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Chemical Separations Processes
for Plutonium and Uranium

AEC Research and Development Report

PROCESSING OF POWER REACTOR FUELS

FIFTEENTH QUARTERLY PROGRESS REPORT

APRIL 1 TO JULY 1, 1961

Compiled by
J. H. Owen

Separations Engineering Division

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina

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PROCESSING OF POWER REACTOR FUELS
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Compiled by

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ABSTRACT

The results of experiments in support of an electrolytic dissolution process for fuel elements clad in stainless steel or zirconium are given. The rate of disintegration of Zircaloy-2 anodes in nitric acid did not vary with acid concentration. Nitric oxide, formaldehyde, and process solvent were found effective in reducing the corrosion of stainless steel equipment that was caused by the chromate present in acid solutions containing dissolved stainless steel. Means were developed to improve the contact between assemblies of stainless steel and the columbium basket of the semiworks dissolver, and an average current of 3000 amperes was achieved. Zircaloy plates were anodically disintegrated at an average current of 1200 amperes.

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PROCESSING OF POWER REACTOR FUELS FIFTEENTH QUARTERLY PROGRESS REPORT APRIL 1 TO JULY 1, 1961

INTRODUCTION

The objective of the development program for processing power reactor fuels at SRP is to demonstrate a technique for dissolving fuels clad with stainless steel or zirconium that is as compatible as possible with the existing plant equipment and with the solvent extraction process that is now being used for aluminum-clad fuels. In recent months, the primary emphasis of experimental work has been on an electrolytic dissolution process in which the cladding and fuel are dissolved in nitric acid(1-7). A 5000-amp dissolver is being operated at the Semiworks to define the problems associated with transferring large amounts of current to mock fuel assemblies from an anode basket made of columbium. An active program in the laboratory has been a study of means of reducing the rates of corrosion of stainless steel in nitric acid solutions containing dissolved stainless steel.

SUMMARY

The rate of anodic disintegration of Zircaloy-2 in nitric acid was not affected by variation of acid concentration from 1 to 10M. Side reactions, which interfere with the anodic dissolution of stainless steel in acid of less than 2M concentration, did not change the rate of disintegration of the Zircaloy from 1.0 ±0.1 gram per ampere-hour.

Cr^{+6} was shown to be the principal cause of corrosion of 304L stainless steel by solutions of nitric acid containing dissolved stainless steel. Corrosion during electrolytic dissolution is low because the Cr^{+6} is reduced to Cr^{+3} by nitrogen oxides liberated at the cathode and retained in the solution, which is not boiled. The oxides of nitrogen formed at the cathode reduce Cr^{+6} to Cr^{+3} at a rate independent of Cr^{+6} concentration in solutions containing up to 1 gram per liter of Cr^{+6} and 30 grams per liter of stainless steel. Means of reducing Cr^{+6} to Cr^{+3} in boiling solutions were studied, to seek ways to limit the corrosive attack on 304L stainless steel vessels when waste solutions are concentrated by evaporation prior to storage. Nitric oxide (NO), formaldehyde, and solvent from the extraction process are effective in reducing the corrosion rate by reducing Cr^{+6} to Cr^{+3}.

The continuing study of electrolytic dissolution in the 5000-amp semiworks dissolver has shown that stainless steel can be dissolved at an average current of 3000 amp. This rate is roughly equivalent to one ton of uranium per day in a plant-scale (10X) dissolver where the ratio of uranium to cladding is 3 to 1. Smoothest operation was obtained when the stainless steel assemblies were completely submerged in the electrolyte and when a weight was used to maintain contact. The capacity of the semiworks dissolver was limited by contact resistance between the columbium basket and the charge. After one million ampere-hours of operation there is still no evidence of corrosion of the 304L stainless steel dissolver vessel by either chemical or stray current effects.

Zircaloy plates were dissolved at an average current of 1100 to 1200 amp at a maximum potential of 15 volts. At this rate more than 2.5 pounds of Zircaloy dissolve in one hour. Proportionally higher rates were demonstrated at higher voltages, although local overheating of the plates and the anode basket was observed. Electrical contact between basket and charge was effectively maintained both by the anode striker, and by a weight that forced the plates against the bottom of the columbium basket.

DISCUSSION

LABORATORY

CURRENT UTILIZATION FOR THE ELECTROLYTIC DISSOLUTION OF ZIRCALOY-2

Work that has been previously reported(7) on the electrolytic dissolution of stainless steel in nitric acid has shown that side reactions decrease the current utilization when the acid concentration falls below 1.5 to 2M. Zircaloy-2 was electrolytically disintegrated in various acid concentrations to determine if similar side reactions interfere with disintegration in low concentrations of nitric acid. No such interference was detected. The current utilization remained at 1.0 ±0.1 g/amp-hr in 1 to 10M and as shown in Figure 1. The rate of 1 g/amp-hr is about 15% higher than theoretically required to oxidize zirconium to Zr^{+4}. Because the current fluctuated as oxide flaked erratically from the metal surface, the product of current and time was measured with a copper coulometer. The weight of zirconium that was oxidized was determined by the loss of weight of the anode and was corrected for the oxide coating remaining on the anode.

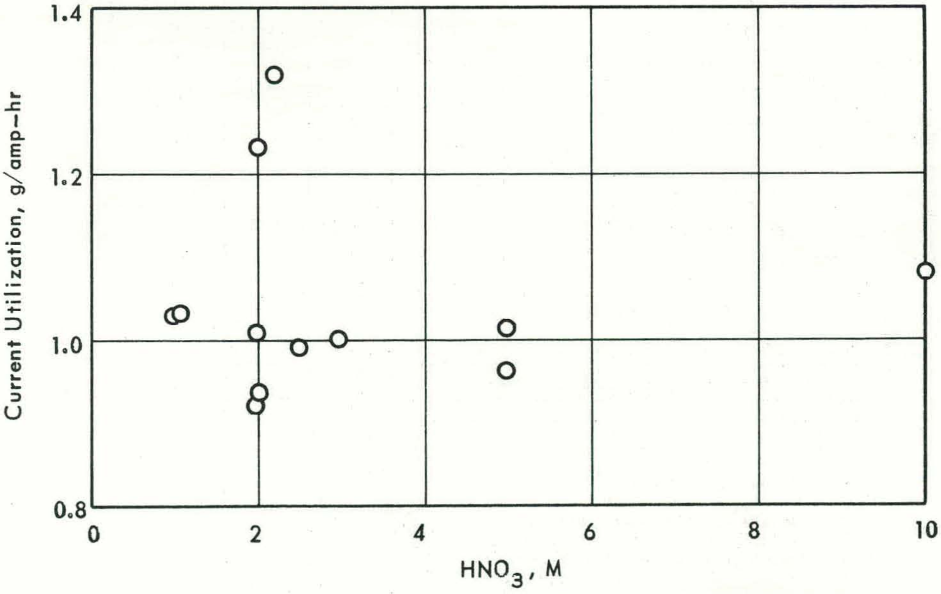

FIG. 1 CURRENT UTILIZATION FOR DISSOLUTION OF ZIRCALOY-2

CORROSION OF STAINLESS STEEL BY SOLUTIONS OF HNO_3 - STAINLESS STEEL

Previous work(7) has shown that the solution resulting from the electrolytic dissolution of stainless steel in nitric acid can be corrosive to stainless steel vessels because the chromium exists as chromate ion (Cr^{+6}) in nitric acid. This corrosion is a problem only when the solution is boiled, as in the evaporation step, and the dissolved stainless steel and nitric acid are concentrated. During electrolytic dissolution, corrosion is not a problem since the chromium is reduced by dissolved oxides of nitrogen to Cr^{+3}.

Figure 2 presents corrosion rates for 304L stainless steel versus chromium concentration. Total chromium, rather than chromate, concentration was used because of the difficulty of analyzing for chromate in the presence of dissolved stainless steel. The corrosion rates in HNO_3-chromate measured by other workers(8,9) are the averages of rates over 48 hours of exposure; the rates were rapidly increasing at the end of these tests. In the SRL tests of solutions containing only HNO_3 - stainless steel, the corrosion rates were found to increase even at the end of 150 hours of exposure. Analysis showed that Cr^{+3}, the predominant chromium ion in the initial solution, was being oxidized to corrosive chromate.

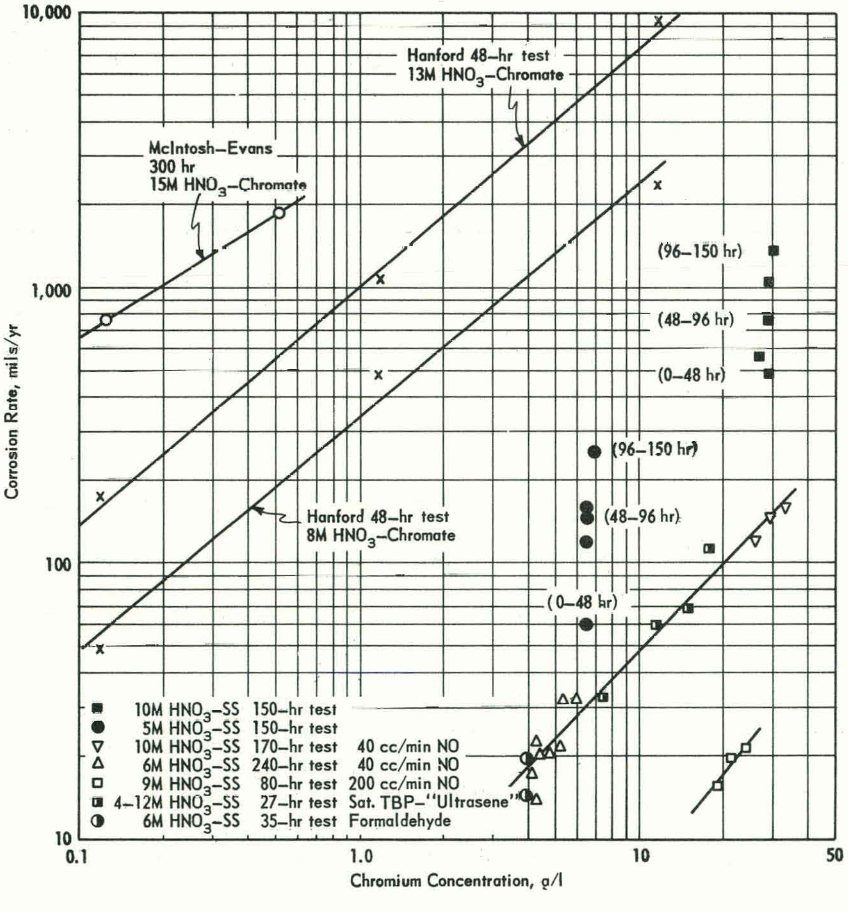

FIG. 2 CORROSION RATE OF 304L STAINLESS STEEL BY BOILING HNO_3–Cr SOLUTIONS

The addition of nitric oxide (NO) to the solution decreased the corrosion rate by reducing much of the chromate to Cr^{+3}. Formaldehyde addition decreased corrosion by lowering the nitric acid concentration as well as by reducing the chromate to Cr^{+3}. To simulate the high activity raffinate from the solvent extraction process, a solution of 3M HNO_3 and 20 g/l stainless steel was saturated with 30% TBP-"Ultrasene". Corrosion rates were measured during evaporation of this solution to 10M HNO_3 and 100 g/l stainless steel. Although the TBP-"Ultrasene" apparently reduced much of the chromate, the corrosion rate averaged 50 to 60 mils/yr during the cycle. Chromate - nitric acid corrosion results in preferential attack of the end grain rather than the rolled surface of a coupon. The corrosion samples used had 16% end grain. Later tests will determine the corrosion rates of rolled surfaces.

After the tests described in the preceding paragraph, a spectrophotometric analysis* for chromate was developed. This analysis required only 0.5 milliliter of solution and permitted continuous assay of chromate without depleting the solution being studied. The analysis was used to follow the changes in chromate concentration during electrolytic dissolution of 304L stainless steel in nitric acid. Data for two runs are given in Figure 3. The initial rise in chromate concentration is due to the Cr^{+6}, which is the form of chromium that is removed from the protective oxide layer. Simultaneously, nitrous acid formed at the cathode reduces Cr^{+6} to Cr^{+3}. Nitrous acid is produced in excess of that needed for Cr^{+6} reduction, and, as the nitrous acid concentration increases, the Cr^{+6} concentration decreases. There is no apparent explanation for the differences between the two runs, except the agitation rates may be different. In other respects the runs were identical.

SEMIWORKS

PROTOTYPE ELECTROLYTIC DISSOLVER

The primary objective of the continuing study of electrolytic dissolution in the 5000-amp semiworks dissolver(7) is to demonstrate that stainless steel and zirconium can be dissolved in nitric acid at an average current of 3000 amp. The achievement of this rate in the semiworks dissolver, in which the anode basket is 5 by 12 inches in plan section, would be equivalent to the demonstration of a capacity of more than one ton of uranium per day in a plant-scale (10X) electrolytic dissolver. During the period of this report, stainless steel pipe and Zircaloy plate in the form of mock assemblies and loose pieces were dissolved to establish the best operating conditions.

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* The spectrophotometric analysis measures the color of a diphenyl carbazide complex of Cr^{+6} at a pH of 3 to 5. The analysis is accurate to ±20% at 0.01 g Cr^{+6}/l in the presence of high concentrations of dissolved stainless steel.

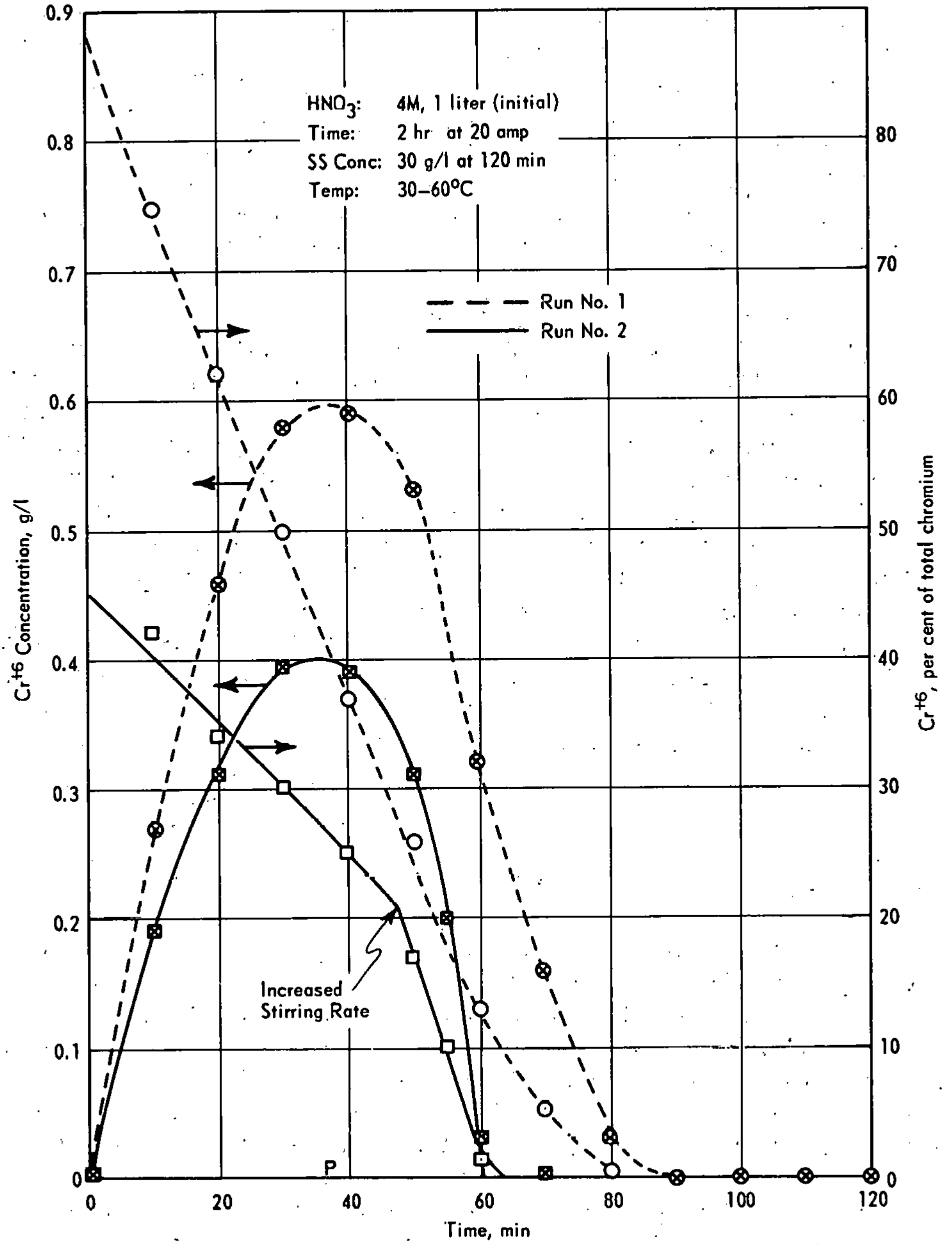

FIG. 3 REDUCTION OF Cr^{+6} TO Cr^{+3} DURING ELECTROLYTIC DISSOLUTION OF 304L STAINLESS STEEL

DISSOLUTION OF STAINLESS STEEL PIPE

The major conclusions that resulted from the dissolution of the assemblies made of stainless steel pipe are that the required capacity (3000 amp) can be achieved, and that the smoothest operation is obtained when the assemblies are fully submerged in acid. The contact resistance between the anode basket and the pieces to be dissolved limits the average capacity of the dissolver. The resistance is initially low, but becomes progressively higher during the run. Decreasing the clearance between anode basket and cathode to less than one inch did not appreciably decrease the cell resistance. There was no evidence of corrosion due to stray currents flowing to a sample of 304L stainless steel that was located 3 inches below the grid on the bottom of the cathode (8 inches below the anode). This observation is significant because it indicates that the electrodes can be located close to the neutral vessel. There is still no evidence of either chemical or stray current corrosion of the 304L stainless steel dissolver vessel after more than one million amp-hr of operation, although this is equivalent to dissolving only 2 tons of stainless-clad UO_2.

Prolonged arcing on the columbium basket above the liquid level will cause the columbium to oxidize. The semiworks anode basket is made of vertical strips of columbium, 1/2 inch wide and 1/16 inch thick(7). Arcing and local overheating above the liquid caused some of the thin strips to fail and caused the current to be carried by less metal. More strips progressively grew hot, oxidized, and failed, until the columbium section of the anode parted completely in a plane parallel to the bottom after about one million amp-hr. The strips that were normally submerged in nitric acid were still in excellent condition. An improved design would provide for full submergence of the fuel and fabrication of the anode basket from more massive metal.

The evidence that mock fuel assemblies dissolve with less trouble than do loose pieces and that total submergence of the assemblies gives improved operation was obtained from several runs. In the first run, two 135-lb assemblies, each of which was 9 ft long and made up of a square array of 1/4-inch stainless steel pipe, were placed vertically in the basket so that only the bottom 3 ft was covered with acid. The initial nitric acid concentration was 4.5M and the temperature was maintained at 85 ±5°C. An average current of 4000 amp was maintained at a maximum potential of 15 v. This average current is about twice that obtained with loose pieces and is thought to be due to more uniform contact of the assemblies with the side of the anode basket. This run was not carried beyond a 50% heel, however, because of arcing and overheating above the liquid, which was serious enough to burn holes in the stainless steel portion of the anode basket. Much of the oxidation of the columbium strips is thought to have occurred during this run, as well as some pitting of the 1/2-inch plate at the bottom of the columbium basket. Efforts to cool the upper sections of the long assemblies by recirculating electrolyte from the dissolver vessel to the top of the anode basket were successful in providing smooth operation. This technique could not be continued in the semiworks dissolver, however, since the upper half of the anode basket is made of stainless steel. Although the stainless steel was not submerged in the acid, sufficient current was conducted by the film of recirculating electrolyte to attack the stainless steel part of the basket.

The fuel assemblies were cut to 2-ft lengths to permit complete submergence during the next run. Two 30-lb assemblies were placed side by side in the basket so that contact was made by the ends of the pipes and the bottom of the basket. With a 100-lb weight on top of the charge to simulate the weight of UO_2 pellets, the dissolution was carried to a heel of less than 2 lb at an average current of 2600 amp and a maximum potential of 25 v. When 9-inch lengths of similar assemblies were stacked horizontally, so that contact at the bottom was made by the pipe surfaces rather than by the ends, a 70-lb charge was dissolved to a heel of less than 2 lbs at an average current of 3000 amp. The striker was used once every 30 seconds, the operation was very smooth, and there was no evidence of arcing or overheating. All components of the charge, including the weight, were submerged. The current had decreased to 500 amp when the run was terminated. The 2-lb heel is probably independent of the initial weight of the charge, so that it would represent a residue of less than 1% for a full charge of 250 to 300 lb of stainless steel.

DISSOLUTION OF ZIRCALOY PLATES

Approximately 250 lb of solid Zircaloy plates were disintegrated in three separate charges to a cumulative 20% heel at a rate exceeding 2.5 lb/hr. It was necessary to use the 100-lb weight on top of the Zircaloy plates to maintain good electrical contact. This weight was equipped with leaf springs to make electrical contact with the walls of the anode. A large part of the input current probably passed through the weight to the charge. Early in the cycle, operation with effective contact from the weight gave an average current of 1500 to 2000 amp at 13 v. Without the weight only half the normal current was possible, and even this could not be sustained for more than one or two hours. The anode striker was used on a 1-minute cycle and was helpful in maintaining contact.

The 2.5 lb/hr rate was attained at a maximum potential of 15 v and corresponds to an average of 1100 to 1200 amp. The current during heel removal was between 500 and 1000 amp; excluding the heel removal period, the current averaged 1500 to 2000 amp. The Zircaloy plates were 3/16 inch by 4-1/2 inches by 8 ft and were submerged to a depth of 3-1/2 ft in 4.5M HNO_3, which was maintained at 90°C. Proportionally higher rates were demonstrated at potentials of 20 v although local overheating of the plates and the anode basket was observed. Relatively poor contact between the Zircaloy plates and the columbium basket, due to the resistance of the zirconium oxide coating on the plates, limits the current flow at 15 v. As in laboratory-scale tests, only 15% of the zirconium dissolved in the nitric acid; the remainder appeared as a fine black sludge of zirconium oxide. This sludge accumulated in the bottom of the anode basket in the first part of the run. Consequently, 1/4-inch holes were drilled in the bottom of the anode to give 6% open area. An air sparge located on the bottom of the dissolver was able to lift the sludge from the anode and disperse it in the electrolyte as the oxide fell from the disintegrating plates.

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