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"Chemical Development for EBR-II Fuel Process 1967-1969"

B. C. Musgrave, Ed., R. G. Butzman, T. L. Evans,

M. E. Jacobson, L. C. Lewis, M. W. Wilding and C. A. Zimmerman

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CHEMICAL DEVELOPMENT FOR
EBR-II FUEL PROCESS 1967-1969

by

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ABSTRACT

The laboratory development work done at Idaho Chemical Processing Plant for the electrolytic dissolution process for EBR-II fuels is summarized. Topics reported include fuel storage, dissolution, characterization of the solid residues resulting from electrolytic dissolution, solvent extraction of uranium from the dissolver product solutions, and corrosion of materials of construction.

SUMMARY

Laboratory development work for the electrolytic dissolution process for EBR-II fuel is reported in detail.

Leach tests of fully irradiated EBR-II fuel in storage basin water have demonstrated that these assemblies, when free of prior cladding failure, can be stored satisfactorily in the basin without contamination occurring. Fission products are leached from segments of declad fuel meat at a rate comparable to earlier results with declad aluminum fuels.

Chemical dissolution of chopped segments of EBR-II fuel pins in nitric acid occurs at a rate sufficiently rapid to guarantee that undissolved fuel slugs will not fall from the partially dissolved cladding to accumulate in the bottom of the dissolver.

Corrosion studies indicate that a titanium dissolver vessel will have a practical operational lifetime. The most vulnerable area was shown to be the titanium cathode. The commonly used decontamination solutions can be used without excessive loss of metal.

The electrochemical behavior of stainless steel alloys, both unirradiated and highly irradiated, have been compared. While it is possible to distinguish between the main types of stainless steel alloys by the EMF vs current density curves, and a significant difference occurs with the most highly irradiated material, all of the materials tested can be expected to dissolve in the electrolytic dissolver without difficulty.

Solid residues resulting from the electrolytic dissolution of EBR-II fuel pins are a mixture of stainless steel particles, silica gel, and insoluble compounds resulting from the fission alloy. If necessary, these can be solubilized by sodium hydroxide fusion followed by dissolution in nitric acid.

Extraction studies of dissolved EBR-II fuel demonstrated that 99.95% of the material would be extracted in three stages. The fine solids which are not removed by the centrifuge will not create any unmanageable difficulty in the extraction column. The first cycle uranium product will be 99.9% free of other metal ions.

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CHEMICAL DEVELOPMENT FOR
EBR-II FUEL PROCESS 1967-1969

I. INTRODUCTION

In future processing campaigns stainless steel clad reactor fuels will be dissolved at the Idaho Chemical Processing Plant (ICPP) in an electrolytic dissolver. Earlier reported investigations have established the feasibility of the electrolytic dissolution process^(1,2,3).

This report covers experiments done to demonstrate the safety of fuel storage in water, the effect of neutron irradiation upon the dissolution of the steel cladding and the fuel alloy, the chemical nature and behavior of the solid residues from dissolution, the extraction coefficients for uranium, and the corrosion of dissolver materials.

An additional document, to be issued shortly, will describe the operation of the pilot plant dissolver with Experimental Breeder Reactor-II (EBR-II) fuel⁽⁴⁾. These current documents, plus the extensive prior work on electrolytic dissolution done at ICPP, are the basis for the design and operation of the electrolytic dissolver being installed at ICPP and for the assurance of feasibility of reprocessing EBR-II fuel.

A schematic representation of the dissolver vessel to be installed at ICPP is shown in Figure 1. The electrolytic dissolution cell is created by a potential applied between the anode (platinum backed with niobium) and the cathode which is the titanium dissolver shell. The fuel charge is held in the perforated niobium basket which is insulated electrically from the anode and cathode by the ceramic button spacers.

When a potential is applied across the dissolver, the fuel charge becomes anodic with respect to the titanium cathode; dissolution then occurs according to the reaction,

Ideally, multiple cells can be set up in such a dissolver configuration. In the voltage gradients imposed across the dissolver, any fuel assembly will become anodic compared to any conductor, including another metal-clad reactor fuel assembly, which is located to the cathodic side of it. A series of cells will then be created with one side of an assembly being cathodic with respect to some other cell-forming material while the other side of the assembly becomes anodic with respect to the cathode of the dissolver or an adjacent fuel assembly.

The electrolyte is circulated through the dissolver from the bottom, then out through the overflow where the gases are allowed to escape. Before the solution is returned to the bottom of the dissolver, a product

Figure 1. Cross section of ICPP electrolytic dissolver.

stream is withdrawn, the circulating stream is cooled in a heat exchanger, and then fresh 8M nitric acid is added to the returning stream. A schematic representation of the process is shown in Figure 2. In this configuration, 90 to 98% of the stream from the dissolver would pass through the overflow of the hydrocyclone to the recirculating stream. The underflow, carrying a maximum possible of the suspended solids, will be used as the product withdrawal stream. An earlier report (5) described the performance of a hydrocyclone which may be used to divert the solids from the recycle stream. The product stream will be fed through the continuous centrifuge for clarification; finally the dissolver product will be extracted with tributyl phosphate and kerosene, or hexone, to recover the uranium. The conceptual flow sheet is shown in Appendix A.

The first fuel scheduled for processing in this dissolver is the driver fuel from the EBR-II. This fuel consists of an alloy of 95% uranium and 5% fissionium. The fissionium fraction of this alloy is approximately 49% molybdenum, 39% ruthenium, 6% rhodium, 4% palladium, 2% zirconium, and 0.2% niobium. The fuel meat is clad in Type 304L stainless steel tubes with a sodium-filled annulus for heat transfer. The fuel pins are arrayed in a Type 304 stainless steel hexagonal tube containing 91 pins per subassembly.

Figure 2. Electrolytic dissolver installation.

II. FUEL STORAGE

The experiments which follow clearly indicate that properly clad EBR-II fuel pins will be inert in the CPP storage basin water and that no hazard of fission product or uranium leaching should be present. However, uranium-fissium alloy in unclad fuel pins will react when exposed to water.

1. Fuel Element Leak Tests of Clad EBR-II Fuel Pins

Prior to processing of EBR-II fuels, it will be necessary to store these fuels for some time, under water, in the ICPP fuel storage basin. The 9-mil, Type 304L stainless steel cladding on these fuel pins will have undergone sensitization in the sodium-cooled reactor environment at approximately 516°C. Since stainless steel in the sensitized condition is known to be susceptible to severe intergranular corrosion attack when exposed to corrosive media⁽⁶⁾, long-term tests were initiated to determine if the ICPP storage basin water would attack the cladding on the irradiated EBR-II fuel pins.

Fully irradiated EBR-II fuel pins were stored in ICPP basin water and tested periodically for fission product leakage. The results of these tests, after twenty-four months of exposure, showed no significant increase in the concentration of radioactive materials during a seven-day test period in the Fuel Element Leak Test (FELT) apparatus⁽⁷⁾; the FELT apparatus is fully described in another report⁽⁸⁾. This is interpreted as indicating that no penetration of the EBR-II fuel element cladding has occurred to date.

The FELT tests were conducted by placing five irradiated EBR-II fuel pins in a stainless steel vessel which was then closed. The vessel was purged with clean water for 24 hours to displace the basin water originally present. A sample of water was obtained at the start of the test and again after seven days exposure to the fuel pins. A comparison of the gamma ray spectra of these two water samples would show an appreciable increase in the concentration of radioactive materials if any penetration of the cladding occurred. The fuel pins were then removed from the stainless steel vessel and returned to storage.

2. Leaching of Unclad EBR-II Fuel Pin Segments

As part of this investigation of the storage of EBR-II fuel in the ICPP storage basin, it was of interest to know the behavior of de-clad, irradiated, uranium-fissium fuel alloy in basin water. In the case of excessive corrosion or fuel cladding failure, leaching of the bare fuel meat could occur at a rapid rate. To determine the leaching to be expected, three tests have been made using unclad segments cut from irradiated EBR-II fuel pins.

The fuel pin segments used had surface areas between 3.1 and 3.5 cm² and were exposed in 3.1 liters of solution. Two of these tests were made in basin water while the third was made using a 6M solution of sodium

hydroxide. The EBR-II fuel element is fabricated with a sodium bond between the cladding and the uranium-fissium alloy fuel pin; therefore a test was made in sodium hydroxide to determine whether any significant change in leaching could be expected due to the reaction of this sodium with water in the event of a cladding failure.

The results of these tests are presented in Figure 3. In all three tests there is an initial rapid increase in the amount of ^{137}Cs in the leaching solution which is probably due to loosely adhering surface material on the fuel pin segment. This initial rapid rise was followed by a period of slow increase or nearly constant values in total ^{137}Cs leached and then by a more rapid leaching action.

The points at which rapid increase in the ^{137}Cs concentration begins are quite different for the two samples that were leached in basin water. The first specimen tested showed a sharp increase after about 1200 hours. This sample was from a subassembly which had achieved an average of 0.45 atom % burnup. The second specimen, 0.98 atom % burnup, showed a sharp increase in leached ^{137}Cs between 500 and 1200 hours.

The third specimen was tested in 6M NaOH. This sample was from a pin which had also received 0.98 atom % burnup. The leaching of ^{137}Cs followed approximately the same pattern as was observed for the 0.45 atom % burnup specimen in basin water.

Corrosion of uranium has been reported to follow a general rate equation^(9,10),

$$W^n = k_n t$$

Where W is some measure of the reaction, such as weight change or reactant product analysis, t is the elapsed time and k_n is an experimental constant. This expression can be rearranged to

$$n \log W = \log k_n + \log t$$

A plot of $\log W$ vs $\log t$ gives a straight line with slope $1/n$. The constant n is determined by whether the corrosion is accelerating or decreasing. If the rate is constant, n is 1.

The corrosion rate for uranium metal was found to have two different rate laws one in the early portion where n was equal to 2.0; after an initial period a sharp break occurred followed by a rate law in which n was approximately 0.44. This sharp change in slope was attributed to rupture of the oxide coating on the metal followed by more rapid attack.

The shape of the leaching rate curves for these EBR-II uranium-fissium alloy pins can be attributed to a similar mechanism. After the initial sharp rise in ^{137}Cs activity all of the test pins showed slowly increasing or nearly constant ^{137}Cs activity until a point was reached at which a much more rapid change in leaching rate occurred. This is consistent with the gradual buildup of an oxide layer as oxidative corrosion of the fuel segment proceeds. At some point in the growth of this oxide, strain leads to rupture of the oxide film accompanied by some possible fracturing of the metal structure underneath. When this

Figure 3. Leaching of ^{137}Cs from unclad EBR-II fuel pins.

fracturing occurs much more rapid attack is possible and the leaching rate of fission products accelerates accordingly.

The differences observed for the two samples leached in basin water can be attributed to the factor-of-two difference in burnup. The more highly irradiated sample will have received more structural damage due to fission fragments and therefore be subject to fracture at an earlier point in the growth of the oxidative corrosion layer. The leaching of a high burnup specimen in 6M NaOH resulted in a longer time to the point at which accelerated leaching occurred. This could be due to the nature of the oxide formed in the base solution or due to the rate at which the oxide is formed. Insufficient data are available to distinguish between these possibilities. In either case the near coincidence between the curves obtained for the 0.45% burnup sample in basin water and the 0.98% burnup sample in 6M NaOH may be fortuitous.

III. DISSOLUTION STUDIES OF EBR-II FUEL PINS

Electrolytic dissolution of the stainless steel cladding exposes the fuel meat to the nitric acid dissolver solution where it may undergo chemical or electrolytic dissolution. If the fuel meat dissolved at a rate which was slow compared to the rate of electrolytic removal of the cladding, an accumulation of undissolved fuel slugs in the dissolver could result in a hazardous situation from a nuclear criticality standpoint. For this reason the dissolution rate of the fuel meat was examined.

1. Dissolution Rate of Fissium-Uranium Alloy

Declad segments of fully irradiated EBR-II fuel pins were dissolved in 8M nitric acid at 60°C. Prior to dissolution of the fuel, the solution was electrolyzed for one hour to establish steady state concentrations of the nitric acid decomposition products. Chemical dissolution of the fuel meat proceeded at about 500 mg/cm²-min.

2. Leaching of Fuel Meat from Chopped Pins

Chopped segments of fully clad unirradiated EBR-II were leached in 8M HNO₃ at various experimental conditions. The dissolution rate was determined at 25, 40, and 60°C. Because the dissolution of uranium is catalyzed by the nitric acid decomposition products, fuel pin segments were dissolved in initially pure nitric acid and in nitric acid which had been partially decomposed by electrolysis. These results are shown in Figure 4.

At 25°C dissolution in the pre-electrolyzed solutions showed an induction period of 7 minutes before the maximum rate was reached; at this temperature the nonelectrolyzed solution required an induction time of approximately 25 minutes to reach the maximum rate.

Figure 4. Effect of solution condition and temperature on the dissolution of EBR-II fuel meat.

Under all of the other conditions tested, dissolution proceeded rapidly from the initial contact with the acid. All of the different dissolutions attained the same maximum rate regardless of the different initial conditions.

3. Electrolytic Dissolution Pattern

Examination of partially dissolved and partially leached EBR-II fuel pins recovered from the electrolytic dissolver pilot plant showed that a definite pattern is set up during the dissolution. Figure 5 illustrates the relative orientation of the fuel pins in the electrolytic dissolver. Since the spacer wires on all pins are wrapped in the same manner, series cells will be set up at the same points between all pins of a given subassembly; the exact points of initial opening will depend on the orientation in which the subassembly is charged to the dissolver. The relative orientation of the subassembly can be varied indefinitely around the lateral axis of the subassembly. For a subassembly oriented as shown in Figure 5, the initial opening will occur at the points equivalent to those designated as A. The sodium bond is dissolved on contact with the acid with the net result that leaching of the partially dissolved fuel pins frequently proceeds along a conical surface after the fuel cladding has opened.

4. Chemical Considerations

The uranium fissium alloy dissolves readily in 8M HNO_3 under the conditions existing in the electrolytic dissolver. Although complete analysis of the extremely complex system resulting from the chemical and electrochemical dissolution of this alloy has not been attempted, some general observations can be made.

a. Electrolytic Reactions

The oxidation potentials for each of the major components of the fissium alloy are listed in Table I. The potentials for the oxidation of iron to the ferrous state and of ferrous iron to ferric are shown for comparison. The oxidation of chromic ion to dichromate which may also occur in the electrolytic dissolver completes the table.

The reactions occurring during the dissolution of stainless steel material have been thoroughly discussed^(1,2). The anodic dissolution of stainless steel leads to Fe(III) , Ni(II) , and Cr(VI) . The Cr(VI) is reduced rapidly by oxides of nitrogen which are present in this system⁽¹⁾.

b. Residues

The solid residues resulting from the chemical or electrochemical dissolution of the uranium-fissium alloy contain little or no molybdenum. None of these solids have been analyzed quantitatively for the fissium elements; however, all of the other components of the fissium alloy are present. The results indicate that molybdenum is quantitatively dissolved; ruthenium is about 20% dissolved with analyses ranging from 10 to 26% as compared to the uranium concentrations. By comparison with the dissolution reactions which do occur, the potentials listed in Table I show

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Points equivalent to those labeled A are the initial points of dissolution of pins nearest the cathode. Dissolution would occur at point B if the assembly were rotated 180° about the lateral axis before charging to the dissolver. As suggested by Figure 6, the ends of pins nearest the anode may be opened first. Only two pins are shown for illustration; the dissolver will be filled with many more pins as well as parts of the hexagonal pin holder.

Figure 5. Pattern of dissolution cell formation on EBR-II fuel elements.

TABLE I. (a,b)

OXIDATION POTENTIALS OF FISSION ALLOY ELEMENTS

<u>Element</u>	<u>Percent of Fission Alloy</u> (c)	<u>Reaction</u>	<u>Potential</u>
Ru	39	$\text{Ru} \rightarrow \text{Ru}^{2+} + 2\text{e}$	+0.1
		$\text{Ru}^{2+} \rightarrow \text{Ru}^{3+} + \text{e}$	+0.25
Mo	49	$\text{Mo} \rightarrow \text{Mo}^{3+} + 3\text{e}$	+0.20
		$\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{MoO}_2 + 4\text{H}^+ + 2\text{e}$	0.0
Pd	4	$\text{Pd} \rightarrow \text{Pd}^{2+} + 2\text{e}$	-0.92
Rh	6	$\text{Rh} \rightarrow \text{Rh}^{3+} + 3\text{e}$	-0.44
Fe	0	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}$	-0.77
		$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}$	+0.44
Cr	0	$2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{e}$	-1.33
		$\text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + \text{e}$	+0.41
		$\text{Cr} \rightarrow \text{Cr}^{2+} + 2\text{e}$	+0.56

(a) W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, 2 ed. Prentice-Hall, 1952.

(b) Robert N. Goldberg and Loren G. Hepler, "Thermochemistry and Oxidation Potentials of the Platinum Group Metals and Their Compounds", Chem. Rev. **18**, 229 (1968).

(c) Smaller amounts of zirconium and niobium are present.

that all of these elements Ru, Rh, Pd, and Mo should dissolve at the anodic potentials reached by the dissolving fuel elements.

Measurement of the amounts of solids produced when stainless steel was dissolved electrolytically, when stainless steel and the fuel meat were dissolved electrolytically and chemically simultaneously, and finally when the fuel meat alloy was dissolved chemically are shown in Table II. Both irradiated and cold fuel pins were examined.

TABLE II.

UNDISSOLVED SOLIDS PRODUCED FROM THE DISSOLUTION
OF EBR-II FUEL ELEMENTS

<u>System</u>	<u>Dissolution Mode</u>	<u>Electrolyte</u>	<u>Temperature (°C)</u>	<u>Percent Solids Produced</u>
EBR-II Fuel Meat	Chemical	0.1-6M HNO ₃	105	2
EBR-II Fuel Meat	Chemical	8	60	<3.1
Fuel Pin	Electrolytic	4	50	2
Fuel Pin	Electrolytic	4	50	2.4
Irradiated Fuel Pin	Electrolytic	4	50	2.5
Irradiated Fuel Pin	Electrolytic	4	50	2.2
Fuel Pin Plus Stainless Steel	Electrolytic	8	65	3.6
Stainless Steel	Electrolytic	8	65	1

From the weight ratio of the stainless steel and uranium charged to the dissolver, the solids formed from the stainless steel and the fuel meat independently should have led to 2.7% total solids in the combined dissolution. The resulting solids amounted to 3.6% of the material dissolved or an excess of 1/3 in the mixed system. The cause of this excess, if it was real, was not determined in these experiments but could be due to coprecipitation of silica gel, iron, chromium, or nickel with the fission residues.

From the composition of the fissium alloy, as shown in Table III, the complete dissolution of the molybdenum fraction plus 20% of the ruthenium will leave approximately 2.2% of the fissium alloy undissolved. This is reasonably close to the observed solids production as shown in Table II. Results to be discussed later in this report, indicate that the ruthenium part of the undissolved fissium elements is present in the elemental form. The other components may also be in the elemental state but this has not been established.

TABLE III.

ESTIMATE OF THE SOLIDS RESULTING FROM EBR-II
FUEL MEAT DISSOLUTION

<u>Percent of Total</u> <u>Fuel</u>	<u>Element</u>	<u>Behavior</u>	<u>Percent</u> <u>Remaining</u>
2.5	Mo	Dissolved	
2.0	Ru	20% Dissolved	1.6
0.3	Rh	Undissolved	0.3
0.2	Pd	Undissolved	0.2
0.1	Zr	Undissolved	0.1
0.01	Nb	Undissolved	<u>0.01</u>
		Total Residue	2.2 %

5. Series Cell Production in the Electrolytic Dissolver

Two experiments in the laboratory dissolver were carried out to compare current utilization for a single-cell system versus a multi-cell system. A four-cell dissolver was constructed using 2-1/2- by 7-1/2-cm electrodes spaced about 5-1/2 cm apart. Within this space, five pairs of

glass rods (3 mm diameter) were mounted vertically in a Teflon "floor" and arranged so that four separate stacks of tubes, one-tube wide, could be accommodated (see Figure 6). The pieces of stainless steel tubing used in the system were 6.5 mm OD and about 5 to 6 cm long. The purpose of the vertical glass rods was to insulate adjacent stacks of tubes from one another and also the end stacks from their respective electrodes. Electrolytic dissolutions were performed with and without the glass rod dividers. The resulting dissolution pattern was very similar across the electrolyzed zone for both the one-cell and the four-cell arrangement; namely, the tubes adjacent to the electrodes were attacked considerably more than the tubes in the central region of the electrolyzed zone.

In the four-cell experiment, measurements were made of the weight losses per cell. Starting with the cell closest to the anode and moving toward the cathode, the individual percentages of the total stainless steel dissolved from the charge were: 35.2, 11.4, 11.8, and 41.6. This illustrates that a substantial amount of the current passed around the ends of the tubes occupying the internal regions of the assembly. The current utilization values were not greatly different -- only about 20% higher for the four-cell system over that of the one-cell system which demonstrates that four electrolytic-cells-in-series were not created by this particular arrangement.

6. Electrolytic Behavior of Cladding Alloys^(a)

Corrosion, passivation and dissolution of metals in electrolyte solutions are electrochemical phenomena. The potential assumed by a pure metal or an alloy in a solution is a measure of the tendency for reaction to occur. Examination of the galvanostatic curves for these materials provides considerable information related to the passivation or dissolution behavior to be expected for these materials in various dissolver systems. When appropriately displayed these measurements can yield information on the potentials at which passivation, breakdown of passive layers, and dissolution should occur.

Since these measurements are more economical to perform, more reproducible, and give more information about the dissolving material than empirical dissolution studies, galvanostatic curves were run for several stainless steel alloys which are or might be used as cladding materials. In addition, the influence on dissolution of very high integral neutron flux has been examined in this manner.

The experimental equipment used for measurement of the galvanostatic curves is shown schematically in Figure 7. Examples of the types of curves obtained for stainless steel alloys of quite different compositions are shown in Figure 8. All curves were obtained in 5M sulfuric acid. The curves show major differences in the region of zero imposed current which reflects different passivity or resistance to corrosion of the alloys in this electrolyte.

(a) This research is described fully in IN-1295. L. C. Lewis and B. C. Musgrave, "The Electrolytic Behavior of Nuclear Fuel Cladding Alloys", to be published.

a. End view showing arrangement of stainless steel tubing and glass rods in the basket dissolver.

b. Top view of the dissolver showing resulting dissolution pattern. Solid areas show regions of complete removal of metal. Shaded areas show regions of attack.

Figure 6. Experimental arrangement for the test of series cell production.

Figure 7. Schematic diagram of galvanostat.

Figure 8. Galvanostatic measurements on various stainless steels.

Galvanostatic measurements were made on samples of a Type 304 stainless experimental subassembly tube which had been irradiated in the EBR-II fast flux for 900 days. Examples of the curves obtained are shown in Figure 9. No effect due to exposure in the reactor which would be significant to the electrolytic dissolution of the cladding alloy used on the EBR-II fuel was noted.

All of the stainless steel alloys examined underwent anodic dissolution at approximately the same potential, about +1.1 V vs S.C.E. Previous studies have shown that all stainless steels and nichrome dissolve satisfactorily in the electrolytic dissolver. These experiments and actual dissolution of irradiated material show that highly irradiated materials will readily dissolve under an imposed potential although detailed examination of the curves for some highly irradiated materials do show significant differences from similar unirradiated alloys.

IV. STUDIES OF SOLIDS RESULTING FROM ELECTROLYTIC DISSOLUTION

The solids found in the dissolver effluent from the electrolytic dissolution of EBR-II fuels are of three types: (a) metal residue dropped from the dissolving stainless steel, (b) metals or oxides (principally ruthenium) remaining from the fissium-uranium alloy, (c) silicic acid formed from the silicon dissolved from the steel. In the nitric acid solution the last tends to bond the other two to metal surfaces of the dissolver and heat exchanger in a detrimental manner.

1. Laboratory Dissolver Studies of Metal Residue from Stainless Steel

Earlier reported laboratory studies⁽¹⁾ were extended to measure the percent formation of undissolved solids during the electrolytic dissolution of stainless steel. The 4-inch long vee-shaped electrolytic dissolver (Model II) which had been used in pilot plant studies⁽³⁾ was modified to serve as the laboratory scale dissolver. The experimental arrangement was much as shown in Figure 2, complete with the heat exchanger, but without the hydrocyclone in the recycle loop.

Earlier laboratory studies of the formation of undissolved solids were carried out at lower acid concentrations than are now planned for the EBR-II fuel dissolution. Studies of the corrosion rates of the electrode materials as a function of acid concentration and current density indicated that the conditions for corrosion resistance were optimum at around 6M HNO₃ and less than 2 amp/cm²⁽¹¹⁾. Attainment of reasonable dissolution rates requires operation at around 1 amp/cm² and over the range of 3.6 to 10 molar nitric acid.

The results obtained are shown in Figure 10. Earlier data from this laboratory are shown on the left of Figure 10. While the percent of undissolved solids generated is not severely dependent on the acid molarity, it is clear that acid concentrations around four to six molar and high current densities plus low temperature lead to a minimum generation of undissolved solids.

- I. $\sim 1 \times 10^{22}$ n/cm² (fast > 0.1 MeV)
 II. $\sim 5 \times 10^{22}$ n/cm² (fast > 0.1 MeV)

Figure 9. Electrochemical effects of fast flux irradiation on Type 304 stainless steel.

Figure 10. Anode sludge produced during electrolytic dissolution of stainless steel tubes.

The solids recovered from the dissolver system were examined under a microscope. Although detailed comparison showed some variations among the recovered solids, there were no major differences among these solids generated in different dissolutions. Silica gel globules were observed among the filtered solids. Large particles were observed which consisted of several grains of stainless steel still bound in the original matrix. These particles, larger than about 100 μ , were generally not carried from the dissolver by the recirculation stream. Smaller particles ranging from less than 1 μ to about 80 μ were distributed throughout the system. An estimation of the particle size distribution showed that the most probable particle size was about 20 to 60 μ . A general trend to larger numbers of particles less than 1 μ in size was noted under those conditions which produced the larger weight fractions of undissolved solids.

2. Characterization of the Solids Remaining from Electrolytic Dissolution of EBR-II Fuel

The electrolytic dissolution of EBR-II fuel yields insoluble residues which are a mixture of insoluble products from the fission fraction of the fuel meat alloy along with stainless steel residues. These solids deposit throughout the recirculation stream, eventually leading to fouling of equipment. Experiments on the effectiveness of a laboratory scale hydrocyclone for concentration of these solids into the product stream have been reported⁽⁵⁾.

Several unirradiated EBR-II fuel elements were dissolved individually in a laboratory scale electrolytic dissolver. These laboratory dissolutions were to generate dissolver product and its attendant insoluble materials for laboratory studies to determine how to best cope with these insolubles in the pilot plant operation.

During these laboratory dissolutions, plant dissolving conditions were simulated as much as possible. The starting electrolyte was prepared to a concentration of 8M HNO_3 , 12 g/l uranium, and 6 g/l ss, which is representative of steady state conditions for the EBR-II flow sheet. The clad fuel pin was cut into 6- to 8-cm lengths for charging into the laboratory dissolver and the remaining space in the electrolysis zone was filled with pieces of stainless steel tubing.

Close observations were made when the nitric acid electrolyte made initial contact with the sodium at the cut ends of the fuel. Because of the open ends of the cladding, the uranium-fission alloy became exposed to the nitric acid upon immersion of the fuel, and chemical dissolution of the alloy was immediately underway. The electrolytic dissolution was continued an additional one to two hours after the fuel alloy was dissolved in order to generate an appropriate ratio of stainless steel-to-fission residue within the dissolver product. The solids concentration of these laboratory dissolver products was

typically in the range of 1.5 to 1.7 g/l with about a 40/60 split of stainless steel sludge to fissium alloy residue.

It was observed that a very slight amount of the sludge in the recirculating electrolyte adhered to the inner walls of the Tygon and glass tubing of the system. The coating was very thin and non-uniform in its distribution.

One batch of dissolver product was prepared which contained fissium type sludge only. Cut fuel element pieces were charged into the laboratory dissolver, following the partial electrolytic decomposition of the nitric acid, and allowed to dissolve chemically.

With the electrolytic dissolution of EBR-II fuel, the occurrence of undissolved solids in the product stream is unavoidable; therefore, some method of solids removal will be necessary. A series of tests was performed in the laboratory to determine how effective centrifugation could be in removing solids from EBR-II dissolver product. The centrifuge installed in TCPP will provide an estimated settling force of 1050 - 1100 g. The residence time for the product stream in the plant centrifuge will vary from 4-1/2 min to 9 min. The test samples were all centrifuged in a laboratory unit at a calculated 1025g. The data appear in Table IV.

TABLE IV.

REMOVAL EFFICIENCY FOR ANODE SLUDGE

<u>Solids Present in Test Sample</u>	<u>Feed Solids Conc. (g/l)</u>	<u>Duration of Centrifugation (min)</u>	<u>Amount of Solids Removed (%)</u>	<u>Solids Conc. in Centrifuged Liquor (mg/l)</u>
ss grains & fissium	~1.7	4.0	96.6	71
ss grains & fissium	~1.6	8.5	99.0	19
fissium	~1.1	4.0	98.3	21
fissium	~1.0	8.5	98.1	22
fissium	~1.0	20.0	99.3	8

At the minimum residence time in the centrifuge approximately 2% of the fissium solids remain suspended; centrifugation at the maximum anticipated residence time, 8.5 minutes, did not give a significantly different result. When stainless steel solids are present, at the minimum centrifuge period a greater fraction of the total solids are left suspended than occurred for the fissium alone. The results at

twenty minutes clearly demonstrate that removal of more than 99% of these solids by centrifugation would be very difficult. Extraction studies reported elsewhere in this report indicate that no particular difficulty will be encountered due to these remaining fine solids.

3. Tests for Electrolytic Dissolution of Dissolver Sludge

A sample of air-dried sludge which had been produced by the electrolytic dissolution of stainless steel was tested for possible complete heel-out dissolution procedures. Attempts at electrolytic dissolution of this material following washing alternately with nitric acid, water and sodium hydroxide showed that the dissolution rate was 1 to 3% of that achieved for stainless steel tubing in the same dissolver configuration. This very low rate indicates that complete electrolytic dissolution of this sludge is impractical.

4. Dissolution of EBR-II Fissium-Alloy Residue

A series of acids was tried for potential usefulness in dissolution of the residue from the dissolution of EBR-II fuel assemblies in the pilot plant. The solids were not significantly attacked by a wide variety of acids or combinations of acids. Fusion of 1 g of the material with 1 g of NaOH and 1 g of CaO gave a product which was soluble in HNO₃ or HCl. This behavior is consistent with that expected for metallic ruthenium (12) and strongly suggests that this finely divided black material is primarily ruthenium metal. An X-ray powder pattern indicated that the fissium solids were amorphous but would not allow differentiation between elemental or compound forms of ruthenium.

V. EXTRACTION OF URANIUM FROM EBR-II FUEL DISSOLVER PRODUCT

1. Extraction Efficiency

An EBR-II fuel pin was dissolved in a laboratory electrolytic dissolver in the presence of excess stainless steel. The product, after analysis, was adjusted to approximately the planned EBR-II fuel reprocessing flow sheet composition(a), then extracted with 10% TBP, scrubbed with a 0.5M Al(NO₃)₃-0.5M NH₄OH solution then stripped with 5 x 10⁻³M HNO₃. The extraction coefficients obtained were 9, 18, and 9 for the first, second, and third extraction stages, respectively. Analysis of the raffinate shows that 0.05% of the initial uranium remained unextracted. Within the accuracy of the experiment <0.6% of the uranium was unrecovered in the stripping step.

A 250 ml sample of electrolytic dissolver product from the pilot plant dissolution (5) was centrifuged at 1000 g for 4.5 minutes, then diluted 1:1 and allowed to stand for 16 hours. An extraction as described above was carried out on this solution. The resulting extraction coefficients for the three stages were 9.4, 11, and 14, and 9, 19, and 15 for duplicate runs. The final raffinate from this extraction also contained 0.05% of the uranium. These experiments indicate that there is no significant factor preventing recovery of uranium in this system.

(a) See Appendix A.

2. Fine Solids Not Removed by the Centrifuge

During the initial contacting of the centrifuged product with the 10% TBP-kerosene, black solids separated at the interface and remained on the walls of the separatory funnel. This material was shown by emission spectrographic analysis to be primarily stainless steel accompanied by smaller but significant amounts of fission residues. This is in agreement with the centrifuge studies which showed that more of the stainless steel particles are left suspended than are fission solids. From extraction studies reported earlier, a solid material separated which was reported to be primarily palladium⁽¹³⁾. In this study ruthenium, rhodium, and palladium were the primary fission elements appearing with the stainless steel solids. The Ru-Pd ratio detected here was approximately three. Considerable attention has been paid to the problem of extractable ruthenium complexes formed in nitrate solutions^(14, 15, 16). Approximately 25% of the ruthenium in the fission alloy is present in solution. This amount of ruthenium is approximately 0.5% of the amount of uranium present in solution. The extraction of a significant fraction of this dissolved ruthenium would result in a uranium product too high in other metals. The TBP-kerosene extract from the first contacting with the aqueous phase contained less than 10 µg Ru/ml. This indicates that significant extraction of ruthenium complexes should not occur.

VI. CORROSION OF ELECTROLYTIC DISSOLVER STRUCTURAL MATERIALS

Tests and observations made on materials of construction of electrolytic dissolver systems as a result of operation and cleaning of the equipment are reported.

1. The Pilot Plant Four-Inch Electrolytic Dissolver

Corrosion experience in both the four-inch titanium and the presently used twenty-four-inch titanium pilot plant electrolytic dissolvers indicate that materials of construction are available to permit operation in this environment under presently proposed conditions.

Corrosion experience in the four-inch dissolver system demonstrated a corrosion rate of less than 0.1 mil per month on the platinum anode. Additional laboratory tests made to compare the corrosion rate of platinum and several of its alloys showed the lowest rate (0.22 mil per month) for a 90% platinum - 10% iridium alloy. Results of these tests which were made in typical four-inch pilot plant dissolver product are shown in Table V.

TABLE V.

PLATINUM ALLOY CORROSION RATES
(mpm)

Platinum	0.26, 0.61, 0.18, 0.42
Platinum-iridium (90-10)	0.22, 0.22
Platinum-iridium (80-20)	0.56
Platinum-rhodium (90-10)	0.45, 0.71
Platinum-rhodium (70-30)	0.82

The niobium basket used in the four-inch dissolver showed a very low weight loss. There was some minor damage as the result of electrical arcing.

The cathode of the four-inch dissolver was the titanium dissolver vessel. This vessel suffered no apparent attack during the short time that it was used.

2. The Pilot Plant Twenty-four-Inch Electrolytic Dissolver

The current twenty-four-inch pilot plant electrolytic dissolver was inspected after 2,000 hours of operation and found to be in excellent condition with no visible weld area attack and with the area facing the niobium (insulating) portion of the anode showing no sign of metal loss. The section of this titanium vessel facing the platinum anode surface, however, has numerous small pits. These pits, up to perhaps 3/32-inch in diameter, have an estimated depth of 15 - 20 mils. Inside of most of these pits were very small particles of bright shiny metal which analysis showed to be stainless steel. No method of formation of these small pits has been clearly demonstrated. Visual examination did not verify either electrical arc damage of the titanium or anodic attack of the titanium due to the small stainless steel particles in the pits.

The active anode surface is a 30-mil sheet of 90% platinum-10% iridium that has been explosively bonded to a 0.250-inch niobium plate. The niobium portion of this anode shows no corrosion damage. The platinum section of the anode has begun to show some attack. Poorer bonding spots are becoming apparent around the edges of the platinum sheet and a wave-like imperfection is visible in several areas. These changes in the appearance of the platinum section of the anode may be inherent in the explosive bonding process and will have to be observed for a longer period of time.

The niobium basket of the 24-inch pilot plant electrolytic dissolver shows no visible sign of corrosive attack. Some damage has occurred due to arcing between the basket and the stainless steel materials dissolved to date.

3. Corrosion of the Electrolytic Dissolver System Materials of Construction by Cleaning and Decontaminating Solutions

Corrosion by decontaminating solutions of two metals of interest in the electrolytic dissolver system--Type 347 stainless steel and titanium--has been previously reported⁽¹⁷⁾. This study covered the following reagents and evaluated both welded and nonwelded test coupons:

- 10% nitric acid
- 10% citric acid
- 2.5% tartaric acid - 10% sodium hydroxide
- 10% oxalic acid
- 0.003M periodic acid - 0.05M nitric acid
- 3% sodium fluoride - 20% nitric acid
- 0.25M phosphoric acid
- Turco 4501 (used as received)
- Turco 4502 (2 lb/gal)

These tests were all run in boiling solutions with the exception of the 3% sodium fluoride - 20% nitric acid solution which was run at 62°C. The results of 360-hour tests indicate that Type 347 stainless steel should not be decontaminated with the 3% sodium fluoride - 20% nitric acid reagent and that the 10% oxalic acid, while acceptable, should be used with caution. The 360-hour test results for titanium indicate that this material should not be decontaminated using 10% oxalic acid, 3% sodium fluoride - 20% nitric acid, or with Turco 4501 reagents, and that the 0.25M phosphoric acid reagent should be used with caution. All other corrosion rates would be acceptable for decontamination purposes.

Additional corrosion tests of five metals used in fabrication of the pilot plant electrolytic dissolvers have been made. These metals were tested in seven different decontaminating reagents at two exposure conditions. The results of these tests, Table VI, indicate that the caustic reagents and the oxalic acid solution tested are generally acceptable for use at room temperature. The 20% nitric acid - 3% sodium fluoride solution should not be used, even at room temperature, unless very difficultly removable contamination is encountered and it becomes desirable to chemically remove some underlying metal. The use of these decontamination agents at elevated temperatures, near the boiling point, should be avoided, if possible, for decontamination of the assembled dissolver system. They might find some usefulness in cleaning individual components on a selective basis.

4. Hydrogen Deterioration of Metallic Niobium Components of the Electrolytic Dissolver System

Hydrogen content up to about 200 ppm has been reported to improve the mechanical properties of niobium; however, serious embrittlement is reported at levels greater than 500 ppm hydrogen⁽¹⁸⁾. A later report gives data which are considerably more restrictive; "At concentrations of 100 ppm, hydrogen causes niobium to fracture in a brittle manner at about half its normal ultimate strength. At 200 ppm of hydrogen,

TABLE VI.

CORROSION OF ELECTROLYTIC DISSOLVER MATERIALS OF
CONSTRUCTION BY DECONTAMINATING REAGENTS

Conditions: A. Four hours immersion at room temperature.
B. One hour immersion in boiling solution.

Decontaminating Reagent	Condition	Copper	Type 304L ss (Welded)	Titanium (Welded)	Platinum	Niobium (Welded)
(mils per month)						
10% Sodium Hydroxide	A	0.4	0.04	Wt. gain	0.04	0.4
	B	3.4	0.4	1.6	Wt. gain	22
20% Sodium Hydroxide	A	0.3	0.04	Wt. gain	0.02	0.5
	B	1.4	0.4	6.6	<0.02	54
10% Sodium Hydroxide 2-1/2% Tartaric Acid	A	0.1	<0.04	0.2	<0.02	0.6
	B	1.1	0.2	53	0.1	34
20% Sodium Hydroxide 5% Tartaric Acid	A	0.1	Wt. gain	0.4	<0.02	0.6
	B	0.6	<0.04	514	Wt. gain	77
Turco 4502 (2 lb/gal) (Alkaline Permanganate)	A	0.8	<0.04	Wt. gain	<0.02	2.5
	B	18	0.5	0.1	Wt. gain	58
10% Oxalic Acid	A	0.7	0.6	0.1	0.02	0.2
	B	17	16	250	Wt. gain	1.4
20% Nitric Acid 3% Sodium Fluoride	A	590	3.4	600	0.02	77
	B	14,000	850	5,000	Wt. gain	1,900

niobium becomes extremely brittle and is easily powdered"(19). This hydrogen uptake could be associated with the caustic wash. If hot caustic wash of the dissolver basket and anode is repeated indefinitely, an unacceptable level of hydrogen could be reached.

Embrittlement by hydrogen could significantly shorten the lifetime for the niobium basket cycled in hot caustic wash. In the face of the conflicting results reported on hydrogen embrittlement of niobium, it appeared to be necessary to re-examine the problem. A short series of tests was made to determine if periodic heel-out procedures using a hot (90°C) 10% sodium hydroxide solution for thirty minutes would be detrimental to the niobium present in the electrolytic dissolver system due to hydrogen penetration. The hydrogen content of an unexposed sample was 2.5 ppm.

A series of samples were subjected to treatment in 8M nitric acid followed by immersion in hot caustic to simulate an electrolytic dissolution and cleanup cycle. These tests were run with and without an anodic current applied during the immersion in acid. The results are listed in Table VII. Cyclic immersion of niobium in nitric acid and sodium hydroxide clearly leads to an increase in the hydrogen content of the metal. The application of an anodic potential to the specimen during the acid immersion may decrease the amount of hydrogen incorporated per cycle, although the difference between experiments 1 and 4 is probably negligible.

A sample of niobium was made anodic to a platinum cathode by 6 V in 8M nitric acid; the specimen became golden in color. After two days the potential was raised to 22.5 V; the specimen immediately became blue in color as the thickness of the oxide film changed. After four days of exposure at 22.5 V, the specimen had suffered a negligible weight loss and the metal contained only 1.7 ppm of hydrogen as determined by the vacuum extraction technique.

A second series of tests was made in which niobium test specimens were cycled between 6M nitric acid for 5 minutes at 60°C and 10% sodium hydroxide for 30 minutes at the boiling point to check the effect of cycling on the hydrogen content. The specimen was made anodic (22.5 V) during exposure in the acid. The specimens were sub-standard size impact specimens (Figure 11) and were tested in a standard Izod "V" notch impact test(20) in air at room temperature. Hydrogen content was determined by the vacuum extraction technique.

Results of these tests are shown in Table VIII. The impact values have not been significantly altered by the amounts of hydrogen that have been absorbed. The hydrogen content after 80 cycles has not reached a level which would appear to be detrimental to the structural integrity of the dissolver basket.

TABLE VII.

HYDROGEN CONTENT OF NIOBIUM SAMPLES
UNDER DISSOLVER CONDITIONS

Sample Treatment	Metal Loss	Hydrogen Content
	(mil)	(ppm)
1. Unexposed specimen	-	2.5
2. Ten cycles: 24 hr in 8M HNO ₃ @ 25°C 30 min in boiling 10% NaOH.	0.03	60
3. Twenty cycles as above.	0.03	100
4. Specimen made 6 V anodic for 2 days, 22.5 V anodic for 4 days, both in 8M HNO ₃ .	nil	1.7
5. Ten cycles: 24 hr in 8M HNO ₃ @ 25°C and at 22.5 V anodic-30 min in boil- ing 10% NaOH.	0.02	41

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Figure 11. Impact specimen.

TABLE VIII.

CYCLIC TREATMENT OF NIOBIUM COUPONS IN
NITRIC ACID AND SODIUM HYDROXIDE SOLUTIONS

Specimen Treatment	Corrosion (by wt. loss) (mpy)	Impact (Avg. of 6 tests) (ft.-lbs)	Hydrogen Content, (Avg. of 2 analyses) (ppm)
Blank	-	9.0(a)	1.6
20 cycles	7.6	8.1	30
40 cycles	7.3	9.7	47
60 cycles	1.7	9.4	72
80 cycles	2.8	7.6	81

(a) Average of 9 tests.

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STREAM	1	2	3	4	5	6	7	7a	8	9	10	11	12	13	14	15	16	17 and 18	19	20	
DESCRIPTION	FUEL CHARGE	DISSOLVENT	DISSOLVER PRODUCT	FEED ADJUSTMENT SOLUTION	DILUTED DISSOLVER PRODUCT	CENTRIFUGED DISSOLVER PRODUCT	CONCENTRATED I BR	I BR	I AF	I AX	I AR	I AP	I BS	I BP	I CX	I CR	I CP	I DX	I DR	I DP	FIRST CYCLE PRODUCT
	(a)			(c)																	
Flow, l/hr		278	278	278	556	556	31	110	587	580	587	580	110	580	300	580	300	15	300	16.6	
SS, g/hr	1660																				
U, g/hr	3340																				
Na, g/hr	38																				
Fissium, g/hr	178																				
H, M	8.00	7.40		3.70	3.70	1.60	0.45	3.59		3.41	0.18	-0.50 ^(d)	0.0	0.005		0.005		0.005	0.09		
NO ₃ , M	8.00	7.80		3.90	3.90	8.68	2.45	4.15		3.97	0.20	1.50	0.05	0.005		0.10		0.10	1.78		
Al, M						1.80	0.50	0.09		0.09		0.50									
SS, g/l		5.98		2.99	2.99			2.83		2.83											
U, g/l		12.00		6.00	6.00	0.71	0.20	5.71		5 x 10 ⁻⁴	5.78		5.74		5 x 10 ⁻⁴	11.10		11.10	200		
Na, g/l		0.14		0.07	0.07			0.06		0.06											
NH ₄ , M						1.80	0.50	0.09		0.09		0.50									
B, g/l (b)	2.0	2.0		1.0	1.0			1.0		1.0											
Fissium, g/l		0.64 ^(e)		0.32	0.16			0.09		0.09											
TBP, %									10		10		10		10						
Diluent									Amaco		Amaco		Amaco		Amaco		Amaco				

Basis: 1 Fuel Subassembly Section (EBR-II)

5.620 kg U
0.064 kg Na
0.300 kg Fissium
2.800 kg SS

(a) One fuel section of a subassembly charged each 101 minutes.

(b) Nuclear poison added as H₂BO₃.

(c) Water

(d) Acid deficient with NH₄OH.

(e) Fifty percent of the fission will be present as solids.

FORM INC-936 (2-60)

APPENDIX A. CONCEPTUAL FLOW SHEET FOR DISSOLUTION AND FIRST CYCLE EXTRACTION EBR-II FUEL.