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THE RECOVERY OF PLUTONIUM FROM METAL WASTES

BY

J. F. FACER AND B. WEIDENBAUM

TECHNICAL SECTION
ENGINEERING DEPARTMENT

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Technology - Plutonium

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THE RECOVERY OF PLUTONIUM FROM METAL WASTES

By

J. F. Facer and B. Weidenbaum

Chemical Process
Separations Technology Unit

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THE RECOVERY OF PLUTONIUM FROM METAL WASTES

INTRODUCTION

The plutonium metal fabrication in the Hanford 235 Building consists of the operations: making castings from plutonium buttons; machining the castings to a given weight; pressing the machined casting; trimming and cleaning the pressed casting; coating the casting; and when necessary, stripping the coating. At the present time only the machining wastes are recycled in the Hanford process. The machining turnings are added to process reduction charges; the dissolved portions of laboratory samples of the turnings are ultimately recycled to the Concentration or Isolation Buildings with other laboratory wastes.

The remaining metal fabrication wastes (including unused portions of laboratory samples, burned turnings and special buttons prepared from scow sweepings) have been stored for future recovery, but such storage requires considerable space(1) and immobilizes product.

The casting skull is the dross of plutonium metal and oxide which remains in the pouring crucible after the plutonium has drained from the pouring crucible into the casting crucible. Skulls represent 80 per cent of the plutonium currently being stored as wastes from metal fabrication operations.

Skulls have been recovered routinely at Los Alamos(2) by dissolution in hydriodic acid and recycle of the resulting solution to the oxalate strike. Installation of the hydriodic acid process at Hanford has been considered undesirable for the following reasons:

a. At Los Alamos buttons produced from skull recovery batches have had higher impurity concentrations than normal(2).

b. The use of hydriodic acid presents a troublesome corrosion problem.

c. Any process change which would eliminate the use of hydriodic acid in the Hanford purification process (e.g. the use of some other reducing agent in the oxalate process or the substitution of a peroxide purification process for

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the oxalate process) would make the recycle of hydriodic acid skull solution a problem.

Any satisfactory skull recovery process might be expected to be applicable to all other metal fabrication wastes except the crucible fragments.

OBJECTIVES

The recovery of plutonium from casting skulls was investigated in this laboratory to develop ways of dissolving plutonium metal and oxide wastes and to evaluate existing Hanford processes as possible methods for recovering plutonium from the dissolved wastes. Experimental work was directed to develop methods that would not require highly corrosive chemicals, in order that glass or glass-lined equipment would not be required in the plant. Exploratory corrosion studies were made with possible materials of construction for the process chemicals studied. The conversion of the metal to oxide was also studied because the dissolution of the oxide formed at relatively low temperatures is much more rapid than the metal.

SUMMARY AND CONCLUSIONS

Plutonium fabrication wastes other than oxides were dissolved in boiling 0.5 to 2 M H_2SO_4 to give a solution with the characteristic blue color of plutonium (III). The solution was oxidized on standing overnight to give plutonium IV with some precipitation unless the hydrogen ion concentration was maintained above 1 M and the solution was protected from air oxidation. A maximum concentration of plutonium in solution of 45 g/l. was obtained when the molar ratio of sulfuric acid to plutonium was 2.0. When larger ratios of acid to metal were used, a blue precipitate, probably plutonium (III) sulfate was formed. The precipitate was readily dissolved in boiling 0.5 M H_2SO_4 or by diluting the hot dissolution mixture with water or 0.5 M H_2SO_4.

Plutonium metal or oxides from casting skulls and other metal processing wastes can be dissolved in a boiling mixture of 8 to 16 M HNO_3 - 0.04 M HF. The time required for complete dissolution of skulls was generally five to ten times longer for a HNO_3-HF mixture than when 0.5 M H_2SO_4 was used. Dissolution time for the mixed acids averaged from one to four hours.

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Variation in the dissolution time from less than one hour to greater than twenty-four hours, however, was observed with the HNO_3-HF mixtures and appeared to depend on the skull weight, specific surface, the oxide content, and particularly on the depletion of the HF, either by chemical reaction with dissolver or by volatilization from the acid mixture.

Either plutonium metal or skull material can be oxidized within two to four hours in boiling 0.5 $\underline{M}$ HNO_3. The green material obtained, plutonium hydroxide or hydrated oxide, can then be dissolved in a half hour or less in boiling 8 $\underline{M}$ HNO_3 - 0.04 $\underline{M}$ HF; sulfuric acid in any strength dissolved only a portion of the green powder even after four hours of refluxing. More rapid oxidation of plutonium metal to the oxide which is readily soluble in the mixed acids can be obtained by autoclaving the metal in water at a temperature above 140° C. for one hour. Steam autoclaving produced a less highly hydrated oxide, which dissolved very slowly and incompletely in the nitric-hydrofluoric acid mixture.

In considering these three methods of handling plutonium metal (and oxide) wastes for use in a plant, the use of the boiling HNO_3 - HF mixture would give the simplest operating procedure. A pre-oxidation with boiling 0.5 $\underline{M}$ HNO_3 prior to the treatment of the waste material with the mixed acids would reduce the extent of the corrosion of the dissolver vessel by shortening the interval for which the boiling mixed acids are required. A shorter processing time, and therefore larger throughput, may also be obtained when pre-oxidation is used. Although the use of the boiling dilute sulfuric acid would be desirable from the corrosion standpoint, its use for a plant process would be precluded because stored metal wastes, or other plutonium that was oxidized, could not be dissolved satisfactorily.

The feasibility of recycling HNO_3 - HF skull solutions to the isolation process as regular plant runs through two peroxide strikes and one oxalate strike was demonstrated in Production Test 234-2 (3). A skull solution purified by one peroxide strike in the laboratory was also processed through the 234-5 Building to yield a satisfactory product.

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Exploratory corrosion studies in the laboratory showed that tantalum and platinum were not attacked by boiling 16 M HNO_3 - 0.04 M HF mixtures, whereas stainless steel types 301, 309, and 347 were penetrated from 0.2 to 0.6 inches per year by the same acid. Studies by the Metallurgy Branch demonstrated that the corrosion rate for Carpenter #20 or chemical lead with boiling 0.5 M H_2SO_4 was less than 20 mils per year.

EXPERIMENTAL

Casting skulls from plant storage or laboratory five gram buttons were used for all dissolution and metal oxidation studies.

Dissolutions were made either in a two necked, two liter, round bottom, pyrex flask equipped with a reflux condenser and heated by a glas-col mantle, or in a cylindrical, stainless steel Type 347 dissolver, six inches in diameter and nine inches high, equipped with a condenser and sample port and heated by a hot plate and infra-red lamp. These vessels were also used for the exploratory corrosion studies.

The normal dissolution procedure using 16 M HNO_3 - 0.04 M HF consisted of: adding the skull material to the dissolver, adding a measured volume of acid, connecting the reflux condenser, and heating the acid to boiling as rapidly as possible with the heaters used for the subsequent refluxing. Refluxing was continued for four hours or longer, and samples were taken after one, two and four hours, for iron, hydrogen ion, and plutonium analyses.

The same procedure was used in sulfuric acid dissolution studies, except that one hour usually sufficed for metal dissolution. Therefore, few tests of longer duration were made.

Solutions for analysis were pipetted from the dissolver while hot (80 to 90° C.). No filtration was necessary for nitric acid skull solution samples, but some sulfuric acid, skull solution samples required filtration to remove finely divided solids.

Laboratory reduction bombs [4] of about 30 cc capacity were employed

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for the autoclaving tests. The plutonium metal was immersed in water for water oxidation and placed in a dry pyrex container which was surrounded by water for the steam oxidation. In both cases the bomb was heated in the resistance furnace (4) used for laboratory reduction studies. The temperature of the bomb was followed by an outside thermocouple and was compared continuously with the furnace temperature. Temperatures were recorded by a Leeds and Northrup, Speedomax recorder.

The usual oxidation procedure was to heat the bomb to 140-150° C., and to shut off the power input to the furnace when a sudden temperature rise occurred because the oxidation was proceeding rapidly. The heat of reaction increased the bomb and furnace temperatures, and the reaction went to completion within an hour without further attention, unless the bomb was quenched in water. When cool, the bomb was vented to allow the hydrogen gas from the reaction to escape. The oxidized plutonium and any liquid oxidizing agent were then transferred to the dissolver.

Oxidation tests with 0.5 M HNO_3 or $HClO_4$ were made by immersing plutonium in a boiling solution of the acid contained in a suitable-sized pyrex flask equipped with a reflux condenser.

Hydrogen in the dissolver gases was aspirated from the dissolver system to an absorption train set up outside the hood consisting of a Schwarz tube filled with ascarite (for gas drying), followed by a copper oxide tube (for hydrogen oxidation), followed by two Schwarz tubes filled with ascarite. The absorption train was checked by aspirating through it the hydrogen generated by a known weight of calcium in water. Recovery was found to be greater than 95 per cent, which was considered adequate for obtaining the information desired.

For the anodic oxidation experiments, current was supplied by two 45 volt dry batteries arranged in series and connected to a 1/4" cylindrical graphite cathode and to a platinum wire anode. The plutonium was suspended in the solution with a platinum wire casing. The spacing between the electrodes was approximately one inch. Because the experiment was only of an exploratory nature, no determination was made of the current density.

Corrosion tests to evaluate a few materials of construction possible for the fabrication of a metal waste dissolver were made in either the pyrex or the Type 347 stainless vessel used for skull dissolution studies. Specimens were insulated from each other and from the container by teflon mounts. No inert container was available for HNO_3 - HF mixtures so some solvent depletion resulted from corrosion of the dissolver as well as from specimen corrosion. Since the tests were of a screening nature, they were shortened to periods of 1/2 to 8 hours and no attempt was made to limit the test to one specimen per container. End-use conditions were simulated during corrosion tests by placing test specimens in the dissolver during skull dissolution experiments.

Corrosion tests with boiling 0.5 $\underline{M}$ H_2SO_4 were made by the Metallurgy Section in one liter pyrex flasks equipped with cold finger condensers. Tests in duplicate were made with each type of metal. The specimens were mounted on glass supports to give test conditions of total immersion, vapor phase, and vapor-liquid interface. All of these tests were made in the absence of plutonium, and only three consecutive tests of 48 hour duration each were made for each specimen.

DISCUSSION AND DATA

Dissolution of Metal Fabrication Wastes

A satisfactory process for the recovery of plutonium from metal wastes should include a rapid method of waste dissolution in a solvent which is compatible with existant Hanford processes and is not too corrosive to equipment. Both plutonium metal and plutonium oxides may be dissolved quite rapidly in HCl, HBr or HI, but these acids are very corrosive and with the exception of HI are not compatible with existing Hanford processes. Hydriodic acid solutions can be recycled only at the oxalate precipitation step in the Purification Building.

Plutonium metal is not dissolved by either dilute or concentrated nitric acid. Although plutonium oxides are manifoldly more soluble in nitric acid than is the metal, nitric acid alone is a poor solvent for metal wastes. However, when nitric acid containing very small concentrations of hydrofluoric acid is employed, the routine dissolution of metal wastes becomes feasible.

Mixtures of nitric and hydrofluoric acids are often used to dissolve metals. The use of HF as an additive to nitric acid for the dissolution of skulls would avoid the use of ions foreign to the plant process. Sodium fluosilicate was found to be equally effective and slightly less corrosive to stainless steel or pyrex (Table II). Presumably other fluorides could also be used.

It was found that casting skulls dissolved quite well in boiling 16 $\underline{M}$ HNO$_3$ - 0.1 $\underline{M}$ HF. The dissolution rate was neither improved appreciably by increasing the HF concentration to 0.25 $\underline{M}$ nor reduced appreciably by lowering the HF concentration to 0.04 $\underline{M}$. Concentrations of 0.02 $\underline{M}$ or less HF were too low for effective dissolution. Nitric acid concentrations of 8 $\underline{M}$ to 16 $\underline{M}$ with HF present seemed equally effective, but a 16 $\underline{M}$ HNO$_3$ - 0.04 $\underline{M}$ HF mixture was used for most tests to keep the volume of solution to a minimum.

Skulls varied from less than ten grams to more than one hundred grams in weight and from 85 to about 95 per cent in plutonium content. The physical condition of skulls varied greatly. Some were massive and metallic, others were made up of several, thin, foil-like layers, and still others had oxidized during storage to a voluminous green powder or, more rarely, to a black powder. Because of these variations, duplicate tests were required to evaluate the solvent. The time cycle for a plant process would have to be very elastic, because of the variation in the physical form of the skulls. The variation in the time required to dissolve skull material is apparent from the data in Table I. It was found that heavy metallic skulls dissolved very slowly (4 to 24 hours or more) in boiling 16 $\underline{M}$ HNO$_3$ - 0.04 $\underline{M}$ HF so that a heel would accumulate if a standard dissolution cycle were used.

The green powder associated with stored skulls was dissolved within an hour by the 16 $\underline{M}$ HNO$_3$ - 0.1 $\underline{M}$ HF mixture. Oxidation of skulls during storage, however, is slow and in no way reproducible. Methods of producing the green powder rapidly were therefore developed during these investigations and are described elsewhere in this report.

Evaluation of the fluoride-containing solvent was hampered by variations due to the depletion of the fluoride from the solvent because of reaction with the dissolver vessel. In glass the fluoride reacted with the container to form fluosilicic acid, which volatilized to render the solvent ineffective after about four hours. In a stainless steel dissolver fluoride depletion was less severe, and skull dissolution was appreciably more rapid.

On an average, about 85 per cent of skull material was dissolved in four hours by treatment with boiling 16 M HNO_3 - 0.04 M HF in a pyrex dissolver. Under identical conditions, more than 99 per cent of the skull material was dissolved in a stainless steel dissolver in 4 hours, and even more rapid dissolution would be expected to occur if a tantalum or platinum clad dissolver were used. It was found that 500 ml. of 16 M HNO_3 - 0.04 M HF should be used for each hundred grams of skull material.

When a pyrex or stainless steel dissolver was used, occasional fortification of the 16 M HNO_3 - 0.04 M HF acid with hydrofluoric acid was found to shorten the required dissolution time. This advantage was most applicable when glass equipment was used. The small quantities of hydrofluoric acid introduced after the initial charge of mixed acids would be difficult to handle and would offer little, if any, advantage to a dissolution process using a platinum or tantalum clad dissolver.

Boiling 1 to 4 N H_2SO_4 dissolved metallic skull fragments completely in less than one hour when two or more mols of sulfuric acid were used for each mol of plutonium. The maximum concentrations of plutonium that were obtained at different molar ratios of sulfuric acid to plutonium were; 45 g. Pu/l. at 2.0, 30 g. Pu/l. at 4.0 and 12 g. Pu/l. at 10. These maximum concentrations did not limit the amount of plutonium metal dissolved. At higher plutonium concentrations, the plutonium metal continued going into solution, but it was immediately precipitated as a blue solid. The blue residue dissolved readily in boiling 0.5 M H_2SO_4 or by diluting the hot dissolution

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mixture with water or 0.5 M H_2SO_4. The amount of sulfuric acid required for plutonium dissolution would be rather high for subsequent use in a single peroxide precipitation process (40 grams of plutonium per liter). By limiting the skull dissolution to the use of 0.5 to 1.0 M H_2SO_4 and a molar sulfate to plutonium ratio of 2.0 to 3.0, a plutonium solution was obtained (40 grams of plutonium per liter and 0.5 - 1.0 M sulfate) which could be diluted to satisfactory feed solution for Hanford's two cycle peroxide process.

When skulls containing some green oxide were dissolved in boiling 0.5 M H_2SO_4, the metal dissolved within 20 to 60 minutes leaving most of the oxide as an insoluble residue. Oxide, prepared by oxidizing plutonium metal in refluxing 0.5 M HNO_3 for several hours, was partially dissolved (16 per cent -3.2 g. Pu/l.) by one hour of refluxing in 0.5 M H_2SO_4 using a sulfuric acid to plutonium molar ratio of 10, but no further oxide dissolution resulted from further treatment in the refluxing solution. Sulfuric acid dissolution data are shown in Table III.

Oxidation of Plutonium Metal and Skulls

Because it was found that both the green and black powders resulting from atmospheric oxidation of skulls dissolved very much more rapidly in boiling 16 M HNO_3 -0.04 M HF than the skull, a rapid method of obtaining such powder was sought.

The green powder was produced slowly from plutonium metal by oxidation with water at 100° C., but at temperatures above 140° C. the oxidation of plutonium metal by water became so rapid that the heat of reaction increased the temperature of the reactants and container. Complete oxidation of either plant casting skulls or laboratory 5 gram plutonium buttons was obtained within one hour by using water at 180° to 240° C. The product obtained by water oxidation at temperatures above 140° C. was a finely divided black solid, which dissolved rapidly in boiling 16 M HNO_3 -0.04 M HF. The chemical reaction is thought to be given by the equation:

$Pu + 4\,H_2O \longrightarrow PuO_2 \cdot 2\,H_2O + 2\,H_2$.

A similar oxidation occurred when steam was used as the oxidizing

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agent instead of water, but the green product could not be dissolved readily in boiling 16 M HNO_3 - 0.4 M HF. On the basis of plutonium content of the oxide products, water oxidation is postulated to produce $PuO_2 \cdot 2\ H_2O$ and steam oxidation is postulated to give $PuO_2 \cdot H_2O$. Atmospheric oxidation gives an oxide with plutonium content corresponding to $PuO_2 \cdot 2\ H_2O$.

The oxidation of plutonium metal by liquid hydrogen peroxide solution at temperatures above 140° C., produced a black product which dissolved readily in boiling 16 M HNO_3 - 0.04 M HF. The only apparent advantage to be gained by using hydrogen peroxide instead of water for plutonium oxidation might be the lower pressure that results in the autoclave. The simplest representation of the reaction might be $2\ H_2O_2 + Pu \longrightarrow PuO_2 \cdot 2\ H_2O$. Actually some decomposition of the hydrogen peroxide would be expected to occur simultaneously; explosive mixtures of hydrogen and oxygen could therefore be a possible hazard. No attempt was made to determine the gas composition after oxidation or to follow the system pressure during oxidation.

Attempts to obtain dissolution of skull material by autoclaving it with 70 per cent HNO_3 at 160° C. produced a cream colored product which was more difficult to dissolve in boiling 16 M HNO_3 - 0.04 M HF than were the black or dark green products obtained by other liquid phase oxidations. The oxidation was not accompanied by a temperature rise such as was noted when water, steam, or hydrogen peroxide was used. Anodic oxidation of plutonium in 35 to 70 per cent nitric acid produced a black product which was readily soluble in boiling 16 M HNO_3 - 0.04 M HF. The oxidation, however, was slow and good contact between the plutonium metal and its supporting anode could not be maintained. The black solid fell to the bottom of the cell and a copious evolution of oxygen came from the platinum wire. The oxidation of the plutonium appeared to be more rapid when 70 per cent HNO_3 was used as the electrolyte than when 35 per cent HNO_3 was used. Oxygen evolution at the anode support might be eliminated by substituting tantalum for platinum, but at best anodic oxidation did not appear promising for use in the oxidation of metallic plutonium wastes. Plutonium oxidation data are given in Table IV.

The most promising method for the oxidation of plutonium metal wastes

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prior to dissolution in boiling 8 to 16 M HNO_3 - 0.04 M HF consisted of immersing the plutonium in refluxing 0.5 M HNO_3 until the plutonium was converted to green oxide. The optimum concentration of nitric acid for the oxidation reaction was 0.5 M but appreciable oxidation was obtained with nitric acid concentrations of 0.1 M to 4.0 M. (Table V). The molar ratio of plutonium to nitric acid was varied from 3 to 1/12 and did not appear to be critical. The function of the nitric acid is not clear, but hydrogen evolution during oxidation with 0.5 M HNO_3 was about 1/10 as large as that obtained by the dissolution of plutonium in 0.5 N H_2SO_4. With boiling 0.5 M HNO_3 complete oxidation of skull material resulted within three hours.

The 0.5 M HNO_3 oxidation process permits one container to be used for both oxidation and dissolution, and no transfer of plutonium-containing material is required between the two operations. The oxide slurry need only be fortified to 8 M HNO_3 0.04 M HF to be ready for dissolution.

Recycle of Skull Solution to the Hanford Process

Nitric acid solution of skull material contained more magnesium (400 ppm) than Hanford oxalate process feed solution (4 to 200 ppm) but all other impurities except lanthanum were present in quantities equal to or less than those present in process feed solution (3). Lanthanum was reported to be greater than 2000 ppm, and similar values are also given for plant feed solution. There is no comparison possible because how much more than 2000 ppm La were present was not determined. Some increase in the lanthanum content of plutonium metal was observed at Los Alamos when skull material was recycled directly to the oxalate process.

In view of the Los Alamos experience recycle of skull solution to the isolation process was therefore studied at Hanford. Approximately 160 grams of plutonium from skulls dissolved in 16 M HNO_3 - 0.04 M HF were processed through one peroxide cycle in the laboratory and as a regular plant run through the purification and metal fabrication processes in the 234-5 Building. Impurity concentrations were satisfactory at all stages of the processing.

Approximately 500 grams of skull material were dissolved in 16 M

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HNO_3 - 0.04 M HF for use in Production Test 234-2. Half of this material was dissolved in glass and half in a stainless steel dissolver, and the two solutions were processed through the Hanford 231 Building as separate runs. The results of this Production Test have been previously reported(3). It was concluded that recovered skull material after two peroxide precipitations could be processed in any manner that could be applied to regular production material. The recommendation was also made that a one peroxide precipitation cycle be tested for 231 Building processing of the skull solution.

Corrosion Studies

Corrosion tests under approximate skull dissolution, process conditions were made with a four hour, specimen exposure to an acid mixture which was initially 16 M HNO_3 - 0.04 M HF during the laboratory skull dissolutions in pyrex or stainless steel dissolvers. Penetration of test specimen coupons was found to be greater in the absence of plutonium than under dissolution conditions. More complete tests, if required, could be made with plutonium-free solutions and would be under more severe conditions than in a plant dissolver.

Of the materials tested, platinum and tantalum were penetrated less than 5 mils per year by the boiling acid or its vapor, stainless steel type 309, (columbium stabilized) was penetrated 100-150 mils by the acid vapors and 150-210 mils by the boiling acid, and stainless steels 304 (extra low carbon), 347, and 347 (tantalum, columbium stabilized) showed greater than 250 mils penetration. In half hour tests 3/4" pyrex glass tubes were penetrated at a rate of one inch per year in the absence of skull material.* Actually, several pyrex flasks were eaten through by the mixed acid during tests. Complete corrosion data are given in Table II.

If the equipment for skull dissolution were not used for more than a few hours per week, the Cb stabilized stainless steel 309 might be expected to serve for dissolver service if checked routinely for pitting or other wear. To be entirely safe in the matter and because the expense for the small dissolver vessel was not excessive, a platinum-clad dissolver has been ordered for plant use.

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*Although these tests indicate that pyrex glass is markedly attacked by a boiling 16 M HNO_3 - 0.04 M HF mixture, Los Alamos has dissolved skulls routinely for six months with a boiling 10 M HNO_3 - 0.05 M HF mixture in a large pyrex tube without any tube failures. An oil bath with immersion heaters is used to heat the pyrex tubes containing the skulls and mixed acids at Los Alamos.

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Corrosion test results from studies made by the Metallurgy Group are shown in Table VII. Carpenter #20 and chemical lead were penetrated less than 20 mils per year by boiling 0.5 M H_2SO_4 in the absence of plutonium. Either material could be used for the dissolver if sulfuric were used for the dissolution. Carpenter #20 would be more desirable from a structural standpoint.

FUTURE WORK

The feasibility of using a combination of one peroxide strike and one oxalate strike for the purification of skull solutions has been demonstrated in the laboratory. Plant testing of this method has been recommended on the basis of the results obtained in Production Test 234-2.

The present work has revealed areas in which the knowledge of plutonium chemistry is scanty. These include the solubility of plutonium (III) sulfate in water and various concentrations of sulfuric acid; the solubility of plutonium oxides in different acids; and the identity of oxides, hydrated oxides, or hydroxides obtained from plutonium metal by different methods of oxidation. It would be helpful in dealing with problems concerning plutonium metal to obtain more information about these subjects.

No inert material has been available for use with boiling 16 M HNO_3 - 0.04 M HF. It will be desirable to obtain corrosion data with this acid mixture in the platinum-clad dissolver, which will be used in the 234 Building to dissolve skull material.

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TABLE I

DISSOLUTION OF CASTING SKULLS IN HNO_3, HF SOLUTIONS

5	6	7	Special -	8	8-A	8-B	9	10	11	12	13	14	15	16	17
1	1	1	4 Buttons	Powder	Slurry	2(4)	5	5	1	1	1	1	1	1	1
14.6	14.7	30.7	18.122	4.8	from 8	--	98.73	134.793	25.86	16.04	20.6	17.35	10.05	31.84	26.73
250	250	250	250	250	250	250	500	500	250	1000	250	250	250	250	250
16 M	16 M	16 M	16 M	16 M	16 M	<16 M	16 M	16 M	16 M	4 M	16 M	16 M	16 M	16 M	16 M
0.04 M	0.08 M	0.04 M	0.04 M	--	0.04 M	<0.04 M	0.02 M	0.04 M	--	0.04 M	0.04 M	0.04 M	0.04 M	0.04 M	0.04 M
--	--	--	--	--	--	--	--	--	0.04 N Na_2SiF_6	--	--	--	--	--	--
Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	Pyrex	STAINLESS STEEL TYPE 347				
15.33	52.27	84.16	15.82	5.993	15.47(3)	142.5	59.8	167.9	65.03	11.00	67.63	CORROSION TESTS WERE RUN SIMULTANEOUSLY			
0.032	0.090	0.206	0.055	--	--	0.113	0.558	0.114	0.084	--	1.460				
13.11	13.2	13.26	13.05	--	--	11.95	--	--	[illegible]	--	12.73				
16.43	54.68	99.54	19.08	--	--	(5) 190.7	(6) 141.5	190.1	74.55	--	81.12	--	--	--	--
0.018	0.101	0.160	0.070	--	--	0.106	0.064	1.175	0.099	--	3.090	--	--	--	--
12.72	13.1	12.29	11.86	--	--	11.59	11.01	--	--	--	--	--	--	--	--
17.22	61.21	110.6	22.51	--	--	--	183.6	(7) 224.9	87.73	18.29	67.94	76.79	58.28	91.46	129.5
0.036	0.109	0.187	0.092	--	--	--	0.090	0.089	0.094	--	3.120	5.699	11.296	3.385	0.404
11.82	13.0	9.6	13.37	--	--	--	11.78	10.25	11.60	--	--	11.46	12.05	7.65	12.72
26	84	75	14	39	100(3)	--	31	62	69	70	--	--	--	--	--
28	88	87	21	--	--	95%	73	71	81	--	--	--	--	--	--
30	98	96	25	--	--	--	95%	82	94	95	--	>99	>99	95	100
Metallic	Considerable Powder	Considerable Powder and Metallic Flakes	--	Powder	Powder	Metallic	4 Powdered 1 Metallic	3 Powdered 2 Metallic	Metallic	Considerable Powder	--	--	Metallic	Metallic	Powder
1 Month	1 Month	1 Month	--	2 Months	--	--	9-13 Months	9-12 Months	2 Months	2 Months	--	3 Months	3 Months	3 Months	10 Months
Pieces and Powder	Pieces	--	Pieces	Powder	--	Pieces	Pieces	Powder and Pieces	Pieces	Powder and Pieces	--	--	--	--	--
	53.547			Slurry	Solution	--	Residue	210.77	Residue	Some	Some	--	--	--	--
89.9				to 8-A	to 8-B	90.3	to 10	90.3	to 12	Residue	Residue	--	--	--	--

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TABLE II

CORROSION OF MATERIALS OF CONSTRUCTION
BY HALIDE-CONTAINING ACIDS USED FOR PLUTONIUM DISSOLUTION

l Conc: of Acid Used	Volume of Acid	Test Container	Area of Specimen	Other Materials Present During the Test	Apparent Penetration(2) Inches Per Year	Basis	Test Conditions
NO_3 0.04 M HF	250 ml.	309 Cb.	9.35 in.^{2}	Stainless Container	0.27	Wt. Loss	Immersion in boiling acid
"	"	"	"	" "	0 during second 4 hrs.	"	" " " "
"	"	"	"	" "	0.40	"	" " " "
"	"	"	"	" "	0.94	"	" " " "
[illegible]	"	"	"	" "	0.78	"	" " " "
"	"	"	"	" "	0.53	"	" " " "
"	"	"	"	" "	0.41	"	" " " "
NO_3 0.04 N Na_2SiF_6	"	"	"	" "	0.12	"	" " " "
NO_3 0.04 M HF	"	Specimen	40.5 in^2	Pyrex Specimen	0.48	(1) Fe in soln.	" " " "
"	"	"	"	" "	0.46	(1) "	" " " "
"	"	"	"	" "	0.30	(1) "	" " " "
0.04 N Na_2SiF_6	"	"	"	" "	0.26	(1) "	" " " "
"	"	"	"	None	0.40	(1) "	" " " "
0.16 N Na_2SiF_6	"	"	"	None	0.83	(1) "	" " " "
0.04 M HF	"	"	"	None	0.60	(1) "	" " " "
"	"	347	4.75 in^2	347 and 347 Ta Cb and Pu	0.21	Wt. Loss	" " " " during skull dissolution
"	"	347	"	347 and 347 Ta Cb and Pu	0.15	"	" " " " " " "
	"	Pyrex	"	347, 347 Ta Cb and 304 ELC	1.81	"	" " " "
	"	"	1.83	347, 309, Cb and 304 ELC	0.42	"	" " " "
	"	"	4.75	309 Cb, 347 TaCb and 304 ELC	8.64	"	" " " "
	"	"	"	309 Cb, 347 TaCb and 347	2.88	"	" " " "
HNO_3 0.04 M HF	"	347	"	347 and 347 Ta Cb and Pu	0.62	"	" " " " " " "
"	"	"	"	347 and 347 Ta Cb and Pu	0.44	"	" " " " " " "
"	"	"	"		Nil	"	Vapor above boiling acid during skull dissolution
"	"	"	"		0.15	"	" " " " " " "
"	"	"	"		0.10	"	" " " " " " "
"	"	"	1.83		0.71	"	" " " " " " "
"	"	"	"		0.70	"	" " " " " " "
"	"	"	"	347 and 309 Cb and Pu	0.51	"	Immersion in boiling acid during skull dissolution
"	"	"	"	347 and 309 Cb and Pu	0.50	"	" " " " " " "
"	"	"	4.75	304 ELC and 347 Ta Cb	0.59	"	" " " " " " "
"	"	"	"	304 ELC and 347 Ta Cb	0.52	"	" " " " " " "
"	"	"	"		0.12	"	Vapor above boiling acid during skull dissolution
"	"	"	1.79		1.87	"	" " " " " " "
"	"	"	12.22		0.04	"	" " " " " " "
"	"	"	12.22	Pt, Pu and 309 Cb	Nil	"	" " " " " " "
"	"	"	4.92	Ta, Pu and Stainless	Nil	"	Immersion in " " " " "

9 Cb is Fe and that only the immersed surface was corroded.

s. Actual penetration would be higher if the acid were not depleted by reaction with the

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TABLE III

SKULL DISSOLUTION IN BOILING SULFURIC ACID

H_2SO_4 Molar Concentration	Mole Sulfate Per Mol Pu	Skull Weight and Condition gms.		Skull Solution After 1 Hour of Refluxing				Color of Residue	% of Pu Dissolved	Further Refluxing				
				g. Pu/l.	g. H⁺/l.	g. Fe/l.	Color			Hours	g. Pu/l.	g. H⁺/l.	g. Fe/l.	% of Pu Dissolved
0.25	2.0	0.81	Flake	27.2	0.32	--	Purple	Olive	92					
0.25	2.0	1.31	Flake	8.56	0.25	0.028	Purple	Olive	29					
0.25	4.6	6.5	Flake	12.72	--	--	"	"	97					
0.25	10.3	0.81	Flake	5.13	--	0.017	"	"	88					
0.75 M H_2SO_4-1 M HNO_3	2.0	1.43	Flake	31.89	--	--	"	"	18					
0.5	1.5	1.89	Powder	11.45	0.11	0.029	"	"	18					
0.5	1.7	7	Flake	18.86	--	--	"	Black	12					
0.5	1.7	0.1	Flake	53.88	--	--	"	"	40					
0.5	2.0	1.47	Powder	48.9[illegible]	0.43	0.039	"	--	82					
0.6	2.0	1.02	Flake	46.6[illegible]	0.35	0.03	"	Blue	78					
0.5	2.6	1.01	Flake	46.62	0.41	0.02	"	"	88					
0.5	3.5	0.89	Flake	32.39	0.72	0.017	"	"	96					
0.5	5.0	0.95	Flake	18.41	0.86	0.01	"	Olive	91					
4.5	10.2	0.73	Powder	12.47	0.82	0.019	"	"	95					
0.5	10.0	1.45	Powder	10.91	--	0.018	"	"	81					
0.5	10.0	2.5	Flake	28.82	--	--	"	--	100					
0.5	2.0	14	Powder and Metal	11.26	0.52	0.007	"	Olive	19	5	12.38	0.51	0.008	29
0.85	5.0	15.4	Metallic	25.11	1.71	0.021	"	"	58	2	42.58	1.50	0.019	96
1.5	1.5	2.39	Powder	35.6	1.05	0.032	"	"	16					
1.5	2.0	2.47	Flake	24.8	1.58	0.034	"	Blue	14					
1.5	4.0	0.56	Flake	30.2	2.27	0.022	"	"	33					
1.5	5.0	1.96	Flake	29.38	1.80	0.018	"	"	41					
1.5 M H_2SO_4-0.05 M HF	2.0	1.43	Flake	16.33	--	--	Brown	Olive	18					
2.0	5.1	0.9	Flake	9.07	--	--	Brown	--	100					
3.0	2.0	2.52	Flake	56.6	3.29	--	Purple	Blue	16					
3.0	4.0	1.99	Flake	38.02	3.13	0.025	Purple	--	21					
3.0	10.0	1.24	Flake	20.9	4.90	0.014	Purple	Dark	29					
8.0	18	0.6	Flake	1.46	--	--	Brown	Pink	12					
18.0	36	0.8	Flake	0.40	--	--	Brown	Pink	3					

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TABLE IV

OXIDATION OF PLUTONIUM METAL

	Button	Button	Button	Button	Button	Button	Button	Skull	Skull
	4.150	4	5.6	2.0	3.5	3	9	13.8	14
	Water	Water	Water	16 $\underline{M}$ HNO_3	15% H_2O_2	90 Volts D.C.	Steam	Steam	Water
	9 ml.	9 ml.	9 ml.	12 ml.	10 ml.		10 ml. H_2O	9 ml. H_2O	12 ml.
	45 Min.	60 Min.	60 Min.	60 Min.	60 Min.	18 Hrs.	30 Min.	60 Min.	60 Min.
.	100-225°C.	15°C. after 0 Min. 60°C. " 10 Min. 115°C. " 20 Min. 135°C. " 30 Min. 198°C. " 40 Min. 210°C. " 50 Min. 200°C. " 60 Min.	140°C. after 0 Min. 140°C. " 15 Min. 190°C. " 16 Min. 190°C. " 25 Min. 180°C. " 30 Min. 170°C. " 40 Min. 140°C. " 60 Min.	160°C.	150-195°C.	Room	145-150°C. For 10 Min. 190°C. 20 Min.	140-210°C.	150-230°C.
s quenched er after s.	Bomb was quenched in tap water after 45 minutes.					70% HNO_3 used as the electrolyte	Bomb was quenched in tap water after 30 min.	Bomb was cooled in air.	Bomb was cooled in air.
BOMBS WERE COOLED IN AIR									
	Black	Black	Black and Green	Cream	Dk. Green	Black	Olive Green	Olive Green	Black and Green
	95	100	100	75	100	30	100	100	100
	4				11		8.27	12.3	13.55
HNO_3 0.04 $\underline{M}$ HF WAS USED FOR ALL DISSOLUTIONS									
	100 ml.			The cream colored material from the HNO_3 oxidation dissolved more slowly than the other products.	250 ml.		Dissolutions were very slow and some residue remained after 3-4 hours in boiling acid.		
	--								--
	100%								100%
							9.94	15.10	17.40
							287	292	307

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TABLE V

THE OXIDATION OF PLUTONIUM METAL BY BOILING NITRIC ACID

Source of Plutonium Metal	Skull	Button	Button	Skull	Skull	Skull	Button	Button	Button	Skull	Button	Skull	Button
Weight of Plutonium, grams	3	3.2	2.8	3	4	7	3	4	3	3	3.4	3	3
Concentration of HNO_3 $\underline{M}$	0.1	0.1	0.33	0.5	0.5	0.5	0.67	0.67	0.67	1.0	1.0	4.0	16
Volume of HNO_3, ml.	375	1000	300	90	250	500	150	150	150	150	100	65	100
Special Conditions	--	--	--					Hg added					Hg added
Hours of Pu immersion in boiling HNO_3	1	1	1	1	17	1	1	1	1	1	1	3	1
Grams Pu per liter of solution	-	0.062	0.221	--	2.22	2.77	--	0.884	0.809	--	1.361	0.10	2.110
% Pu dissolved	--	2	2	--	55.6	20	--	3.3	4.9	--		3	6.7
% Pu converted to oxide or nitrate*	50	12	11	90	100	80	20	10	20	75		50	--
Hours of Pu immersion in boiling HNO_3	2			2		24		3		2	3		
Grams Pu per liter of solution	--			--		3.05		0.931		--	2.717		
% Pu dissolved	--			--		20		3.5		--			
% Pu converted to oxide or nitrate*	80			99		100		15		90			
Hours of Pu immersion in boiling HNO_3	3			3		48				3			
Grams Pu per liter of solution	--			15.32		3.71				1.52			
% Pu dissolved	--			45		20				7.5			
% Pu converted to oxide or nitrate*	100			100		100				100			
Hours of Pu immersion in boiling HNO_3						72							
Grams of Pu per liter of solution						4.09							
Final Volume, ml.						280							

* Determined by metallic residue weight.

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TABLE VI

SPECTROGRAPHIC ANALYSIS OF SKULL SOLUTION

	ppm, Based on Plutonium	
Impurity	Skull Solution Z-10-2-9	Average Feed Solution(5.) to Hanford Oxalate Process October 1950
Al	40	43
Ba	< 20	< 20
Be	< 0.02	< 0.02
Ca	100	55
Cd	< 10	40
Co	< 20	30
Cr	40	2500
Hg	< 200	< 200
In	< 100	3
La	> 2000	2000
Li	< 2	3
Mg	400	120
Mn	10	375
Na	100	125
Ni	20	2.50
Pb	< 100	45
Sr	< 4	< 4
Zn	< 100	< 100
Tl	< 100	< 100

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TABLE VII

CORROSION OF MATERIALS OF CONSTRUCTION BY BOILING

0.5 M H_2SO_4

Metal	48 Hr. Period	Penetration in Inches Per Month Vapor Phase	Interface	Liquid Phase
Chemical Lead	First	0.0001	+ 0.0015	+ 0.0011
	Second	0.0011	0.0013	0.0001
	Third	0.0002	0.0004	0.0010
	First	0.0048	+ 0.0035	+ 0.0007
	Second	0.0008	0.0027	0.0001
	Third	0.0006	0.0006	0.0009
	Average	0.0013	0.0017	0.0007
Stainless #316	First	0.0014	0.0002	0.0001
	Second	0.0065	0.0682	0.0653
	Average	0.0039	0.0342	0.0327
Duriron	First	0.0002	0.0036	0.0061
	Second	0.0001	0.0011	0.0009
	Third	0.00005	0.0009	0.00025
	Average	0.0001	0.0019	0.0024
Carpenter #20	First	0.00032	Nil	Nil
	Second	0.00032	Nil	0.00004
	Third	Nil	0.0016	0.0018
	First	Nil	Nil	0.0037
	Second	0.0001	Nil	Nil
	Third	Nil	Nil	0.00001
	Average	0.0001	0.0003	0.0011

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