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REPROCESSING OF POWER REACTOR FUELS

NINTH QUARTERLY PROGRESS REPORT

OCTOBER 1, 1959 TO JANUARY 1, 1960

Compiled by

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Separations Engineering Division

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ABSTRACT

Pressure and mechanical vibration are effective in maintaining continuous anodic dissolution in HNO_3 of stainless steel contained in an electrolytically inert anode basket. Zirconium metal can be electrolytically disintegrated in HNO_3 by the same technique; in this case 85% of the zirconium precipitates as ZrO_2 and only 15% remains in solution. When Zr - 10% U alloy is electrolytically disintegrated in HNO_3, 60 to 80% of the zirconium precipitates as ZrO_2, carrying 10% or more of the uranium.

The constituents of a charge of PRDC elements - zirconium and U-Mo alloy - were dissolved in a two-step process with HNO_3 and HF. The rate of dissolution of irradiated PRDC fuel is one to two times that of unirradiated fuel.

Previous reports in the series are DP-283, DP-318, DP-319, DP-338, DP-393, DP-421, and DP-439.

CONTENTS

LIST OF TABLES AND FIGURES

REPROCESSING OF POWER REACTOR FUELS
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INTRODUCTION

Studies continued on the electrolytic dissolution of both stainless steel and zirconium in nitric acid. These metals are the primary materials used for cladding power fuel elements. Since neither can be dissolved chemically in pure nitric acid, electrolytic dissolution in this medium is under study as an alternate process that is compatible with the stainless steel construction of the separations plant. The development of a process for dissolving elements clad in stainless steel has advanced to a semiworks scale. The process for zirconium and zirconium alloys is still under evaluation in the laboratory. The status of the progress in both programs of study is reported herein.

This report also includes the results of additional tests on chemical dissolution of PRDC elements in a HNO_3-HF solution. This process is presently favored for reprocessing these elements, which are zirconium-clad U-Mo alloy. At the relatively low concentration of HF required to obtain satisfactory rates of dissolution of the elements, corrosion of the plant equipment can be held to a tolerable level.

SUMMARY

Electrolytic dissolutions of stainless steel in HNO_3 have been operated continuously for periods up to 22 hours. Contact between the stainless steel and the electrolytically inert anode basket was maintained by applying additional weight to simulate the effect of UO_2 cores for the slugs and by intermittent vibration of the basket. The electrical "shadowing" of pieces of stainless steel in the interior of the charge was demonstrated.

Only 15% of the zirconium metal electrolytically disintegrated in nitric acid remained in solution as ZrO^{++}. The remainder precipitated as ZrO_2. The split between soluble and insoluble species was insensitive to a fourfold change in acid concentration and a threefold change in current density. Electrolytic disintegration of Zr - 10% U alloy effected the solution of 22 to 40% of the zirconium, the remainder precipitating as ZrO_2. The loss of uranium to the precipitate was greater than 10% in all tests. The loss decreased with increasing concentration of acid, but no definite correlation of loss with temperature was observed.

A simulated charge of PRDC elements was dissolved by the two-step process that was described previously. All of the zirconium of the charge dissolved in five hours in 1M HNO_3 - 0.075M HF. The U-Mo alloy was completely dissolved in an additional five hours, after the free fluoride was complexed with $Al(NO_3)_3$ and the concentration of HNO_3 was increased to 3M.

Test specimens of declad, irradiated PRDC fuel dissolved in 3M HNO_3 at rates one to two times as great as those for unirradiated controls. One test piece clad with 8-mil zirconium dissolved satisfactorily in 3.0M HNO_3 - 0.075M HF. Penetration rates ranged from 10 to 24 mils per hour for the irradiated specimens.

<center>DISCUSSION</center>

ELECTROLYTIC DISSOLUTION

STAINLESS STEEL

Two series of electrolytic dissolutions of long duration have been carried out on charges of randomly packed segments of stainless steel. For these runs the scale-ups were about 30 and 300 times the earlier tests reported in the Seventh and Eighth Quarterly Progress Reports[6,7], in which the experimental arrangement was described. The primary purpose of the tests was to demonstrate that electrolytic dissolutions could be continued for extended periods of time without loss of electrical contact between the inert metal anode basket and the small segments of stainless steel, which are collectively the anode.

Laboratory

Two electrolytic dissolutions of 2-inch lengths of 1/2-inch stainless steel tubing (800 to 1000 gm) were performed in a tantalum basket, 1 foot high and 3 inches in diameter. The electrolyte was 4M HNO_3, and all the pieces were submerged. The current was maintained between 50 and 100 amperes. The first run was carried to 73% completion and the second to 88% completion with current utilizations of 0.6 and 0.7 gm/amp-hr, respectively. With a 1.8-kg weight applied to the top of the randomly packed segments, no loss of contact was observed throughout the runs. The dissolutions were not carried to completion only because the resistance of the cell ultimately became too great, due to the decreasing surface area of the charge. A moderate amount of finely divided sludge, identified as particulate stainless steel, settled to the bottom of the dissolver.

Semiworks

Several extended electrolytic dissolutions have been performed in a niobium basket 6 inches in diameter. The initial charges were 7 to 11 kg of 5-inch segments of 1/4-inch stainless steel pipe. The cathode was constructed of niobium sheet. Twenty-two hours were required to dissolve about two-thirds of a 7-kg charge in 7M HNO_3 at 70°C. Repeated intermittent vibration was necessary to maintain the current at 400 amperes. A weight was applied to the charge to simulate conditions for a charge of the same volume of UO_2 slugs. Currents and voltages between the electrodes were recorded during the

<center>- 5 -</center>

run and are shown in Figure 1. The smooth voltage curve is the average of a series of sawtooth curves, the discontinuities of which were produced when the anode basket was jarred. The decrease in current near the end of the run occurred when the extent of vibration was diminished. Throughout the run the electrolyte was recirculated, which prevented accumulation of the sludge in the bottom of the basket. Current utilization for the run was about 0.6 gm/amp-hr.
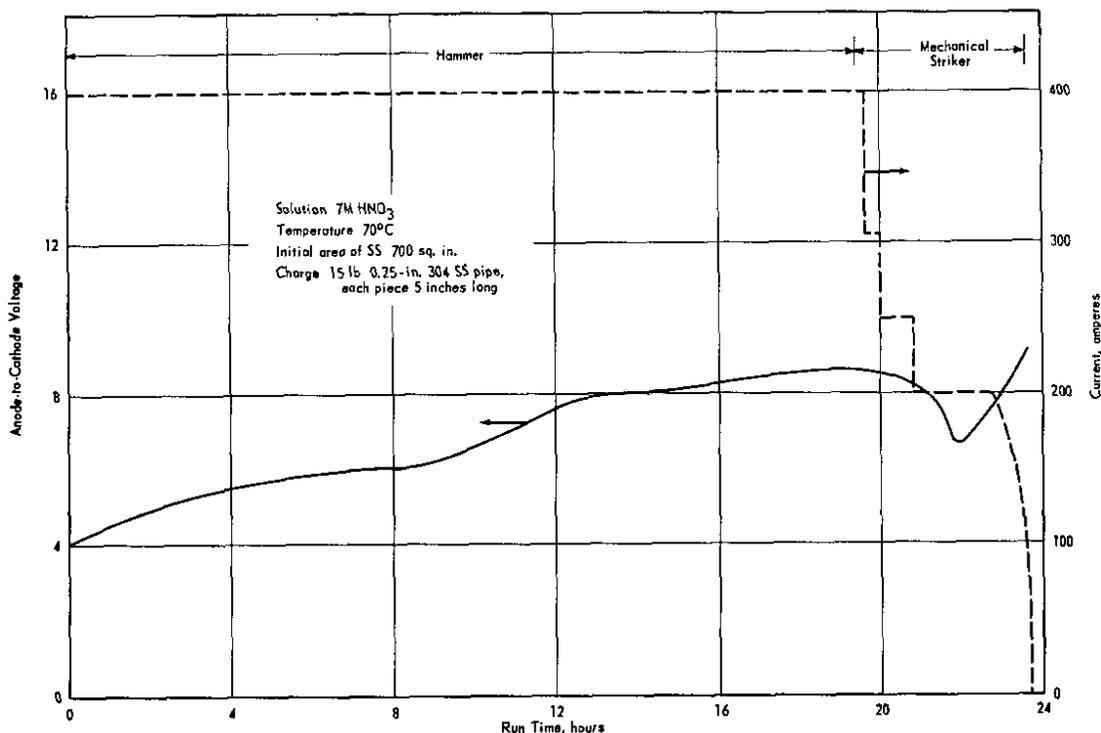
FIG. 1 ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL

Electrical Shadowing

In a full-scale electrolytic dissolver, there will be electrical "shadowing" of the stainless steel near the center of a containing anode basket. The magnitude of this effect was demonstrated by a simple laboratory test. Electrolytic dissolution of a charge of three concentric rings of vertically stacked segments of 1/2-inch stainless steel tubing produced a much greater loss in weight for the outer ring. After passage of 60 amp-hr of charge, the pieces in the outer ring had lost an average of 3.0 gm each; whereas the average loss in weight was 0.4 gm for each piece in the middle ring and 0.3 gm for each in the inner ring.

Probably the natural realignment of pieces in the charge, following consumption of those in the outer shell, will permit smooth operation as dissolution proceeds toward completion. This result has been observed for a charge of pieces of stainless steel. It must be verified, however, for a charge of UO_2 slugs clad with stainless steel.

- 6 -

ZIRCONIUM

The electrolytic dissolution of zirconium metal in nitric acid is
characterized by the precipitation of large quantities of ZrO_2, as
described in the Eighth Quarterly Progress Report[7]. Six tests
have been made on reactor-grade zirconium to determine the effect of
acid strength and current density on the split between the soluble
ZrO^{++} and the insoluble ZrO_2 that results from the electrolysis.
The results are shown in Table I. About 15% of the zirconium that
is electrolytically disintegrated remained in solution in all the
cases tested. Neither changing the concentration of the acid from
4 to 16M nor the current density from 0.13 to 0.41 amp/cm² affected
the quantity of the zirconium put into solution. Current utilization
ranged from 0.8 to 1.3 gm/amp-hr. Tests are planned with uranium and
UO_2 slugs clad with zirconium or Zircaloy to evaluate the potential
for an electrolytic decladding process, with codissolution of the
core, in pure nitric acid. The engineering problems associated
with maintaining electrical contact and the potential for explosion
at the interface between the cladding and a uranium metal core must
be determined.

TABLE I

Electrolytic Dissolution of Zirconium in HNO_3

HNO_3, M	Anode Current Density, amp/cm²	Current Utilization, gm/amp-hr	Zr Dissolved, %
4	0.19	0.8	14
10	0.13	0.8	16
10	0.13	1.0	15
10	0.26	1.3	15
10	0.41	1.1	14
16	0.24	1.1	14

Zr-U ALLOY

Electrolytic dissolution in HNO_3 is a possible technique for
reprocessing power fuel elements with cores of Zr-U alloy. As
discussed in the previous quarterly report[7], a large fraction of
the zirconium precipitates as ZrO_2. If the loss of uranium can be
kept low, say to less than 5%, such a process would be of particular
interest for elements with Zr-U cores of high zirconium content,
since most of the zirconium would be removed at the dissolution step.

A series of eleven runs on the electrolytic dissolution of
Zr - 10% U alloy have been completed. The technique differed from

that used for stainless steel only in that a single slab of metal was used for the anode. Temperature and acid concentration were the chief variables. All available data are presented in Table II. The results in general have been erratic with no definite trends emerging. Between 22 and 40% of the zirconium dissolves during electrolysis, and a small additional fraction dissolves during digestion of the residue with boiling nitric acid. In the runs thus far, a substantial quantity of the uranium has precipitated with the ZrO_2. Loss of uranium to the precipitate decreases with increasing acidity, but no correlation between the loss and the temperature for the electrolysis has been observed. The addition of $Al(NO_3)_3$ also proved ineffective in decreasing the uranium loss. This was tried because aluminum ion reportedly stabilizes Zr(III) in nonaqueous solutions and might also have a similar transient effect in the aqueous system, thereby decreasing the quantity of precipitate and reducing the uranium loss. Digestion with boiling nitric acid is partially effective in recovering the precipitated uranium, and additional effort will be made to reduce loss by postelectrolysis leaching. Work is currently in progress to determine the chemical state of uranium in the precipitate in order that techniques to reduce the loss can better be devised.

TABLE II

Electrolytic Dissolution of Zr - 10% U Alloy in HNO_3

Temperature During Electrolysis, °C	HNO_3, M	$Al(NO_3)_3$, M	Leaching With Boiling HNO_3, hr	Zr Dissolved During Electrolysis, %	U Loss to ZrO_2 Ppt., %	
					After Electrolysis	After Leaching
20-90	4	0	1.5	30	(a)	52
20-100	10	0	2	33	46	34
70-107	16	0	2	25	37	12
120	16	0	9	40	(a)	31
110	10	0.5	None	22	73	--
85-114	13	0.4	None	24	69	--
14-46	16	0	1.5	35	(a)	19
15-30	16	0	2	22	36	25
14-20	16	0	2	26	41	24
18-46	16	Sat'd	None	23	31	--
16-20	16	Sat'd	2	38	13	11

(a) Residue digested in original dissolver solution immediately after electrolytic dissolution.

CHEMICAL DISSOLUTION OF PRDC ELEMENTS

SIMULATED CHARGE OF PRDC ELEMENTS

Semiworks tests have confirmed the applicability of a two-step dissolution procedure[5] for PRDC elements in HNO_3-HF solution. The simulated charge consisted of a 12-lb "core" of U - 10% Mo alloy in the form of 150-mil rolled plate. The "cladding" was 0.7 lb of 10-mil zirconium sheet. "Decladding" was accomplished by immersing the charge in boiling 1M HNO_3 - 0.075M HF. After five hours, all the zirconium and about half of the alloy had dissolved. For "core" dissolution the free fluoride was complexed with 0.2M $Al(NO_3)_3$ and the concentration of HNO_3 was increased to 3M. The residual charge was completely dissolved after boiling for an additional five hours. A tan-colored deposit settled on the heating coils and the bottom of the dissolver during the dissolution. The material is being identified.

IRRADIATED PRDC FUEL

The rates of dissolution of five irradiated, declad specimens of U - 10% Mo alloy in 3M HNO_3 were one to two times as great as that for unirradiated alloy. Each specimen was 0.1 inch in diameter and weighed less than 1 gm. The zirconium cladding had been removed from the specimens prior to their receipt. Material at the surface of some of the test pieces was insoluble in 3M HNO_3, but dissolved readily when the solution was made 0.03M in HF. Therefore, it is believed that there was either some residual cladding or a diffusion layer of Zr-U at the surface. A sixth sample, clad with 8 mils of zirconium, was dissolved in 3.0M HNO_3 - 0.075M HF. The interior of this sample dissolved readily, but a very thin coating, presumably ZrO_2, did not. Such a coating is not anticipated on the elements from the sodium-cooled Detroit-Edison reactor.

The irradiated samples were dissolved in 200 ml of solution in glass apparatus. Data from the dissolutions are listed in Table III. Each of the declad samples of irradiated alloy was dissolved simultaneously with a sample of unirradiated alloy in order to compare the rates of dissolution and the over-all behavior. The irradiated samples in Tests 1 through 4 dissolved normally, except for small particles that were insoluble in 3M HNO_3 but soluble in dilute HF. During the dissolution of samples in Tests 5 and 6, the interior of the samples disintegrated during dissolution. In contrast to Tests 1 through 4, an insoluble coating that almost completely covered the sample was present in Tests 5 and 6; thus attack by the acid at the ends of the sample and through cracks in the coatings may have caused the disintegration.

TABLE III

Dissolution of Irradiated PRDC Fuel

Test	Burnup, total atom %	Enrichment, %	Dissolvent[a]	Average Rate of Penetration, mils/hr	
				Unirradiated	Irradiated
1[b]	<0.1	Natural U	3M HNO$_3$	10.2	9.8
2[b]	<0.1	Natural U	3M HNO$_3$	7.9	20.7
3[b]	<0.1	Natural U	3M HNO$_3$	10.3	23.7
4[b]	1.3	11.54	3M HNO$_3$	9.6	9.5
5[b,c]	2.0	11.54	3M HNO$_3$	9.3	9.5
6[c,d,e]	0.4	19.35	3M HNO$_3$ - 0.075M HF	--	14.4

(a) All samples were dissolved at the boiling point with total reflux. The final dissolver solutions contained <15 gm of total metal per liter.
(b) Small particles from surface were insoluble in HNO$_3$, but dissolved when solution was made 0.03M in HF.
(c) Interior disintegrated during dissolution.
(d) Specimen 6 was clad with 8 mils of zirconium.
(e) Thin coating, presumably ZrO$_2$, did not dissolve.

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