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ELECTROLYTIC DISSOLVER FOR PLUTONIUM METAL

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ELECTROLYTIC DISSOLVER FOR PLUTONIUM METAL

INTRODUCTION

The Plutonium Reclamation Facility has the capability of recovering plutonium from scrap metal. The present head-end process requires that plutonium metal buttons be cut into pieces, burned, screened, and if necessary, pulverized to eliminate clinkers. The resulting PuO_2 is then combined with nitric and hydrofluoric acids in a batch pot dissolver. Often several hours of heating and agitation are required to handle difficult-to-dissolve PuO_2 . The plutonium solution is then delivered to a holding tank for use as feed to the solvent extraction columns.

The proposed electrolytic process consists of placing plutonium metal between two electrodes immersed in nitric acid and passing current through the metal. The side facing the cathode dissolves, forming plutonium nitrate. The process is simple, requires considerably less operator time per kilogram of metal dissolved, and can also be used to dissolve a wide variety of plutonium alloys--clad and unclad. The process has been developed extensively both at Savannah River and Idaho Chemical Processing Plant. It has been adapted to plutonium button dissolution by studies in the Plutonium Engineering Development Laboratory, coupled with further development work at Pacific Northwest Laboratory.

This report presents the evaluation of electrolytic dissolution and its application to plutonium metal. It also presents suggested design criteria for a production unit.

SUMMARY AND CONCLUSIONS

Laboratory tests have demonstrated that plutonium metal, as well as aluminum, stainless steel, Hastelloy C, and other alloys, can be electrolytically dissolved in nitric acid using the "solution contact" approach. Two sources of plutonium metal were evaluated, weapons' grade and a special reactor grade (42% ^{240}Pu , 12% ^{241}Pu) from Savannah River, both yielding a dissolution rate of approximately one gram per ampere-hour. A current flow of 150 amperes was attained at 12 volts (limit of the power supply) and higher current should be possible at increased voltage. Since no fluoride was used in the actual dissolution, glass and 304 stainless steel components provided satisfactory performance. Preliminary investigations on the sludge formed (less than 1%) during electrolysis showed it to be soluble in a low fluoride-high nitric wash.

The proposed electrolytic dissolver is recommended to replace the present metal dissolution process for the following reasons: (1) eliminates button sectioning--entire buttons are dissolved; (2) eliminates metal burning; (3) eliminates powder handling; (4) eliminates PuO_2 dissolution; (5) reduces solids going to the recovery columns; (6) simple to operate; (7) relatively independent of plutonium metal source; (8) reduces operator time resulting in decreased cost and operator exposure; and (9) will directly dissolve many types of plutonium alloys and cladding materials.

DISCUSSION

ELECTROLYSIS THEORY

The transfer of electrons across an electrically conducting fluid accompanied by the generation of a neutral species at the electrodes is called electrolysis. The cations pick up electrons at the cathode, while the anions lose electrons at the

anode, both ions becoming neutral. An example of this process is shown in Equations 1 - 3 representing electrolysis of a molten salt.

In this system the passage of electrons through the molten salt results in the formation of sodium metal and chlorine gas. Using plutonium as an anode, a tantalum cathode immersed in a nitric acid dissolvent results in reactions shown in Equations 4 - 6 upon passing current between the electrodes.

The actual stepwise mechanism is considerably more complex and is accompanied with minor side reactions. It is important to note that hydrogen is not one of the major electrolytic products.

The voltage required for the reaction to proceed depends on the electrode composition, the electrode-liquid interface resistance, polarization (local increase of one ion species over the other) and the ohmic resistance of the solution. For the reactions represented by Equations 4 - 6 in 8M nitric acid, the voltage required is between 2 1/2 and 3 1/2 volts. The interface and solution resistance control at low current density (2 amps/cm²). Above 2 amperes/cm², anode polarization becomes influential and eventually dominates.

The theoretical amount of metal that is dissolved can be

determined from Faraday's Law which states that the passage of one Faraday through a solution of AgNO_3 will deposit one gram equivalent weight of silver. Equations 7 and 8 can be used to calculate the number of grams which will dissolve (or deposit, depending on the current direction and anode material) by multiplying the number of Faraday's by the gram equivalent weight of the element.

$$\text{gram equivalent weight} = \frac{\text{atomic weight (in grams)}}{\text{valence change}} \quad (7)$$

$$\text{Faraday's} = \frac{\text{amp-hr} \times 3600 \text{ coulombs/amp-hr}}{96,501 \text{ coulombs/Faraday}} \quad (8)$$

PREVIOUS WORK

Idaho Chemical Processing Plant, Nuclear Reactor Test Station

Idaho Chemical Processing Plant (ICPP) is one of the major contributors in the development of electrolytic dissolution of nuclear fuels.⁽¹⁻⁶⁾ Idaho Chemical Processing Plant is involved with processing a variety of fuel element designs contained in a broad range of materials. Thus their entry into this area was the desire to develop a universal head-end process for their fuel reprocessing facility.

Electrolytic dissolution was a leading contender for the head-end process, but it had one major disadvantage. This was maintaining electrical contact with the fuel elements after the bundle constraints were dissolved. The problem was solved with what ICPP calls the "solution contact" approach. This consists of placing the fuel elements in a basket located between the electrodes as shown in Figure 1.

By positioning the fuel elements between the electrodes, the electrons are forced through the fuel elements as they pass from one electrode to the other. This results in the side of the fuel elements facing the anode becoming cathodic and, correspondingly, the side facing the cathode becomes

FIGURE 1
ELECTROLYTIC DISSOLVER

anodic. Dissolution takes place at the anodic surface.

The primary disadvantage of the solution contact technique is that there are two parallel paths available for current flow between the electrodes--one through the material for dissolution and a direct path through the solution. However, as Table I shows, the experimental and calculated current utilization are generally within a few percent of each other. This result is obtained by ensuring that the resistance through the material to be dissolved is much lower than the resistance through the solution.

TABLE I
APPLICATION OF ELECTROLYTIC DISSOLUTION IN
NITRIC ACID TO VARIOUS ALLOYS

<u>Alloy</u>	<u>Theoretical* Current Utilization g/amp-hr</u>	<u>Experimental Current Utilization g/amp-hr</u>	<u>Wt% of Undissolved Alloy</u>
Chromium	0.324	0.333	0.4
Inconel X	0.752	0.742	0.3
Hastelloy C	0.738	0.742	9.3
303 SS	0.598	0.587	0.3
345 SS	0.594	0.601	1.2
316 SS	0.605	0.598	0.3
Aluminum	0.335	0.414	1.0
Inconel	0.788	0.748	0.5
Nichrome V	0.745	0.742	0.5

* Calculated using Equations 7 and 8.

A materials analysis program was undertaken at ICPP which included materials for the basket, electrodes, and the containment vessel (Figure 1).

The basket was necessary to contain the multi-element fuel sections within the electric field, to eliminate electrode shorting, and to prevent arcing which could damage the electrodes. The basket material had to be metal to withstand the

mechanical abuse of having fuel assemblies dropped into it. It also had to withstand high radiation dosage and to be an insulator to prevent the short-circuiting of the electrodes through the basket. The problem was solved using one of the "valve" materials--niobium and tantalum are examples. These materials form a high resistance coating when made anodic, preventing further current passage. Niobium and tantalum were also well suited to back the platinum anode, providing strength and preventing current from passing to the vessel wall. Of the container and cathode materials tested, titanium and Carpenter-20 were the most promising, with titanium being the final choice.

A number of cladding shapes, bundle geometries, some containing UO_2 -cermet fuel were dissolved.⁽¹⁾ The results were encouraging enough to go ahead with the full-scale dissolver now in the final fabrication stages at ICCP.

Off-gas samples obtained from several of the runs gave a gas evolution rate of $3.6 - 14 \times 10^{-3}$ SCFM/amp-hr. Hydrogen content of the undiluted gas varied from 3.6 to 5.6%. This rate was considered insufficient to create an explosive condition because the in-leakage of air diluted the gaseous products of dissolution four to one.

Sludge and heel cleanout tests were conducted using caustic (NaOH), concentrated nitric acid, and several nitric acid-fluoride ion solutions. Caustic was found effective over a concentration range of 5 to 30% if used at 95 °C. Caustic has one major disadvantage--it can result in hydrogen embrittlement. Another effective sludge remover was 2M HF-6M HNO_3 at 65 °C.

Savannah River

Savannah River has also evaluated electrolytic dissolution as a head-end process.^(7,8) Their demonstration dissolver is

also wedge-shaped, with an active dissolution zone 19 inches wide, tapers from 5-1/2 inches to 1 inch thick, and is roughly 3-1/2 feet deep. Power is supplied by a 600 kW transformer-rectifier that produces 10,000 amperes of direct current. Power controls can automatically maintain either constant current or voltage.

A campaign was initiated to test the dissolver by recovering 232 kg of ^{235}U from 3300 kg of stainless steel. Over a two-month period, the dissolver was operated 1004 hours at 35 to 40 volts and 8000 to 9500 amps. Final operating conditions were essentially identical to the startup parameters, indicating no significant corrosion or damage occurred during operation.

One of the Savannah River investigations directly applicable to this study was the determination of the conditions necessary to prevent hydrogen embrittlement of the cathode. Hydrogen embrittlement which occurs when the absorbed hydrogen concentration exceeds 200 ppm can be eliminated using a solution with a minimum nitric acid concentration of 6M and a nitrate ion concentration of 7M. Nitric acid concentrations lower than this will cause embrittlement and eventual disintegration of the cathode.

LABORATORY TESTS

Cold Laboratory Evaluation

An investigation was initiated to determine the types of materials that could be dissolved using electrolytic dissolution. Initial cold tests were conducted using the jacketed glass vessel shown in Figure 2. The platinum anode and tantalum cathode were connected to 304 stainless steel buss bars by means of 1/4 inch tantalum rods welded to the 2 x 2-1/4 inch electrodes. Power was supplied by an 8 volt, 50 ampere direct current plating power supply.

Aluminum, 304 stainless steel, and Hastelloy C discs 3 to

FIGURE 2
LABORATORY DISSOLVER

4 inches in diameter and a half inch thick were used to verify the results of previous investigators and evaluate the behavior of this particular system. The tests were conducted in 8M HNO_3 at 50 to 65 °C and resulted in a percent Theoretical Current Utilization (TCU is the theoretical amount which will dissolve per ampere-hour of current) for aluminum of 95%, 304 stainless steel of 80%, and Hastelloy C equal to 73%. A small amount of sludge formed during the dissolution of the stainless steel and Hastelloy C.

Plutonium Dissolution

A system similar to the cold laboratory dissolver was used to investigate the dissolution behavior of plutonium metal. The button was positioned vertically between the electrodes in a dissolvent of 8M HNO_3 . The concentration was maintained during dissolution by the addition of 15.8M HNO_3 . An operating current of 30 to 40 amps at 8 volts (maximum for the power supply) was used to dissolve the button at 50 to 60 °C.

No problems were encountered during the dissolution with a solution concentration of 380 g/liter being easily obtained. The resistance of the solution remained constant over most of the range, decreasing 20 to 30% at the higher plutonium concentrations. The actual current utilization varied from 0.8 to 1.2 grams per amp hour with the lower value being obtained at low (less than 100 g/liter) plutonium concentration. This is considerably lower than the calculated TCU of 2.2. An improved dissolver design which restricts current flow around the button is expected to improve the current utilization. Some very fine particles formed during the metal dissolution which settled out overnight, forming a coating on the vessel bottom. Their dissolution is discussed in the subsequent section.

DEMONSTRATION DISSOLVER

Demonstration tests using an advanced dissolver design utilized a special reactor grade plutonium (42% ^{240}Pu , 12% ^{241}Pu) as source material. The resulting fluoride-free plutonium nitrate solution was subsequently used by the Pacific Northwest Laboratory Critical Mass Laboratory.

The dissolver system, based on work performed at Atlantic Richfield Hanford Company (ARHCO), was designed, constructed, and operated at Pacific Northwest Laboratory.⁽⁹⁾ Figure 3 shows a sketch of the system. Details of the electrode designs are shown in Figures 4 and 5. The horizontal electrode placement was chosen for several reasons:

- It allowed construction of a cathode which would follow the dissolving face of the button. Letting the cathode gravity settle against the top side of the button minimizes heat generation and improves current utilization.
- Reduces operator exposure.
- Improves current utilization during the final stages of dissolution when the button begins to disintegrate. In a vertical dissolver the pieces fall to one end of the basket with the result that little current passes through the metal.

The dissolver itself was fabricated from 5-inch glass pipe with the various ports constructed from 1-inch glass pipe. The anode (bottom electrode) has a tantalum base to which a 20-mil thick, 3-1/2 inch diameter piece of platinum was electron beam-welded. The 4-inch diameter cathode was fabricated from a sheet of 1/16 inch thick tantalum. Holes were drilled through the disc to contain the nonmetallic inserts which allowed the cathode to follow and yet not contact the button. The basket was fabricated from a polyethylene bottle

FIGURE 3
DEMONSTRATION DISSOLVER

FIGURE 4
TANTALUM CATHODE

FIGURE 5
PLATINUM ANODE

by drilling holes in the bottom and mounting spacers to allow solution flow between the anode and the basket bottom. The heat exchanger and holdup tank were fabricated from 304 stainless steel and connected to the dissolver vessel with polyethylene tubing.

Solution from the top of the electrolytic dissolver is circulated through the holdup tank and heat exchanger, then returned to the dissolver through 3/8 inch OD, 3/16 inch ID tantalum tubes welded to each electrode. Returning the cooled dissolvent in this manner serves the following functions:

1. Removes current-generated heat at the junction of the power cable and tantalum buss tube as well as the tube itself.
2. Flushes the bubbles produced during electrolysis away from the electrode surfaces, the button, and the basket. A buildup of bubbles in these locations can seriously restrict current flow.
3. Increases the amount of current that can be passed before polarization becomes a serious resistance.

The system was operated on a batch basis by filling the dissolver system with 8M HNO₃ and operating the dissolver until a certain concentration of plutonium was reached. The nitric acid concentration varied as a function of process requirements (see Equations 4 - 6).

Results

A minimum of data were taken during the demonstration run due to requirement that the assignment be completed as rapidly as possible. The dissolver was operated on a 24-hour-per-day, five-day-a-week basis. Operating conditions were 40 to 50 °C and 150 amps at 8 to 10 volts D.C. Very little change in solution resistance was noted during the dissolutions cycle.

Apparently $\text{Pu}(\text{NO}_3)_4$ compensates for any loss of HNO_3 . It was observed that the limiting resistance for this system was the open area in the basket bottom.

Several problems were encountered during the dissolution of the eight buttons. One was hydrogen embrittlement of the cathode resulting from allowing the HNO_3 to vary as a function of the system demand. As indicated earlier in the study, maintaining the HNO_3 concentration above 6 molar will eliminate this problem. The second area of concern was the formation of sludge (less than 1 percent of the button and passing a 5-micron filter) generated during dissolution. Preliminary investigations indicate a flush containing 0.05M F^- in 8 to 10M HNO_3 will remove the majority of sludge. The laboratory dissolver has been operated in the presence of F^- at these levels with no obvious detrimental effect on the electrodes.

Further development work will include verification of previous work and recording of data not taken in the previous study.

EQUIPMENT DESIGN CRITERIA

A schematic of a two-dissolver module is shown in Figure 6. The recommended basis for designing the equipment is the use of a 250 amp, 30 volt power supply for each dissolver. The design parameters for each major component are presented in the following discussion.

Dissolver Vessel

The dissolver vessel shown in Figure 7 should be adequate for handling buttons or smaller material. Either Pyrex glass or Kynar could be used; both have their advantages and disadvantages. Pyrex has the advantage that it is inexpensive and the vessel can be fabricated locally on short notice. It does have the disadvantage of being fragile. Kynar, on the other

FIGURE 6
PROPOSED ELECTROLYTIC DISSOLVER SYSTEM

FIGURE 7
PROPOSED ELECTROLYTIC DISSOLVER

hand cannot be broken but is expensive, difficult to obtain, and must be fabricated in the Shop. Adequate space must be allowed for the basket and an annulus for solution to flow from the anode to the overflow port. The off-gas port should be through the lid to minimize entrainment and thus increase the scrubber life.

Electrodes

The electrode designs shown in Figures 4 and 5 are adequate for the production model. Tantalum or niobium serve as a base for the anode and as the material of construction for the cathode. The weld joint between the buss tube and the electrode should be a full penetration weld, if possible, to minimize resistance at this point. A 10-mil platinum facing is recommended.

Basket

The basket design is determined by the stage of the dissolution cycle in progress. Ideally, the basket would be completely open at the bottom, allowing unrestricted current flow. Toward the end of the dissolution cycle when the button begins to break up, a basket with small holes (3/16 inch diameter or smaller) will ensure the plutonium stays in the electrical field while preventing a short circuit from occurring across the electrodes. A choice somewhere between these two designs will be necessary for a single basket operation.

Power Supply

A D.C. power supply capable of supplying 250 amperes at 30 volts per dissolver is recommended. Independent adjustment of current and voltage would provide maximum flexibility for handling materials other than buttons. Each of the dissolvers should be equipped with volt, ampere, and ampere-hour meters.

A resettable and total ampere-hour meter combination will allow a double-check on current usage and also provide for direct readout of the ampere-hours to which a given button has been subjected. The ampere-hours can be used as an indication of dissolved plutonium.

Heat Exchangers

A heat exchanger for each dissolver is recommended so that completely independent operation (other than the power supply) is possible. Each should be sized to handle the maximum design load of 7.5 kW at 2° °C inlet temperature with the maximum dissolver temperature at 50 °C. If nitric acid and a low fluoride (8 to 10M HNO₃, less than 0.05M F⁻) wash are used as dissolvents, 304 stainless steel would probably be adequate as construction material. If higher fluoride levels above 0.05M F⁻ are continuously used, consideration should be given to more exotic materials.

Scrubber

There seems to be a conflict between Savannah River⁽²⁾ and ICPP⁽¹⁾ concerning amount of hydrogen generated during electrolysis in nitric acid. Savannah River found an undetectable amount, ICPP 5.6%, when dissolving nichrome. Assuming the maximum off-gas rate obtained at ICPP and diluting the off-gas to twice its original volume (4.1% is the minimum possible explosion mixture) will require a scrubbing capacity of 7 SCFM per dissolver.

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