to increase the agitation by boiling.

The HRT chemical processing plant is using a segmented jacket, tantalum lined dissolver as described (Figure 1) with a reflux system of the type shown for the Unit Operations glass lined dissolver (Figures 2 and 3). Details of the CPP reflux and accessory system installation are shown by ORNL drawings D-26388, D-27409, and D-27410.

6.2 Simulated Corrosion Product Preparation

The history of synthetic corrosion and fission products was found to greatly affect the ease of dissolution; therefore, the preparation procedure was selected to give a history resembling that expected in the HRT. Large amounts of these simulated corrosion products were prepared for solids behavior studies in the HRT Mock-Up and in the HRT Chemical Processing Plant.

About 400 g of mixed simulated corrosion product oxides were prepared by solution of the following salts followed by precipitation, filtration, washing, and digestion:

240 g $Zr(SO_4)_2$

257.2 g $Fe_2(SO_4)_3$

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Fig. 2. UNOP Corrosion Products Solids Dissolver.

FIG. 3 HRT - CP
GLASS-LINED DISSOLVER

1.25 g CuSO_4

156 g $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$

The precipitation was by addition of 4 N NH_4OH to the salt solution at 60-70°C until a pH of 7 was obtained. The supernatant liquid was removed from the settled hydroxides by decantation. After four demineralized H_2O washes by decantation, the solids were filtered and slurried with one liter of 10 g U/l as UO_2SO_4 solution. Concentrated H_2SO_4 was added to give a pH of 2, and the slurry was autoclaved with 500 psi of O_2 over pressure at 300°C. About 16.5 g of mixed rare earth sulfates was added to some batches before autoclaving. Composition of the dry oxides was intended to be 47% ZrO_2 , 40% Fe_2O_3 , and 13% Cr_2O_3 .

After some initial batches of oxides were reported to have high halide contents by chemical analyses, two 4 N NH_4OH washes prior to the water washes and a subsequent H_2SO_4 wash to pH 7 were added to the procedure. Material prepared by using these extra wash steps showed lower halide concentrations by analyses, but material later prepared without NH_4OH or H_2SO_4 washes showed even lower halide concentrations. The reason for these indicated halide concentration differences was not determined.

6.3 Phosphoric Acid as an Alternate Dissolution Reagent

Dissolution of corrosion and fission products in phosphoric acid was developed in the laboratory and was demonstrated by two dissolutions in a glass dissolver. Since the product of the sulfuric acid dissolution was more desirable for further processing, was more stable, and had a lower solids content, work on the use of phosphoric acid was terminated after sulfuric acid dissolution was demonstrated to be practical.

The corrosion and fission product solids were dissolved by adding 15-20 ml of 85 wt% H_3PO_4 per gram of solids and heating to 230°C. Water was driven off and pyrophosphoric acid was probably formed. The resulting clear green solution was cooled and was diluted with 20-27 ml of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ solution saturated at 75° per gram of initial solids. The dilution with $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ was to increase the stability of the dissolved salts. The two dissolutions in the glass dissolver appeared complete, but crystalline material formed after dilution and cooling.

Corrosion tests indicated that selection of a dissolver material would not be a problem. Samples of Durimet 20, lead, and 304, 316, and 347 stainless steels were exposed at room temperature and the boiling point to dissolver product (after the $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ dilution). Only lead showed any significant attack (see Table 6); the others showed no weight change or small weight gains.

Table 6. Corrosion of Lead in Phosphoric Acid Dissolution Product

Exposure Conditions	Corrosion Rates in mils/yr for Exposure Time of				
	24 hrs	48 hrs	72 hrs	96 hrs	168 hrs
Circulated Solution at Room Temperature	----	24.4	----	29.3	30.6
In Boiling Liquid	420	960	1090	----	----
Vapor Above Boiling Liquid	1.22	----	1.16	----	----

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