THE IMPREGNATION OF GRAPHITE WITH
NEPTUNIUM OXIDE

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1. INTRODUCTION	1
2. SUMMARY	1
3. MATERIALS	2
3.1 Graphite	2
3.2 Neptunium	2
3.3 Uranyl Nitrate	4
4. IMPREGNATION PROCESS	4
4.1 Impregnation	4
4.2 Drying	6
4.3 Calcination	6
5. EXPERIMENTAL RESULTS	7
6. DISCUSSION	10
6.1 Impregnation	11
6.2 Drying	12
6.3 Calcination	13
7. PROCESS EVALUATION	14
8. RECOMMENDATIONS	15
9. REFERENCES	15

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1. INTRODUCTION

The use of aluminum as the matrix in the preparation of neptunium target elements results in a high Pu^{236} content in the Pu^{238} due to a γ -n reaction. It has been proposed that a composite neptunium oxide-graphite element be substituted to eliminate the γ -n reaction. At the request of Douglas United Nuclear, Battelle-Northwest is evaluating two methods of preparing the neptunium oxide-graphite composites. The Materials Department is investigating the preparation of composite pellets prepared by cold pressing graphite-neptunium oxide powder mixtures. The Chemistry Department studied the preparation of oxide-graphite composites by impregnating graphite with a neptunium solution and subsequently calcining the neptunium to the oxide. This report summarizes the results of this study.

2. SUMMARY

A total of eight graphite pieces were impregnated with neptunium oxide for use as target elements in experimental Pu^{238} production. The neptunium content of each element varied from 37.1 to 41.4 grams with a total of 316.4 grams of neptunium in the eight elements.

The impregnation process consisted of soaking the graphite element (TSF grade graphite) in neptunium nitrate solution to fill the voids, drying the element to remove the excess water, and then calcining at 1000°C under an argon atmosphere to convert the neptunium to the oxide. The entire cycle required approximately sixteen hours, and four to five cycles were required to reach the desired neptunium concentration of forty grams per element.

After completion of the impregnation process, the elements were transferred to the Materials Department for canning.

3. MATERIALS

The specifications set forth by DUN required that the materials used in preparing the target elements be suitable for reactor use. The following sections describe all of the materials used in preparing the elements.

3.1 Graphite

The graphite used in preparing the target elements was National Carbon Company grade TSF (equivalent to the old grade GBF), a highly purified grade of nuclear graphite. A summary of the properties of this material is given in Table I.

Two types of graphite shapes were used in preparing the target elements:

1. A solid cylinder having a diameter of 1.505 inches and a length of 8.510 inches.
2. An annular cylinder with an outer diameter of 1.505 inches, inner diameter of 0.500 inches, and a length of 8.510 inches. Upon completion of the impregnation process a rod of TSF graphite was inserted into the annular element to increase the element density.

The graphite shapes were machined from cylindrical stock with the grain of the graphite paralleling the longitudinal axis of the element. The machined pieces were leached in boiling 8N nitric acid for several hours, prior to impregnation, to remove impurities and particulate matter which may have been present. The graphite was then washed with distilled water and dried at 250-300°C.

A high porosity graphite (National Carbon Company Grade 60) having greater than 50% void space was also used in some later test experiments to determine the effect of porosity on the impregnation process. It was not used, however, in preparing any of the target elements.

3.2 Neptunium

The neptunium used in preparing the target elements was received from Isochem Inc. (now ARHCO) as a concentrated nitrate solution. The composition

TABLE I

Properties of TSF Graphite

Density (g/cm ³)	1.71
Specific Resistance (μΩ-cm)	
With Grain	932
Across Grain	1190
Thermal Expansion Coef. (10 ⁻⁶ °K ⁻¹)	
With Grain	~ 2.22
Across Grain	~ 3.77
Tensile Strength (lbs/in ²)	
With Grain	~ 1440
Across Grain	~ 1260
Compressive Strength (lbs/in ²)	
With Grain	~ 5990
Across Grain	~ 5960
Ash Content (wt. %)	< 0.01
Boron (wt. %)	0.00002
Gas Evolution (cc/gm at 1500°C)	0.17
σ _a (Millibarns)	3.52

TABLE II

Composition of Neptunium Solution Used in Impregnation

Np	398 g/liter
H ⁺	9.48 N
NO ₃ ⁻	14.0 M
Density	1.75 g/cm ³
U	0.05 g/liter
Pu239	0.11 g/liter

Ag	50 ppm	Li	< 10 ppm
Al	50	Mg	20
As	< 20	Mn	10
Bi	< 1	Mo	< 5
Ca	20	Na	2000
Cd	< 1	Ni	5
Cr	20	P	< 100
Cu	< 1	Si	50
Fe	600	Ti	< 2
Ge	5	V	< 10
K	20	Zr	10

of the solution is given in Table II. The solution was prepared by R. S. Kingsley (Plutonium Chemistry Laboratory - Isochem, Inc.) by concentrating the neptunium product solution from the Purex Plant. The concentrating was accomplished by evaporating the solution in a titanium evaporator. The maximum concentration was determined by the solubility of neptunium in the cold solution which was approximately 410 grams per liter.

3.3 Uranyl Nitrate

In checking out the impregnation process, several trial runs were made in which graphite pieces were impregnated with depleted uranium. This was done using a uranyl nitrate solution. The solution was prepared by dissolving micronized uranium dioxide in nitric acid to give a uranium concentration of 500 grams per liter.

4. IMPREGNATION PROCESS

The process used to impregnate graphite with neptunium oxide is a modification of the process developed by DeHollander⁽¹⁾. It consists of (1) saturating the graphite with neptunium solution, (2) drying the impregnated graphite to remove the water, and (3) calcining the dried element to convert the neptunium to the oxide. Each of the three steps is discussed in detail below.

4.1 Impregnation

A weighed graphite shape which has been leached with nitric acid and dried is immersed in the neptunium nitrate solution. The containment vessel is sealed and a vacuum applied (see Figure 1-A) to remove the air trapped in the void space of the graphite. The vacuum is maintained about five minutes and released. This step is repeated several times until gas evolution has ceased.

The graphite element, which is now partially saturated with solution, is removed from the vessel and allowed to drain for a few minutes to remove any excess solution. Under normal conditions less than a milliliter of solution will drain from the element. The element is then weighed to

AImpregnation Equipment BDrying Equipment CCalcining EquipmentFigure 1

EQUIPMENT FOR IMPREGNATING GRAPHITE WITH
NEPTUNIUM OXIDE

determine the volume of solution which has been taken up by the graphite.

Normally this will amount to about 80% of the initial void space of the graphite.

4.2 Drying

The impregnated graphite element is then placed in a device where it can be rotated with its longitudinal axis in a horizontal position (see Figure 1-B). The element is rotated at a speed of approximately 30 RPM while being heated with a heat lamp to evaporate the water and nitric acid and convert the neptunium to a solid form. The rate of heating must be quite slow to insure that a uniform distribution of the neptunium is obtained. If the element is heated too rapidly, gas evolution in the center portions of the graphite can force solution to the periphery of the graphite and give an uneven neptunium distribution. Too high a rotational speed can have the same effect.

Normally, the graphite is heated to about 250°C under the heat lamp. The entire drying cycle takes about eight hours. The rate of heating should be as uniform as possible from room temperature to the final 250°C to prevent solution flow.

4.3 Calcination

Upon completion of the drying step the element is placed in a vycor tube which is in turn placed in a vertical tube furnace (Figure 1-C). The vycor tube is purged with argon and slowly heated to 1000°C under a flowing argon atmosphere. Nitrate decomposition becomes apparent at about 400°C and is essentially complete at 600-650°C. The neptunium in the graphite is converted to the oxide.

The element is maintained at 1000°C for a short period of time and then cooled to room temperature under argon. The element is weighed and its neptunium content is determined by weight gain, assuming that the weight increase is NpO_2 .

The complete impregnation-drying-calcination cycle takes about sixteen hours. If additional neptunium impregnation is required the entire cycle is repeated.

5. EXPERIMENTAL RESULTS

A total of eight neptunium oxide impregnated graphite target elements were prepared. The composition and physical characteristics of the eight elements are summarized in Table III. The neptunium concentration desired was forty grams per element. As can be seen from the table the actual concentrations varied from 37.1 to 41.4 grams per element. The large number of variables involved in the impregnation process made it difficult to control the neptunium level of the impregnated element within $\pm 5\%$ of the desired concentration. Those elements with neptunium contents below the desired level could have been reimpregnated to a higher level but this was not done because of the time requirement of the program.

The only non-destructive method available at this time for determining the neptunium content of an impregnated element is by weight gain of the graphite section during the processing. This assumes that no graphite is lost and that any weight gain is due to neptunium oxide (NpO_2). DeHollander⁽¹⁾ reported in his work with PuO_2 impregnation of graphite that when graphite is saturated with nitric acid and then heated to 1000°C under argon a weight loss of graphite amounting to about 1% occurs. With elements of the size used in this work this would amount to about 4 grams loss per element. However, when we heated graphite elements in a similar manner a weight loss of only 0.1-0.2 grams per element was detected. This would indicate that basing the neptunium content on the weight gain of the element should be accurate to about $\pm$ one gram when four-five impregnation cycles per element are used.

TABLE III

Composition and Physical Characteristics of
NpO₂ Impregnated Elements

Element No.	Type	Weight (Grams)		NpO ₂ (Grams)	Np (Grams)	Density (g/cm ³)		Final Dimensions (Inches)	
		Initial	Final			Initial	Final	Diameter	Length
1	Solid	408.5	450.6	42.1	37.1	1.65	1.81	1.506	~8.510
2	Solid	402.7	449.1	46.4	40.9	1.63	1.81	1.506	~8.510
3	Solid	407.5	452.5	45.0	39.6	1.65	1.82	1.508	~8.510
4	Solid	410.1	452.6	42.5	37.5	1.66	1.82	1.507	~8.510
5	Annular	346.5*	389.6*	43.1	38.0	-	1.76**	1.503	~8.510
6	Annular	343.8	390.2	46.4	40.9	-	1.76	1.509	~8.510
7	Annular	345.6	392.6	47.0	41.4	-	1.77	1.506	~8.510
8	Annular	364.3	410.8	46.5	41.0	-	1.82	1.507	~8.510

* The weights given for the annular elements do not include the weights of the graphite inserts.

** Includes the weight of the graphite insert.

A neptunium material balance for the entire impregnation program shows a substantial neptunium loss that cannot be accounted for at this time (see Table IV - Column 2). However, a discrepancy in the amount of material received from Isochem based on Isochem analyses and BNW analyses could possibly account for a substantial portion of the neptunium unaccounted for at this time. In addition, if the graphite losses during impregnation and calcination were greater than expected from the preliminary tests, this could account for a portion of the neptunium loss.

TABLE IV

Neptunium Material Balance for Impregnation Program

	<u>Isochem Analysis</u>	<u>BNW Analysis</u>
Neptunium Received From Isochem	458.8 g	414.6 g
Neptunium Transferred to Materials Department	316.4 g	316.4 g
Neptunium Returned to Isochem (Based on BNW Analysis)	89.1 g	89.1 g
Neptunium Unaccounted For	53.3 g	9.1 g

While the target elements were being prepared, two small graphite samples were impregnated to the same approximate oxide content as the elements. These samples were used for chloride and off gas analyses. The specifications set by Douglas United Nuclear calls for the following impurity levels in the elements:

Chloride	35 ppm maximum
Nitrogen	125 ppm maximum
Other Non-Condensable Gases	75 ppm maximum

The chloride analysis gave a value of < 10 ppm, which is the detectable limit of the analytical method used. The off gas analysis, however, showed that the impregnated graphite adsorbed substantial amounts of gas when exposed to air after completion of the calcination step. The analytical sample which had been exposed to air for about one week after being calcined and before analysis gave the following off gas analyses*:

Volume: $3.12 \text{ cm}^3/\text{g}$ of sample

Composition:	CO_2	6.1 Mole %	373 ppm
	CO	13.6	530
	O_2	15.0	668
	N_2	57.4	2240
	H_2	7.1	20
	Ar	0.6	35
	He	< 0.01	< 0.1
	CH_4	0.2	4

* The off gas analysis procedure consists of placing the sample in a tantalum crucible in a vacuum system, evacuating the system, and then heating the crucible under vacuum to 1000°C . The total gas evolved upon heating is collected, its volume measured, and its composition determined by mass spectrograph.

The volume of gas evolved far exceeded the specification limit set by DUN. By heating the elements under vacuum to a high temperature and then exposing to air only briefly prior to canning it is possible to reduce the adsorbed gases to an acceptable level. Analysis of a graphite sample given such a treatment showed the following composition:

Volume:	0.62 cm ³ /g of sample	
Composition:	CO ₂	76.5 mol %
	CO	19.7
	O ₂	0.2
	N ₂	1.1
	H ₂	2.3
	Ar	< 0.01
	He	< 0.01
	CH ₄	2.3

The CO and CO₂ are due to the reaction between graphite and the oxide. This would not be a problem in a sealed system since the equilibrium partial pressure of the CO and CO₂ would be very low at the element temperature in the reactor. The total of the other gases is low enough that they would not be a problem. Therefore, by outgassing the graphite elements under vacuum prior to canning it is possible to meet the DUN specifications.

6. DISCUSSION

In impregnating the eight graphite elements for use in the test program, the process and equipment used were those which appeared best suited to a laboratory development program from the standpoint of the limited time and funds available. The exact procedures and equipment used would not be directly applicable to a production operation. In the following paragraphs the various steps of the process will be discussed in detail with special emphasis on how the process could be applied to a production operation.

6.1 Impregnation

In impregnating the graphite matrix with neptunium oxide four to five impregnations were required to reach the desired neptunium concentration of forty grams per element. Table IV shows a typical impregnation study in which four cycles were required. There are several ways in which the number of cycles required could be reduced:

1. Change the impregnation step so that essentially 100% of the void space is filled each cycle.
2. Use a more porous graphite.
3. Use a solution having a higher neptunium concentration.

There are two ways in which the extent of impregnation could be increased. One is to heat the neptunium solution to the boiling point during the impregnation cycle. This helps remove the gases trapped in the graphite matrix and will give essentially 100% saturation. The second method is to apply a vacuum to the graphite matrix before it is immersed in the neptunium solution. This procedure will also give close to 100% saturation of the graphite. Neither process was used in preparing the test elements because of the extra equipment involved, but either could be applied very easily to a production operation. If the heated solution technique is used, care must be taken to see that water is not evaporated to the point where precipitation of the neptunium occurs.

TABLE IV

Typical Impregnation Study

<u>Annular Cylinder Matrix</u>	<u>1st</u> <u>Cycle</u>	<u>2nd</u> <u>Cycle</u>	<u>3rd</u> <u>Cycle</u>	<u>4th</u> <u>Cycle</u>
Initial Element Weight (grams)	345.6	363.6	375.9	384.9
Weight Calcined Element (grams)	363.6	375.9	384.9	392.6
Neptunium Oxide in Element (grams)	18.0	30.3	39.3	47.0
Neptunium in Element (grams)	15.8	26.6	34.6	41.4

If a high porosity graphite is used as the target matrix it should be possible to impregnate to the desired neptunium content with one or two

cycles. With a graphite matrix having a porosity of 50% a single cycle would theoretically give greater than forty grams neptunium per element assuming 100% saturation and 400 gram per liter neptunium solution. A test run was made using uranium solution and National Carbon Company Grade 60 porous graphite to determine the extent of impregnation. The test conditions and results are summarized in Table V. From these results it can be seen that using a solid porous graphite matrix an impregnation of forty grams neptunium per element could be achieved with a single impregnation cycle.

TABLE V

Impregnation Test Using Porous Graphite

Graphite Matrix	National Carbon Company Grade 60	
	Length	8.50
	Outer Diameter	1.50
	Inner Diameter	0.75
	Porosity	51%
	Void Volume	92.5 cm ³
Uranium Solution	Uranium	360 g/liter
	Density	1.65 g/cm ³
Results	Solution Uptake	89 cc
	% of Saturation	96 %
	Calcined Oxide	37.8 grams
	Uranium	32 grams*

*Assuming uranium is present as U_3O_8 .

6.2 Drying

The basic problem in drying the saturated graphite element is to insure that solution flow does not occur during drying. If solution flow does occur, an uneven distribution of neptunium in the graphite matrix is the result. It was shown by DeHollander⁽¹⁾ that if the saturated graphite is dried in a stationary position gravitational force will cause the heated solution to flow to the lower portions of the graphite. To prevent this it is necessary to rotate the graphite. Even with rotation some solution flow will occur if the drying rate or rotational speed are too high. This is

evidenced by "blistering" on the surface of the graphite. The drying rate must be sufficiently slow that evaporation proceeds from the outer periphery of the graphite inward to the center of the element. If evaporation occurs in the center portions of the graphite before the outer portions are dry the solution will be forced to the periphery and result in uneven distribution. With too rapid a rotational speed centrifugal force will force solution to the periphery of the element. With neptunium solution of the composition used in this work a rotational speed of about 30 RPM appears to be optimum, although speeds as high as 50 RPM do not appear to be deleterious.

At the time this work was performed there were no nondestructive methods available for determining the neptunium distribution in the graphite matrix. Destructive methods were used with uranium impregnated elements, however, and these tests showed that the impregnation procedure described in Section IV gave a uniform oxide distribution. For example a uranium impregnated element (40 g U/element) was sectioned into four equal sections and then burned in air to oxidize the graphite. The residual uranium oxide for each section was weighed and the weights agreed within 0.1-0.2 grams ($\pm 1\%$). When the graphite was oxidized away the uranium oxide retained approximately the same shape as the graphite matrix, and there was little visual evidence of uranium concentration at the periphery as compared to the center of the shape.

6.3 Calcination

The primary objectives in calcining the elements are to (1) insure that the neptunium is converted to the oxide, and (2) be certain that all of the water and residual gases are removed. The first can be accomplished by heating the elements to 1000°C in a flowing argon system. To reach the second objective, however, it is necessary to subject the elements to a high vacuum and temperature prior to canning. Between the vacuum heating and canning step the elements should be exposed to air for as short a time as possible. Since the rates of oxygen and nitrogen adsorption on the elements appear to be fairly

slow, some exposure to air can be tolerated, but should be reduced as much as possible.

In analyzing the impregnated graphite for residual gases some carbon monoxide and carbon dioxide are formed by the reaction of the graphite with the neptunium oxide. In a sealed system, such as a canned element however, the equilibrium partial pressure of the CO and CO₂ would be quite low at the temperatures involved and these gases would not present a problem as far as can pressurization is concerned.

Based on the data supplied by National Carbon Company, TSF graphite should evolve about 0.17 cm³ of gas per gram of graphite when heated to 1500°C. Since the impregnated graphite, after exposure to air for substantial periods of time, shows a much greater gas evolution (approx. 20X) this would indicate that the neptunium oxide is primarily responsible for the gas evolution. It is possible that some activation of the graphite surface has occurred to increase gas adsorption on the surface, but this does not appear to us to be very likely.

7. PROCESS EVALUATION

Based on the limited amount of work performed on the impregnation process the following evaluation of the process can be made:

1. Graphite can be impregnated to the desired neptunium level by repeated impregnation cycles. With graphite of medium porosity (approximately 26% voids) 4-5 cycles are required.
2. With correct processing, the neptunium distribution within the graphite matrix is fairly uniform.
3. Gas evolution from a calcined element is high unless the element is subjected to a high vacuum at 700-1000°C. After evacuation the element can be exposed to the air for short periods of time prior to canning without gas evolution becoming a problem.

4. By using a high porosity graphite (approximately 50%) the number of impregnation cycles required can be reduced to one or two.
5. The laboratory procedure used for impregnation can be easily scaled up to a production operation with a few minor modifications in equipment design. However, unless porous graphite can be used, the over-all time requirements of the process, due to repeated cycles, make it appear to be impractical for a production operation.

8. RECOMMENDATIONS

If the impregnation process is to be used for Pu²³⁸ target element production it is recommended that the following studies should be made:

1. The use of porous graphite as the target matrix should be thoroughly investigated. If porous graphite cannot be used, the impregnation process does not appear to be feasible due to the repeated cycles required.
2. A method for determining the neptunium content of the calcined element, other than weight gain, should be developed. Material balance analyses do not appear to be sufficiently accurate to give a satisfactory measure of the neptunium content.
3. A nondestructive method for determining the neptunium distribution in the graphite matrix should be developed.
4. Leaching and burning studies, aimed at developing a process to recover neptunium and Pu²³⁸ from irradiated elements should be initiated.

9. REFERENCES

1. W. R. DeHollander, General Electric Company, Unpublished Data, 1959.