PREPARATION AND CHARACTERIZATION OF
 $\text{NpO}_2\text{-CaO-ZrO}_2$ TARGET RODS FOR Pu^{238} PRODUCTION
IN COMMERCIAL WATER REACTORS

by

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY.	1
INTRODUCTION	1
MATERIAL SELECTION	4
Target Constituents	4
Cladding Components	8
PELLET PREPARATION	16
Target Specifications	16
Target Fabrication	17
Zirconia Pellet Fabrication	22
PELLET CHARACTERIZATION	25
Chemistry	25
Metallographic Examination.	31
Autoradiography	35
PROPERTY MEASUREMENTS	39
Thermal Expansion.	39
Thermal Cycling	41
COMPATIBILITY TESTING	43
ENCAPSULATION AND QUALITY ASSURANCE	47
Weld Qualification	47
Encapsulation Procedures	51
Cleaning and Inspection.	52
SHIPMENT AND ASSEMBLY.	55
DISCUSSION AND CONCLUSIONS	55
ACKNOWLEDGMENTS.	58
REFERENCES.	58
APPENDIX.	A-1

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SUMMARY

Two neptunia-zirconia-fueled target rods, each containing four sections of different neptunia concentrations, were fabricated and loaded into Connecticut Yankee Reactor* for irradiation. Nominal compositions of the target pellets in the sections were 15.18, 28.06, 48.76, and 77.22 w/o NpO_2 , with the balance of material being calcia-stabilized zirconia. Conventional ball-milling, cold-pressing, and sintering techniques were utilized for powder blending and pellet fabrication. Chemical analysis studies performed on selected pellets showed that total gas, moisture, and hydrogen contents, were considerably less than specified tolerances. Metallographic examination revealed a uniform porosity and grain structure which indicated that the distribution of constituents was homogeneous. This fact was essentially confirmed by autoradiographic examination. Limited thermal expansion and thermal cycling tests were performed on various pellets to confirm their conformance to design specifications and resistance to fracture during irradiation. All work was conducted according to rigid pellet fabrication and weld specifications as well as stringent quality assurance procedures for each phase of the assembly operation.

INTRODUCTION

By the end of the decade the needs for Pu^{238} are expected to exceed, by appreciable margins, present capabilities for production of this isotope within the USAEC Laboratories. This projection, to a great extent, depends heavily on continuation of existing space programs, but no major realignment is foreseen that would circumvent the need for radioisotope power sources. On this basis, then, one must look to commercial reactors as the only truly economical means of meeting the required production capacity.

A theoretical study of the feasibility of converting Np^{237} to Pu^{238} in commercial water reactors⁽¹⁾ was conducted by Southern Nuclear Engineering (SNE) under sponsorship of the Isotopes and Materials Branch of the USAEC in 1969. This work concluded that the approach was practical and the cost of Pu^{238}

* Owned by Connecticut Yankee Atomic Power Company.

could be reduced appreciably with preservation of adequate profit margins for the utilities. Questions still remained regarding limitations of the one-dimensional model used for the calculations and the unavailability of experimental data related to the characteristic behavior of neptunium in a light-water-reactor neutron environment. A project definition phase of a program aimed at generation of experimental and analytical data necessary to the critical analyses of the concept through use of a one-dimensional finite difference computer model was initiated by SNE in 1970⁽²⁾. This effort led to an agreement whereby Battelle's Columbus Laboratories (BCL) was responsible for the fabrication of two NpO_2 target assemblies which were to be irradiated in Connecticut Yankee Reactor owned by Connecticut Yankee Atomic Power Company (CYAPC). Design drawings with full specifications, and the results of multidimensional calculations for the target rods in a pressurized water reactor have been reported⁽³⁾.

Specifications called for the fabrication of two target rod assemblies, each consisting of four separate sections with different neptunium compositions and mass-volume relationships, as listed in Table 1. The target material was to be composed of neptunium dioxide mixed with a suitable diluent in the form of pellets sintered to a fairly high density to promote heat transfer. Seamless Type 304 stainless steel tubing was specified as the cladding material. Fin-shaped spacers were located on the top ends of each segment of the targets to position the rod within the thimbles of the control rod assemblies which were chosen for the irradiation.

Battelle's responsibility in the overall program was focused on experimental development and conduct of full quality assurance procedures for cladding examination, pellet fabrication, pellet characterization, some physical property measurements, rod segment welding, shipment, and final assembly and welding at the reactor site. This report covers the specifications and detailed process operations that were employed to fulfill this responsibility.

TABLE 1. SPECIFIED NEPTUNIUM CONTENT OF
VARIOUS TARGET ROD SEGMENTS

Segment		Neptunium Density, g per cm ³	Total Volume of Fuel Segment, cm ³	Total Mass of Neptunium, g
1A	2A	5.44	18.88	102.69
1B	2B	2.72	18.88	51.35
1C	2C	1.36	18.88	25.67
1D	2D	0.68	81.17	55.20

MATERIAL SELECTION

Target Constituents

Only a few properties of NpO_2 have actually been reported in the literature, and to complicate the situation further there are virtually no data relating to fabrication behavior. Ackermann, et al.⁽⁴⁾, previously worked with small quantities of NpO_2 to study its vaporization characteristics. Their work showed that NpO_2 was the principal vapor species although a tendency to become hypostoichiometric and form a lower oxide (probably Np_2O_3) through loss of NpO was found at high temperatures. In this respect the phase relationships found in the neptunium-oxygen system seem to closely resemble those established for plutonium-oxygen.

The theoretical density of NpO_2 was calculated to be 11.13 g per cm^3 based on the lattice constant value of 5.434 Å reported by Ackermann, et al.⁽⁴⁾. This information was of immense value throughout the program since it provided a means for calculation of reliable theoretical densities of neptunia solid solutions with the diluent material. These data in turn aided the interpretation of the sintering behavior as the approach to theoretical density was realized. Since little more was known of the intrinsic behavior of NpO_2 an assumption was made that its melting point, and phase interactions, would closely parallel those of UO_2 and PuO_2 based on the periodic table relationships of this family of actinide compounds. Moreover, the sintering characteristics of NpO_2 were assumed to be about the same as those of UO_2 and PuO_2 , which effectively bracketed the temperature range for attaining maximum densification between 1500 and 1700 C.

The optimum target appeared to be columns of pellets consisting of a dispersion of NpO_2 in some diluent added to reduce self-shielding of the neptunium. The term dispersion, as used here, is probably a misnomer since some solubility, perhaps complete, would be predicted under the sintering conditions imposed to obtain pellets with a high degree of resistance to fracture and spalling coupled with the optimum attainable heat transfer. Materials and techniques normally used for target fabrication⁽⁵⁾, e.g., powder metallurgical preparation of aluminum compacts with a uniform dispersion of NpO_2 , were unsuitable for this study because of the high temperatures involved in the irradiation. As a means of making a selection a list of some of the more important desired

characteristics of the diluent material was formulated, as given below:

- (1) Low neutron cross section
- (2) Good irradiation stability in a water reactor neutron spectrum
- (3) Excellent high-temperature stability, e.g., to temperatures near the melting point of NpO_2 or $\sim 2000^\circ\text{C}$ (3632°F)
- (4) High probability of predictable uniform sintering characteristics based on behavior with other actinide dioxides, e.g., UO_2 and PuO_2
- (5) Compatible with Type 304 stainless steel cladding at 600°F , the normal reactor water temperature during operations.

Other factors taken into consideration were the low calculated heat evolution from the target rod pellets and almost negligible problems of swelling from fission products, etc., normally associated with reactor fuels.

Based on the above criteria a decision was made to utilize CaO-stabilized ZrO_2 in solution with the NpO_2 . ZrO_2 was considered to be more favorable than Al_2O_3 because of possible deleterious side reactions associated with aluminum. Calcia stabilization of the zirconia appeared mandatory because of the complete lack of data on the $(\text{Np},\text{Pu})\text{O}_2$ - ZrO_2 system and the wide range of compositions called for in the target specifications.

Neptunium dioxide for this study was obtained from the Atomic Energy Commission via the Savannah River Plant. The powder was light green in color and was received with the specification sheet shown in Table 2. As a general observation, the impurity content of the NpO_2 powder, as determined by spectrographic analysis, was about the same as that expected in commercial-grade UO_2 and PuO_2 powders when the limits of detection and the spectrum of elements examined were evaluated. The low plutonium content of this material was considered to be essential for the planned irradiation to avoid excess fissioning within the targets.

The calcia-stabilized zirconia powder for use as the diluent with the neptunium dioxide was procured from the Zirconium Corporation of America (ZIRCOA). This material was ordered as nuclear-grade powder containing 10 to 12 w/o calcia of minus 325 mesh ($< 44\text{-}\mu$ particle size). A typical chemical analysis for impurities in the powder furnished by ZIRCOA is given in Table 3 together with the results obtained at Battelle-Columbus. As can be seen, the Battelle analysis is in fairly good agreement with that of the manufacturer. The relatively high silicon and sulfate contents of the powder were recognized as factors which could lead to fabrication difficulties but no other substitute material could

TABLE 2. RESULTS OF CHEMICAL ANALYSES ^(a) ON NpO₂
POWDER RECEIVED FROM SAVANNAH RIVER

Run Identification	010HB-14
Oxide Weight, g	850.0
Neptunium Oxide Assay, %	99.54
Neptunium in Neptunium Oxide, %	88.1
Neptunium Weight, g	745.37
Thorium, w/o oxide	0.14
Uranium, w/o oxide	L 0.10
Weight loss at 800 C, w/o oxide	0.21
Total Plutonium w/o oxide	0.02

Plutonium Isotopic Distribution

²³⁸ Pu	78.32
²³⁹ Pu	18.98
²⁴⁰ Pu	2.19
²⁴¹ Pu	0.376
²⁴² Pu	0.140

Spectrographic Analysis, ppm

Al, 150	Fe, 200	Ni, L50
B, L20	K, L 200	P, L500
Be, L10	Mg, 10	Pb, L10
Ca, L50	Mn, L 50	Si, L100
Cd, L10	Mo, L 10	Sn, L50
Cr, 30	Na, L 20	Zn, L200
Cu, L50		

(a) L = less than.

TABLE 3. TYPICAL AND ANALYZED IMPURITIES IN THE
CALCIA-STABILIZED ZIRCONIA POWDER^(a)

Impurity	Impurity Content, ppm	
	Typical ZIRCOA Analysis	BCL Analysis
Aluminum	100-300	40
Boron	0.5-2	<5
Cadmium	<10	<10
Chlorine	10-20	40
Cobalt	<10	<10
Chromium	10-30	10
Copper	<25	<10
Iron	85-400	150
Hafnium	50-100	<100
Magnesium	100-150	50
Manganese	<10	5
Nickel	N.A.	20
Lead	<25	<10
Silicon	280-600	300
Tin	≈10	<10
Titanium	<10	20
Vanadium	≈10	<10
SO ₄	100-400	30
Loss on ignition	0.3% max	N.A.

(a) ZIRCOA reactor-grade zirconia containing 10 to 12 w/o CaO.
N.A. = not analyzed.

be obtained in time to meet the commitments of the program. Removal of chlorine during sintering was expected; therefore, the high chlorine content of the powder did not present any cause for concern.

The stabilized zirconia powder was then examined by metallographic techniques in an effort to further characterize the material before blending with the neptunia. A photomicrograph from the mounted and polished powder specimen is shown in Figure 1. As expected, the particles were irregular in shape, and a cursory size analysis indicated that approximately 80 percent of the powder was $\leq 10 \mu$ in maximum width. No similar evaluation of the NpO_2 was conducted; however, it was concluded that the particle size of the two constituents was sufficiently fine to give a highly sinterable powder blend with reasonable ball-milling periods.

Cladding Components

Type 304 stainless steel tubing for the target rods was supplied by Nuclear Materials and Equipment Corporation. This tubing, which conformed to the specification NPS-20A-Rev 1 (Reference NUMEC Drawing 10B323) was completely qualified for use in Connecticut Yankee core reload assemblies. The four tubes received for this program were each approximately 10 ft long, and these were identified as S-557, -562, -566, and -569. Dimensions of this reactor-grade fuel rod tubing were 0.433 in. in OD with a 0.0165-in. wall thickness. Results of chemical analyses for each of the tubes are presented in Table 4, along with the mill heat analysis and ASTM and SNE specifications. In general, all of the elements were within the standard specifications with the exception of the chromium content of Tube S-569, which was slightly on the low side. Battelle analyses for gaseous impurities fall within the ranges normally expected for these elements.

Further characterization included metallographic examination of transverse and longitudinal sections from each of the tubes. Typical microstructures of the various tube sections are shown in the photomicrographs of Figures 2 and 3 for Tube S-566. All of the sections were examined first in the as-polished condition to obtain a true picture of the inclusion distribution and then in the etched condition for grain size evaluation. Small amounts of stringer-type inclusions seen in Figure 2b were present in all of the specimens examined in the longitudinal direction. These stringers were often found close to the

500X

As Polished

2F350

FIGURE 1. TYPICAL CaO -STABILIZED ZrO_2 PARTICLE
CONFIGURATION AND SIZE DISTRIBUTION

TABLE 4. CHEMICAL ANALYSIS DATA FOR TYPE 304 STAINLESS STEEL TARGET TUBE MATERIALS^(a)

Element	Specification Analysis		Mill Analysis ^(d)		Battelle Analysis of Indicated Tube ^(e)			
	NUMEC ^(b)	SNE ^(c)	Heat	Check	S-557	S-562	S-566	S-569
Oxygen	-	-	-	-	150 ppm	200 ppm	175 ppm	235 ppm
Hydrogen	-	-	-	-	4 ppm	7 ppm	4 ppm	3 ppm
Nitrogen	-	-	-	-	510 ppm	660 ppm	640 ppm	520 ppm
Carbon	0.08 max	0.04-0.08	0.04	0.04/0.04	0.038	0.041	0.037	0.035
Phosphorus	0.040 max	-	0.025	0.008/0.008	0.026	0.027	0.025	0.024
Sulfur	0.030 max	-	0.015	0.010/0.009	0.013	0.013	0.012	0.013
Chromium	18.0-20.0	-	18.89	18.30/18.30	19.6	18.7	18.5	17.8
Nickel	8.00-11.0	-	10.17	9.94/9.88	10.2	10.5	9.9	9.8
Manganese	2.00 max	-	1.17	1.13/1.15	1.23	1.01	1.13	0.94
Silicon	0.75 max	-	0.32	0.343/0.347	0.28	0.28	0.41	0.3
Cobalt	-	0.08 max	0.028	0.002/0.002	0.070	0.070	0.075	0.075
Boron	-	-	0.0005	<0.0005/<0.0005	N.A.	N.A.	N.A.	N.A.

(a) Analysis data given as w/o unless otherwise indicated.

(b) NUMEC specification indicates material to conform to ASTM Standard A-213-66.

(c) SNE specification is same as NUMEC except for carbon and cobalt, as indicated.

(d) Mill analysis provided by Superior Tube Company for Heat No. M2918. Check analysis is at finish of processing.

(e) Samples taken from sections removed from one end of each tube. N.A. = not analyzed.

100X

As Polished

2F340

a. Transverse Section

100X

As Polished

2F341

b. Longitudinal Section

FIGURE 2. UNIDENTIFIED INCLUSIONS (DARK) IN MATRIX OF SEAMLESS
TYPE 304 STAINLESS STEEL TUBING

100X

Etched

2F342

a. Transverse Section

100X

Etched

2F343

b. Longitudinal Section

FIGURE 3. TYPICAL MICROSTRUCTURE OF TYPE 304 STAINLESS STEEL TUBING SHOWING GRAIN STRUCTURE AND STRINGER INCLUSIONS

surface, as is evident in Figures 2b and 3b. Generally, the microstructures were typical of those expected for this grade of stainless steel tubing. One of the tubes, S-566, appeared to have a somewhat higher concentration of inclusions; therefore, this length of tubing was held in reserve and utilized for preliminary testing of weld parameters and as cladding for compatibility capsules. Boroscope examination was conducted on all tubing after cutting to size. Some small pits and scratches were identified on the interior of all of the tubes but in no case were these considered to be of sufficient magnitude to preclude the use of a tube for a target segment. However, as a result of this evaluation all tubes were classified and subsequently utilized according to this listing.

Type 304 stainless steel rod for the various end fittings and other hardware components was procured in accordance with the SNE specification (Reference Drawing SNE69-646-11). The Battelle chemical analysis of this material is given in Table 5 together with the SNE specifications and the certified mill analysis. Concentrations of all elements were within the expected ranges. The high cobalt content allowed for the stainless steel rod was appreciably above the generally accepted limit; however, it was necessary to relax the specification for cobalt somewhat in order to obtain material that would satisfy the immediate needs of the program. This bar stock was the only lot of stainless steel commercially available at the time the order was placed. Although stainless steel with a lower cobalt content can be obtained on special order, several months are required for delivery and the quantity of steel ordered must be appreciably greater than warranted for this investigation.

Cursory evaluation of the effects associated with the high cobalt content of the cladding end fittings indicated that some degree of perturbation of the gamma scans of the target rods would be expected on postirradiation examination, but no serious or insurmountable problem was thought to exist. Metallographic examination of transverse and longitudinal center sections from the rod stock yielded the expected microstructures, as shown in Figure 4. Comparison of these microstructures with those of Figures 2 and 3 shows that the average grain size of this material was considerably greater than that of the cladding.

TABLE 5. CHEMICAL ANALYSIS OF TYPE 304 STAINLESS STEEL ROD
USED FOR TARGET END COMPONENTS AND OTHER HARDWARE^(a)

Element	Specification Analysis ^(b)	Certification Analysis ^(c)	Battelle Analysis
Oxygen	-	-	600 ppm
Hydrogen	-	-	< 1 ppm
Nitrogen	-	-	300 ppm
Carbon	0.04-0.08	0.057/0.059	0.065
Phosphorus	0.045 max	0.022/0.023	0.027
Sulfur	0.030 max	0.021/0.019	0.025
Chromium	18.00-20.00	18.40/18.50	18.5
Nickel	8.00-12.00	8.36/8.36	8.25
Manganese	2.00 max	1.51/1.52	1.65
Silicon	1.00 max	0.52/0.52	0.46
Cobalt	0.15 max	0.13/0.13	0.12
Molybdenum	-	0.26/0.26	N.A.
Copper	-	0.20/0.20	N.A.

(a) Analysis data in w/o unless otherwise specified. N. A. = not analyzed.

(b) SNE Drawing 69-646-11 specifies ASTM Standard A-276, Type 304, centerless ground, Condition A, except for carbon, 0.04 to 0.08 w/o, and cobalt, 0.15 w/o max.

(c) Certified analysis from Williams and Company on Universal Cyclops Heat No. G5433.

100X

Etched

2F381

a. Transverse Center Section

100X

Etched

2F383

b. Longitudinal Center Section

FIGURE 4 MICROSTRUCTURE OF TYPE 304 STAINLESS STEEL ROD STOCK

PELLET PREPARATION

Target Specifications

Initially it was thought that extensive parametric processing studies could be avoided since normal stringent performance characteristics associated with a reactor fuel were not specified for the targets and there was no necessity for maintenance of excessively precise restrictions on density. However, as the work progressed and the goals of the program became more well defined it became obvious that there was a need for target pellet specifications equivalent in many ways to those for the fuel so as not to jeopardize the operation of the reactor. This was further deemed necessary when the additional value of experimental data generated on pellets with a uniform density was considered in light of more ambitious goals for the program. In addition, a rigid diametral tolerance gave some assurance that appreciable void volume would form within the targets if the fuel-cladding gap closed during the course of the irradiation. The requirement for uniform clearance thus minimized the probability of breachment of the cladding. Control of pellet diameter was also found to be of significance since this dimension affects the NpO_2 concentration per unit length, which when held constant provides a means of mapping the flux of the reactor through determination of the change in Pu^{238} concentration over the length of the target segment.

In view of the above, a pellet specification was written toward the completion of the program. This document is given as the Appendix to this report. The standards imposed on the target material closely parallel those normally required for UO_2 fuel. The only exceptions occur in the allowable impurity elements, particularly in regard to the total equivalent boron content since reactivity of the target rod was of no consequence, and in the dimensional limits of surface flaws. Otherwise, the acceptable amount of chlorine, hydrogen, and total gas was the same as for the reactor fuel pellets. These limits and the consequences of preparing pellets that could not meet the specifications were factors that profoundly influenced the techniques chosen for pellet fabrication; these are discussed below.

Target Fabrication

Since data pertaining to the densification behavior of NpO_2 were virtually nonexistent, initial studies were directed toward obtaining a cursory understanding of the powder blending characteristics and the change in density that could be expected on sintering the various compositions of interest. It was expected that this work would then provide the basic information needed to make adjustments in the processing scheme and thus zero in on the fabrication parameters that would meet the goals established for this phase of the program.

Neptunium concentrations specified for each of the target segments are given in the tabulation of Paragraph 5.1 of the Appendix. These values, which range from 77.22 to 15.18 w/o NpO_2 , essentially encompass the entire phase system in the pseudobinary NpO_2 -(10 w/o CaO-ZrO_2). Accordingly, an appreciable change in blending and densification characteristics could be expected for these compositions due to the tremendous difference in properties between the components.

As a first step in the investigation, various techniques for blending of the NpO_2 and 10 w/o CaO-ZrO_2 powders were evaluated according to the relative probability of obtaining a homogeneous dispersion of NpO_2 in the sintered pellets. This was necessary because many standard methods are unsuitable for blending of powders with widely different densities, as is the case with NpO_2 and calcia-stabilized ZrO_2 , which have densities of 11.13 and about 5.0 g per cm^3 , respectively. A decision was eventually made to blend the powders by wet ball milling, on the basis of experience at Battelle with mechanically mixed UO_2 and PuO_2 together with an evaluation of previous work on UO_2 - PuO_2 - ZrO_2 fuels⁽⁶⁾.

Approximately 30-g powder batches* of various compositions were blended for the preliminary sintering trials. Each powder batch was blended for 8 hr in a rubber-lined mill containing zirconia balls and filled with distilled water. The powder slurry was then removed, dried, and screened prior to

* As defined in the Appendix, Paragraph 7.2.1, a batch of powder is defined as a blend of the initial constituents to obtain a specific composition.

pressing. Considerable foaming occurred during milling due to the sulfate content of the stabilized zirconia powder, but aside from some inconvenience on cleaning there was no deleterious effect on the dried powder. All work on this and other phases of the effort connected with pellet fabrication was conducted in glove boxes containing a dry nitrogen atmosphere. Pellets approximately 0.45 in. in diameter and 0.65 in. long were uniaxially cold pressed at 20,000 and 40,000 psi and sintered in a high-temperature resistance furnace employing a tungsten mesh heater at temperatures ranging from 1300 to 1800 C. An atmosphere of either flowing argon-8 v/o hydrogen or pure nitrogen was used throughout the sintering cycle. Pellets were placed on one of several tiers of a tungsten holder, which was positioned well within the hot zone of the furnace heater. Densities of the pellets were determined from their physical dimensions and weights. Theoretical densities of the various target segment compositions were calculated from a derived theoretical density for NpO_2 , based on the lattice constant data, together with an estimated density for 10 w/o CaO-ZrO_2 obtained from the manufacturer.

A compilation of the various process parameters investigated and the resulting densities of the pellets is given in Table 6. Duplicate pellets of the 48.76 and 77.22 w/o NpO_2 compositions were cycled to progressively increasing temperatures to determine the effect of temperature on shrinkage behavior. In addition, small amounts of mechanically dry-blended powder containing 77.22 w/o NpO_2 , together with the as-received NpO_2 , were pelletized and sintered at increasing temperatures to obtain a measure of the benefits of reduction in particle size through ball milling. As soon as the data indicated that densities on the order of 90 percent of theoretical could be attained by high-temperature firing, batches of several hundred grams of powder were wet blended for a period of 24 hr and subsequently evaluated for densification characteristics.

Generally, sintering temperatures on the order of 1700 or 1800 C were needed to attain densities near 90 percent of theoretical with powder that was wet milled for 8 hr. Shrinkages were quite high and comparatively nonuniform, i.e., shrinkage was far greater in the radial direction than in the longitudinal direction and pellets were hourglass shaped or tended to be larger in diameter at one end. This behavior was attributed somewhat to the pressing techniques, but powder characteristics were thought to be primarily responsible. This was evident from the number of fissures, blow holes, and in some cases raised areas

TABLE 6. RESULTS OF INITIAL SINTERING STUDIES OF VARIOUS NpO_2 TARGET ROD PELLETS

Segment	Nominal Composition, w/o NpO_2	Ball-Milling Time, hr	Densification Pressure, psi	Sintering Temperature, C	Sintering Atmosphere	Density of Material		Diametral Shrinkage, percent
						G per cm^3	Percent of Theoretical ^(a)	
D	15.18	8	40,000	1700	Ar-8 v/o H_2	4.93	90.2	16
		8	40,000	1700	Ar-8 v/o H_2	4.98	91	-
		8	20,000	1700	Nitrogen	4.92	90.2	17
		8	20,000	1800	Nitrogen	5.07	92.7	17.6
		24	20,000	1800	Nitrogen	5.22	95.5	13.2
		24	20,000	1800	Nitrogen	5.25	96	13.3
		24	20,000	1700	Nitrogen	5.18	94.8	12.7
		24	20,000	1600	Nitrogen	4.97	91	11.4
		24	20,000	1675	Nitrogen	5.17	94.6	-
		24	20,000	1675	Nitrogen	5.16	94.4	12.4
		24	20,000	1675	Nitrogen	5.13	93.8	12.7
C	28.06	8	40,000	1700	Ar-8 v/o H_2	5.37	90.7	-
		8	40,000	1700	Ar-8 v/o H_2	5.28	89.1	-
		8	20,000	1700	Nitrogen	5.38	91	18.2
		8	20,000	1800	Nitrogen	5.38	91	18.1
		24	20,000	1675	Nitrogen	5.47	92.4	-
		24	20,000	1675	Nitrogen	5.39	91	12.9
B	48.76	8	20,000	1300	Nitrogen	4.53	66.3	9.1
		8	20,000	1500	Nitrogen	5.13	75	13.3
		8	20,000	1700	Nitrogen	6.04	88.3	17.2
		8	20,000	1800	Nitrogen	6.03	88.3	17.6
		24	20,000	1675	Nitrogen	6.37	93.2	13.7
A	77.22	8	20,000	1300	Nitrogen	5.67	65.2	11.1
		8	20,000	1500	Nitrogen	7.16	82.5	17.6
		8	20,000	1700	Nitrogen	7.15	82.5	18.0
		8	20,000	1800	Nitrogen	7.74	89	19.9
		24	20,000	1675	Nitrogen	8.70	100	16.8
		24	20,000	1675	Nitrogen	8.54	98.2	16.5
A	77.22	Dry Blended	20,000	1400	Nitrogen	5.63	64.7	9.3
				1500	Nitrogen	6.04	69.4	11.4
				1600	Nitrogen	6.58	75.6	14.2
				1700	Nitrogen	7.14	82	16.9
				1800	Nitrogen	7.14	82	-
-	100	As Received	20,000	1400	Nitrogen	8.55	76.6	-
				1500	Nitrogen	8.69	78	-
				1600	Nitrogen	-	-	-
				1700	Nitrogen	8.71	78	-
				1800	Nitrogen	8.71	78	-

(a) Based on calculated theoretical densities of the 15.18, 28.06, 48.76, 77.22 and 100 w/o NpO_2 compositions of 5.46, 5.92, 6.84, 8.70, and 11.13 g per cm^3 , respectively. Calcia-stabilized ZrO_2 theoretical density is estimated to be 5.0 g per cm^3 .

(b) Same pellet(s) sintered at increasing temperatures.

seen on the surface of the pellets which were apparently caused by impurities present in the as-received powders.

In comparison, pellets pressed from the dry-blended and as-received powders attained densities of only 82 and 78 percent of theoretical when sintered at temperatures up to 1800 C. This behavior demonstrated the greater activation of the wet-milled powder and enhanced densification through sintering that could be obtained by particle reduction. An additional and significant observation was the similarity among the surface characteristics of the pellets prepared from the dry-blended, as-received, and wet-milled powders. Further examination of the pellets by standard metallographic techniques showed that the porosity distribution was for the most part quite uniform except for occasional large void areas which appeared to be caused by gas formation from impurities. These voids were generally of less magnitude in the pellets prepared with wet-milled powders. This information together with the somewhat greater dimensional uniformity of these pellets suggested that a longer ball-milling time would be of value in enhancing ultimate densification and reducing surface defects. No evidence of metallic impurities was found in any of the microstructures and all specimens appeared to have a fairly equiaxed grain configuration indicative of a single-phase $\text{NpO}_2\text{-CaO-ZrO}_2$ solid solution. Similarly, there was no indication of the presence of the ZrO_2 monoclinic phase when the specimens were examined with polarized light.

Further reference to Table 6 shows that there was no increase in sintered density from either the use of high densification pressure, e.g., 40,000 psi as compared to 20,000 psi, or the change of sintering atmosphere from pure nitrogen to argon-8 v/o hydrogen. Data pertaining to the densification characteristics of pellets prepared from the large batches of powder milled for 24 hr are also shown. A general increase in density was noted with the longer ball-milling time for all compositions but the change was more significant in the pellets with the higher NpO_2 content. This trend is more readily seen by comparison of the data pertaining to the 77.22 w/o NpO_2 powder batches where material ball milled for 8 hr achieved a density of only 82.5 percent of theoretical on sintering to 1700 C, while the 24-hr-milled powder treated in the same manner sintered to densities close to the calculated theoretical value. Another quite noticeable change occurred in the shrinkage characteristics of the powder milled for the longer period. By referral to Table 6 it can be readily seen that the diametral shrinkage of pellets with

sintered densities in the range of 90 to 95 percent of theoretical was considerably less than found in earlier work. For example, initial shrinkage values generally fell within the range of 17 to 18 percent when the various powder blends were sintered at about 1700 C for 2 hr. Calculations also indicated that the shrinkage was nonuniform, with the ratio of the diametral to longitudinal change being about 1.7. In comparison, the somewhat finer powder produced by milling for 24 hr generally showed a diametral change of about 12 percent and more uniform shrinkage behavior, with a ratio of the percent change in diameter to length of about 1.1. The trend was similar to that observed for overall densification, i.e., the greatest amount of diametral shrinkage occurred in the 77.22 w/o NpO_2 composition and the dimensional nonuniformity or degree of hourglass configuration was also greatest in this material.

A cursory study of the sintering characteristics of the 24-hr-milled 15.18 w/o NpO_2 powder showed that hourglassing could be minimized by sintering at 1800 C; however, the densities of these pellets were near 96 percent of theoretical, which was greater than desired since by this time all process parameters were adjusted to the projected 90 percent density value. When the sintering temperature was lowered to 1600 C, dimensions of the pellets were generally somewhat irregular, indicative of nonuniform shrinkage within the fired specimens. Although the calculated densities of pellets sintered at 1600 C were very close to the desired value of 90 percent of theoretical the best compromise in regard to dimensional stability and appearance was obtained by treatment at 1675 C. Time did not permit the same type of study with other compositions. In any event, the 1675 C sintering temperature was found to be satisfactory for the 28.06 and 48.76 w/o NpO_2 compositions as well. A decision was made to lower the sintering temperature of the 77.22 w/o NpO_2 pellets to 1600 C on consideration of the near theoretical densities attained by firing at the slightly higher temperature of 1675 C.

Throughout the above effort, shrinkages were obtained on one or two pellets of a given composition and these data were then used to calculate the die sizes needed to prepare densified pellets within several thousandths of an inch of the specified mean diameter of 0.3825 in. Early results immediately indicated the difficulties associated with an original intent to sinter the pellets to size. Therefore, dry centerless grinding was incorporated into the fabrication process as an additional but necessary step to insure uniform clearance between the pellets and cladding wall.

A flow diagram outlining the various process steps utilized in the fabrication of the target pellets is shown in Figure 5. This general scheme was used to prepare six batches^{*} of pellets, as described in Table 7. All pellets were centerless ground to a diameter of 0.383 ± 0.001 in. The densities shown in Table 7 were obtained on randomly selected pellets. All values were quite close to the mean for the various batches of material. This excellent reproducibility was achieved only through exceedingly close control of all process variables including pressing techniques, heating and cooling rates during sintering, and gas flow through the furnace.

Zirconia Pellet Fabrication

According to specifications, each end of the four target segments composing the two rods required nonfissile zirconia pellets to act as barriers between the hot center of the target columns and the stainless steel components. Characterized calcia-zirconia powder, obtained for preparation of the target pellets, was also used for this purpose.

Pellets were pressed from the stabilized zirconia powder at a pressure of 60,000 psi and subsequently sintered at 1800 C for 2 hr. Heating and cooling rates ranged between 200 and 300 C per hr. A flow of pure nitrogen was maintained through the furnace during the entire sintering cycle.

Dimensions of the densified pellets were 0.433 to 0.438 in. in diameter by about 0.5 in. long. All pellets were dry centerless ground to a diameter of 0.384 ± 0.001 in. and ends were faced to leave the pellets at their maximum length. Determinations of the density of several pellets gave values ranging between 90 and 93 percent of theoretical.

* Paragraph 7.2.1 of the Appendix defines a pellet batch as those compacts pressed and sintered under identical conditions in the same furnace cycle.

FIGURE 5. PROCESS FLOW DIAGRAM FOR PELLET FABRICATION

TABLE 7. PROCESS PARAMETERS AND DENSITIES OF NpO_2 TARGET PELLETS

Target Segment	Batch Identification	Nominal Composition, w/o NpO_2	Densification Pressure, psi	Temperature of Nitrogen Sinter, C	Density, ³ g per cm^3	Density Percent of Theoretical
1A	4	77.22	20,000	1600	8.61	99.0
					8.65	99.4
					8.65	99.4
2A	4	77.22	20,000	1600	8.61	99.0
					8.61	99.0
					8.61	99.0
1B	5	48.76	20,000	1675	6.15	90.0
					6.13	89.7
					6.16	90.0
2B	5	48.76	20,000	1675	6.18	90.4
					6.14	90.0
					6.20	90.6
1C	6	28.06	20,000	1675	5.42	91.6
					5.42	91.6
					5.51	93.0
2C	6	28.06	20,000	1675	5.31	89.7
					5.45	92.1
					5.40	91.3
1D	2	15.18	20,000	1675	5.10	94.0
					5.11	94.0
					5.13	94.6
	1	15.18	20,000	1675	5.12	94.5
					5.13	94.6
					5.08	93.6
2D	3	15.18	20,000	1675	5.03	92.8
					5.04	92.9
					5.12	94.5

PELLET CHARACTERIZATION

Chemistry

Two pellets were selected from each batch of material for chemistry studies. One of these was used for immediate analysis of total gas, moisture, spectrographic impurities, NpO_2 , CaO , and ZrO_2 . The other pellet was stored as an archive sample to be available if needed during examination of the targets after irradiation. Specifications also called for the determination of the typical hydrogen content of the gas released from the pellets and measurement of the chlorine content of a typical 15.18 w/o NpO_2 pellet. The latter analyses were to serve as backup data if total gas and moisture approached or exceeded specifications.

Gas collection and moisture analysis were conducted in low-volume glass apparatus that had been thoroughly outgassed by heating and evacuation. The apparatus was divided into two sections by appropriate valves, with the lower section containing the pellet and moisture probe and the upper section, a pressure gage and collection bulb. The analytical procedure consisted of heating a pellet to 1000 C in a system previously evacuated to 10^{-6} torr with a mercury diffusion pump, followed by immediate collection and analysis of all evolved gas. Each pellet was held at temperature for 30 min. The moisture content of the gas was monitored continually by an EMF probe^{*}, and the amount of total gas was obtained by measurement of the pressure changes in the calibrated volume portion of the apparatus.

The results of these analyses are given in Table 8. In all cases the total gas was far less than the 0.05 cm^3 per g specified for the target pellets, and the moisture content was exceedingly low at less than 1 ppm. Although samples of evolved gas were taken from all pellets only one was analyzed, as per previous agreement with CYAPC and SNE. This approach seemed quite reasonable in view of the fact that all pellets received the same prior treatment and the total gas and moisture contents were generally very low. The values obtained from the mass spectrometric measurement of the gas from a 77.22 w/o NpO_2 pellet are given in Table 9. As can be seen, the off gas was composed

*Panametrics hydrometer, Model 1000, Waltham, Massachusetts.

TABLE 8. TOTAL GAS RELEASE AND MOISTURE CONTENTS
OF SELECTED NpO_2 PELLETS

Sample Designation	Nominal Composition w/o NpO_2	Gas Volume, cm^3 per g (STP)	H_2O , ppm
22	15 (Batch 1)	0.0022	< 0.38
36	15 (Batch 1)	0.0079	0.08
34	15 (Batch 2)	0.0050	< 0.10
38	15 (Batch 3)	0.0280	< 0.10
28	28	0.0270	0.05
30	48	0.0240	< 0.10
21	77	0.0150	0.10

TABLE 9 RESULTS OF MASS SPECTROMETRIC ANALYSIS
OF GAS FROM 77 w/o NpO_2 PELLET

Species	Amount, v/o
CO_2	0.98
Air	0.60
Oxygen	0.32
CO	57.6
Nitrogen	25.6
Hydrogen	10.1
C_2H_6	0.59
CH_4	0.16
SO_2	<0.02
H_2O	3.9
Unknown component	0.27

primarily of nitrogen and carbon monoxide. Hydrogen, which was to be held to < 10 ppm, was present in an insignificant amount.

By analogy in processing, it can be assumed that the distribution of the various species present in the evolved gas did not change appreciably with composition. It is interesting to note that conversion of the percentage moisture in the gases to ppm by weight yielded values ranging between 0.9 and 0.07, which is in relatively good agreement with the results obtained by use of the electrolytic probe. This correlation essentially substantiated earlier predictions that very little hydrogen and moisture would be found in the pellets. In addition, since the total amounts of evolved gas were all quite low, one can be quite confident that there was no introduction of impurities into a particular pellet batch that would have gone undetected by the procedures used in these analyses.

A separate determination of the chlorine content of the 15.18 w/o NpO_2 composition was conducted to obtain some indication of the amount of this impurity present after processing. A pellet of the high- ZrO_2 composition was chosen for analysis because of the high chlorine content of the as-received calcia-stabilized zirconia powder. The analytical technique employed for the measurement involved pyrohydrolysis by passage of a moisture-saturated argon gas stream over a crushed pellet while it was being heated at 950 C. The gas was passed through a solution of potassium acetate and acetic acid which was treated with mercuric thiocyanate in ethanol containing ferric alum, and this solution was then read spectrophotometrically. A value of about 8 ppm chlorine was obtained by use of this analytical method. This result showed that chlorine was removed in processing and was within the limit of 10 ppm established in the target specification. Although other batches of pellets were not analyzed for chlorine, from all indications these compositions would contain far less of this impurity than the 15.18 w/o NpO_2 material.

After completion of the total gas analysis, the pellets were broken and divided to obtain sections for general spectrographic analysis and metallography. Sections for spectrographic analysis were specifically taken from the surface of the pellets in an effort to obtain analyses that would be representative of the highest levels of impurities that could be expected in these materials. As seen from the results of this work, shown in Table 10, the impurities present in various material batches were of little consequence aside from those of iron, magnesium, manganese, chromium, and silicon. Generally acceptable impurity levels

TABLE 10. IMPURITIES PRESENT IN SELECTED PELLETS FROM VARIOUS BATCHES OF MATERIAL AFTER SINTERING

Element	Impurity Content, ppm							UO ₂
	Sample 22, 15 w/o NpO ₂ (Batch 1) ²	Sample 36, 15 w/o NpO ₂ (Batch 1) ²	Sample 34, 15 w/o NpO ₂ (Batch 2) ²	Sample 38, 15 w/o NpO ₂ (Batch 3) ²	Sample 28, 28 w/o NpO ₂	Sample 30, 48 w/o NpO ₂	Sample 21 77 w/o NpO ₂	
Bi	<2	<2	<2	<2	<2	<2	<2	2
B	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	1
Cd	<5	<5	<5	<5	<5	<5	<5	1.0
Cr	80	95	95	95	85	80	80	500.0
Cu	11	3	5	11	3	2	2	25.0
Fe	375	280	520 ^(a)	700 ^(a)	375	125	220	500.0
Li	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.1
Mg	200	200	225	200	200	200	150	50.0
Mn	75	95	50	55	75	12	75	10.0
Mo	<6	<6	<11	<11	<6	<11	<6	150.0
Ni	8	<8	25	35	8	<12	<8	300.0
P	<210	<210	<210	<210	<210	<210	<210	-
Pb	40	40	<4	<4	40	<4	<40	20.0
K	<125	<125	<250	<250	<125	<250	<125	-
Si	110	70	300	300	60	80	<34	500.0
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
Na	80	50	<40	<40	80	<40	160	-
Sn	20	20	10	20	20	10	20	5.0
V	<11	<11	<11	<11	<11	<11	<11	1.0
Zn	<50	<50	<50	<50	<50	<50	<50	20.0

(a) Contaminated with iron during sampling

for UO_2 pellets are given in this table for comparison.

Chemical analysis for neptunium content was conducted according to the following procedures. Duplicate samples of the pellets weighing about 0.3 g were initially dissolved in nitric acid with slight additions of hydrofluoric acid to aid dissolution. These solutions were evaporated twice and the agglomerate was redissolved in dilute sulfuric acid. The resulting solution was then fumed to remove traces of nitric acid and passed over a Jones reductor (zinc mercury amalgam) to adjust the valence of the neptunium. Final titration was conducted with ceric ammonium sulfate.

The procedures utilized for the ZrO_2 and CaO determinations were adaptations of standard methods for these elements. Portions of the pellet were crushed and dissolved in HNO_3 -HF. Neptunium (IV) was then separated from the calcium and zirconium by absorption on a Dowex 1x8 resin. Effluent from the column containing both calcium and zirconium was then treated separately to obtain constituent analyses.

For zirconium a solution of diammonium phosphate was added to precipitate ZrP_2O_7 . This precipitate was filtered from the solution, ignited at 1000 C to form ZrO_2 , and weighed to obtain the amount present. The remaining solution was then treated with oxalic acid to precipitate calcium oxalate, which was filtered and redissolved in dilute sulfuric acid. This solution was then titrated with a standard KMnO_4 solution to obtain the amount of calcium present.

All of the wet chemical analysis results are given in Table 11. These data, for all practical purposes, are adequate to verify the nominal compositions of the initial powder blends within about 10 percent. However, there was an obvious discrepancy between nominal and measured compositions which increased with increasing neptunium content. Due to this disparity the neptunium analysis of the 77.22 w/o NpO_2 sample was repeated with more care applied toward the various steps in the procedure. Reproducibility on the second run essentially verified the first results. In backup to this effort, a follow on investigation of chemical behavior was initiated as part of the experimental program to be carried out during the next fiscal period.

Several explanations of the observed results seem reasonable but all are associated with a bias in the neptunium determination and any interpretation of the data along these lines must also take into account possible slight material gains which could have occurred during ball milling. For example, all samples

TABLE 11 SUMMARY OF MAJOR OXIDE CONSTITUENT ANALYSES
FOR VARIOUS BATCHES OF TARGET PELLETS

Nominal Composition, w/o NpO_2	Batch	Sample	NpO_2 Content, w/o	ZrO_2 Content, w/o	CaO Content, w/o	Total Constituents ^(a) , w/o
15.18	1	22 ₁	15.20	71.65	13.34	100.19 high
		22 ₂	14.35	70.64	12.93	97.92 low
15.18	1	36 ₁	14.94	71.28	11.88	98.52 high
		36 ₂	14.94	68.46	12.30	95.28 low
15.18	2	34 ₁	14.98	72.49	12.75	101.75 high
		34 ₂	14.98	74.02	12.65	100.12 low
15.18	3	38 ₁	14.91	71.55	11.79	100.21 high
		38 ₂	14.90	73.51	11.71	98.16 low
28.06	6	28 ₁	25.34	62.06	9.61	100.39 high
		28 ₂	25.25	65.04	10.01	96.92 low
48.76	5	30 ₁	43.05	48.07	8.44	99.56 high
		30 ₂	42.96	47.75	8.43	99.14 low
77.22	4	21 ₁	74.69	20.48	4.69	100.05 high
		21 ₂	68.21	20.67	4.69	93.09 low
		21 ₁	69.26	-	-	-
		21 ₂	67.92	-	-	-

(a) Values listed are the totals of the high and low determinations for each oxide component.

were dissolved with difficulty and residues would probably follow some pattern in relation to the neptunia content. Then too, interfering ions could have been present during the determination or the valence state of the neptunium may not have been adjusted properly prior to titration. In any case, future studies will pay considerable attention to techniques which will obtain rapid and complete dissolution of the samples from the pellets since this was one of the difficulties that could have contributed to the apparent errors in the results. In addition controlled potential coulometry will be utilized to obtain the neptunium analysis in a manner consistent with the latest analytical methods for the actinide element in solution.

Metallographic Examination

Standard metallographic procedures were used to mount, grind, and polish samples from pellets designated for chemistry studies. An attempt was made to obtain longitudinal sections for examination but in most cases the pellets fractured into several pieces which were not truly representative of this configuration. Microstructures of the various pellet sections are shown in Figures 6 through 11. A slight chemical attack of the pore areas was noted when the samples were etched to obtain grain structure. This behavior should be taken into account when the pore areas are compared with apparent void volumes for each composition, easily derived from the density values given in Table 7. Offhand, there appears to be a good correlation between the observed porosity and the amounts thought to exist from the density calculations, i.e., the densities of 90 to 94 percent of theoretical are consistent with the microstructures. The very high densities of 99 percent of theoretical (see Table 7) determined for the 77.22 w/o NpO_2 pellets was verified by the microstructure of this material seen in Figure 11. Only a few pores present at the triple points of the grain boundaries are in evidence. This examination together with the density results also tends to confirm the nominal composition of this material as being very close to 77 w/o NpO_2 .

The grain size for various batches of pellets was quite uniform, considering the wide range of compositions prepared. Average values determined from the photomicrographs varied from 8 to 10 μ . This factor, in conjunction with the uniformity of observed porosity in all specimens, pointed to the conclusion that the distribution of the neptunia and stabilized zirconia was homogeneous.

500X

Etched

PL8736

FIGURE 6. TYPICAL MICROSTRUCTURE OF NOMINAL 15.18 w/o NpO_2
COMPOSITION AFTER SINTERING AT 1675 C FOR 2 HR²
(PELLET BATCH 1)

500X

Etched

PL8749

FIGURE 7. MICROSTRUCTURE OF TYPICAL PELLET FROM BATCH 2
CONTAINING 15.18 w/o NpO_2

500X

Etched

PL8753

FIGURE 8. MICROSTRUCTURE OF TYPICAL PELLET FROM BATCH 3
CONTAINING 15.18 w/o NpO_2

500X

Etched

PL8741

FIGURE 9. MICROSTRUCTURE OF NOMINAL 28.06 w/o NpO_2 COMPOSITION
(PELLET BATCH 6) AFTER SINTERING AT 1675 C FOR 2 HR

500X

Etched

PL8745

FIGURE 10. MICROSTRUCTURE OF NOMINAL 48.76 w/o NpO_2 COMPOSITION (PELLET BATCH 5) AFTER SINTERING AT 1675 C FOR 2 HR

500X

Etched

PL8731

FIGURE 11. TYPICAL MICROSTRUCTURE OF NOMINAL 77.22 w/o NpO_2 COMPOSITION (PELLET BATCH 4) AFTER SINTERING AT 1600 C FOR 2 HR

Note high density typified by absence of large pore volume (black areas).

Autoradiography

The procedure utilized for autoradiography was one developed for routine examination of plutonium-containing material. These checks were conducted on each of the metallographic specimens to obtain a positive record of the uniform distribution of the component materials and as a necessary criterion to comply with the pellet specifications. As can be seen in the Appendix (Paragraph 5.11), areas with neptunia concentrations of greater than 200 μ were unacceptable.

The examination technique consisted of placing the polished and cleaned surface of the metallographic samples in contact with a very fine grain photographic film^{*} in total darkness. To prevent alpha contamination of the film a thin sheet, < 0.001 in. of polyester⁺ was placed over the specimen surface. Previous work showed that this thin layer of polyester has very little effect on alpha particle resolution. All samples were weighted throughout the time of exposure to maintain intimate contact of the polished surface with the polyester and film. Exposure periods ranged from 20 to 30 min for all compositions, with the shorter time giving the best results for the specimens containing the highest concentration of neptunia.

Negatives produced from the developed film were enlarged eight times to obtain the autoradiographic prints shown in Figures 12a through 12f. No significant dark areas or variations in contrast, which would indicate a nonuniform distribution of neptunia were found on any of these prints. In several instances very small light areas can be seen which are attributed to incomplete removal of plutonium particles[‡] from the specimen surface during cleaning. Striations on the autoradiograph of the 48.76 w/o sample (Figure 12e) are scratches made during placement or removal of the sample from the film since an almost identical exposure showed the same type of marks on the opposite end. Furthermore, the autoradiograph of the 77.22 w/o neptunia sample (Figure 12f) shows a dark curlicue emanating from an apparent imperfection on the surface which is probably a remnant from the cloth used for cleaning. The obvious sharp delineation of surface imperfections is a good indication of the resolution of

* Kodak contrast process Ortho film.

+ Melinex polyester film, Type S.

‡ Loose contamination from the glove boxes.

8X

a. 15.18 w/o NpO_2 (Batch 1)

PL8869

8X

b. 15.18 w/o NpO_2 (Batch 2)

PL8866

FIGURE 12. AUTORADIOGRAPHS OF VARIOUS METALLOGRAPHIC SPECIMENS

8X

c. 15.18 w/o NpO_2 (Batch 3)

PL8871

8X

d. 28.06 w/o NpO_2

PL8863

FIGURE 12. (Continued)

8X

PL8864

e. 48.76 w/o NpO_2

8X

PL8858

f. 77.22 w/o NpO_2

FIGURE 12. (Continued)

the technique. Therefore, these autoradiographs generally verify the metallographic observations and are further evidence of the homogeneous nature of all the pellets.

PROPERTY MEASUREMENTS

As part of the overall evaluation of the pellets an effort was made to determine the thermal expansion characteristics of the 15.18 w/o NpO_2 material and the thermal cycling behavior of all compositions. These measurements, although not intended to be thorough investigations, were considered to be the minimum backup data needed to provide some assurance that design parameters were correct and the targets would perform as expected after placement in the reactor.

Thermal Expansion

The 15.18 w/o NpO_2 composition was selected for measurement because the possibility of a phase transformation was highest in this material and deviations from design values would have the greatest effect since these pellets make up the longest length target specimen of approximately 43 in. An existing recording dilatometer was used for the measurement. This apparatus was calibrated with a high-purity alumina specimen prior to the run with the unknown. The specimen consisted of two pellets stacked to give an overall length of about 1 in. These pellets were slowly heated to 1000 C in a period of about 12 hr. Flowing high-purity nitrogen was used as a protective atmosphere throughout the time of measurement.

The thermal expansion curve depicting dilation as a function of temperature is shown in Figure 13. No discontinuities were observed in the temperature range studied. The linear thermal expansion coefficient of 8.2×10^{-6} per C (4.56×10^{-6} per F) calculated from these data was somewhat less than expected based on an assumed behavior for NpO_2 similar to that of PuO_2 and existing data for ZrO_2 . In any case, this measurement was satisfactory to show that design values were conservative for this and probably other target segments.

FIGURE 13. THERMAL EXPANSION CURVE OF THE 15.18 w/o NpO_2 MATERIAL

Thermal Cycling

Fairly early in the program it was apparent that some degree of testing would be required to verify the thermal shock resistance of the pellets under simulated reactor conditions. Compositions thought to have the least resistance were those containing the greatest amount of zirconium dioxide, a material known to have excellent insulating properties and generally poor thermal shock behavior. Neptunia was assumed to behave similarly to urania, but the lack of properties data on this material contributed to an uneasiness regarding its actual behavior in the reactor. The possibility of pellet fracture and ratcheting of the cladding prompted considerable thought directed to cycling tests. Further incentive to conduct these tests was provided by the inadvertent rapid cooling of a furnace from high temperatures during one of the initial sintering runs which resulted in fracture of an entire batch of 15.18 w/o NpO_2 pellets.

A decision was made at this time to conduct a limited series of thermal cycling experiments that would simulate cooling of the pellets during a reactor scram, the most rapid transient expected throughout the irradiation period. To obtain a series of curves approximating this condition, SNE conducted a computer analysis which determined the rates of cooling of various radial nodes for each different target composition. The results of this work are given in the SNE report describing their experimental and analytical program⁽³⁾. An attempt was then made at BCL to approximate the curves for the centerline transients. Three thermal cycles consisting of a slow heatup, a short hold, and rapid cooling were performed on the various different target pellets. Tests were performed in a low-heat-capacity furnace to facilitate cooling. In addition, the furnace was purged with helium at a high flow rate the instant that power to the furnace was turned off. This procedure gave quite rapid cooling, but even under these conditions the actual curves obtained on the pellets deviated appreciably from the calculated ones, as may be seen in Figure 14. It should be noted that the maximum temperature reached in the various tests increased with the neptunia content of the pellets. Also, all three thermal cycles were identical; therefore, the curves given in Figure 14 are a composite of the typical behavior observed for specific compositions. Pellets containing 15.18 w/o NpO_2 (Segment D) were not cyclic tested since calculations indicated that the maximum center temperature of the target segment loaded with this material would be only several hundred degrees Fahrenheit above the ambient water temperature of the reactor.

Although the cooling curves obtained on the pellets are significantly different from the calculated centerline curves, it can be rationalized that these tests were as severe as the cyclic changes actually expected for the average radial node of the targets and, hence, are satisfactory for the purpose intended. In fact, the test performed may be overly severe because cooling was initiated from temperatures considerably higher than those calculated for the midradial nodes.

All pellets were examined closely for cracks after testing and in no case was a pellet changed from its original appearance. Therefore, these studies showed that the pellets could withstand the severest transient expected during irradiation, which could only be possible in the unlikely event of a reactor scram.

FIGURE 14. COMPARISON OF CALCULATED AND MEASURED TEMPERATURE CYCLES OF VARIOUS NpO₂ TARGET COMPOSITIONS

COMPATIBILITY TESTING

Demonstration of the long-term compatibility of the pellets with the Type 304 stainless steel cladding under conditions far exceeding those expected within the reactor was required as part of the testing phase of the program. However, no definite criteria existed as to the best conditions for these tests so a temperature of 500 C (932 F) for a period of 1 month was chosen as a satisfactory goal. This decision was based primarily on the choice of a reasonably high testing temperature which would be, in effect, an accelerated test equivalent to a 1-yr treatment of the cladding at the normal reactor operating temperature of 315 C (600 F). In addition, UO_2 and PuO_2 are known to have no solid-state interaction with stainless steel at 500 C; therefore, identical behavior for the NpO_2 target pellets would demonstrate the similarity of this material with common fuels.

One pellet of each target composition was encapsulated under conditions identical to those described later for the target rods, i.e., in helium, by TIG techniques. After heat treatment the capsules were examined in the longitudinal direction for diffusion interaction between the pellets and the cladding wall. No evidence of a solid-state reaction was found on any of the capsules; however, close examination of the cladding revealed areas of grain pullout which in some instances affected 20 percent of the cladding wall. A typical microstructure of an affected area is shown in Figure 15. Disturbed areas were found in all of the capsules but there was no indication of a systematic change in the depth of penetration with pellet composition.

At this point in the program the seriousness of the situation was assessed and steps were taken to obtain as much information as possible in the short period of several weeks available before a final decision was mandatory in regard to loading of the target rods into the reactor during the Spring refueling operation. Specifically, it was decided to section all of the metallographically mounted cladding specimens in the transverse direction to obtain a separate view of the phenomenon, which might aid interpretation. One cladding specimen with the most severe grain pullout was repolished and examined on the electron microprobe. Finally, additional capsules were made up and heat treated according to the conditions listed in Table 12. In addition, several experts on stainless corrosion within Battelle were consulted as to the possible significance of the problem and rate of attack expected at the somewhat lower temperatures

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FIGURE 15. TYPICAL APPEARANCE OF LONGITUDINAL SECTION FROM TYPE 304 STAINLESS STEEL CAPSULE WHICH CONTAINED PELLET AFTER HEAT TREATMENT AT 500 C (932 F) FOR 1 MONTH

Note grain pullout (black areas) and grain separation (black outline) near the surface of the cladding.

TABLE 12. SUMMARY OF HEAT-TREATMENT CONDITIONS
FOR THE SECOND GROUP OF TEST CAPSULES

Capsule Identification	Description	Heat Treatment	
		Temperature	Time, days
1	Blank (helium filled)	500 C (932 F)	12
2	15.18 w/o NpO_2 pellet	315 C (600 F)	10
3	Al_2O_3 grinding medium (pieces)	500 C (932 F)	12
4	NpO_2 pellet (pieces)	500 C (932 F)	12
5	CaO-stabilized ZrO_2 pellet	500 C (932 F)	9
6	UO_2 pellet	500 C (932 F)	9

(600 F) of actual reactor operation. Though no specific cause could be sited, the general consensus of opinion was that the phenomenon would not occur at 600 F even under prolonged periods of more than a year.

Examination of the cladding sections mounted in the transverse direction confirmed the fact that the pullout was localized to a number of areas on the inner surface of the cladding. Electron microprobe examination showed that there was no penetration of neptunium, calcium, or zirconium into the cladding. The specimen was also checked for other impurities that could have inadvertently been present on the surface of the pellets, e.g., aluminum, silicon, manganese, sulfur, and chlorine. None were found. Although this examination was inconclusive as to the cause of grain pullout, it unquestionably verified the absence of diffusional attack of the cladding which was the initial goal of these studies.

Further efforts were directed toward the metallographic examination of the capsules assembled and heat treated as indicated in Table 12. Since the heat treatment was substantially shorter, significant changes in the cladding were not expected. However, by this time there was a strong indication that the grain pullout was related to sensitization of the stainless steel (precipitation of chromium carbides at the grain boundaries) and somehow tied to the numerous inclusions (see Figures 3 and 4) present in certain sections of the cladding material. Based on this assumption, the type of grain structure and grain size present after heat treatment were noted and compared to those found initially as a means of obtaining some indication of a change in the stainless steel that could be related to carbide precipitation.

Pullout to the extent seen previously was not detected in any of the capsules from this group but a blank capsule containing only pure helium and another containing the UO_2 pellet exhibited very slight grain separation in some areas, forming what appeared to be the initial stages of the process. Grains in these and some of the other stainless steel capsules heat treated at 500 C (932 F) were more equiaxed and the etchant attack produced a fairly clear delineation of the grain boundaries. In comparison, the grains of the capsule containing the 15.18 w/o NpO_2 pellet remained unchanged after the heat treatment at 600 F. No attack of the cladding was seen in any of the capsules, including those containing pure NpO_2 , pure ZrO_2 (calcia stabilized), and the alumina bonding medium. Based on these results, the pellet gas analyses, and discussions with representatives from SNS (AEQ), SNE, and CYAPC, a decision was made to proceed with the irradiation of the NpO_2 target rods. Plans were also made to conduct out-of-pile compatibility tests during Fiscal Year 1972 to obtain backup

information on the long-term lower-temperature behavior of the pellets and cladding. These tests will be quite valuable in the postirradiation assessment of changes that may occur in the cladding while the rods are in the reactor.

ENCAPSULATION AND QUALITY ASSURANCE

As a necessary part of the project all work from this point forward was conducted according to written quality assurance procedures to insure proper assembly and checking of the target rod segments. This phase of the effort included construction of a welding alignment bench, determination of welding parameters through prequalification testing, weld qualification, and writeup of procedures for assembly, welding, decontamination, visual inspection, helium leak testing, and radiography. These procedures were then submitted to SNE for approval prior to actual conduct of the various operations.

Weld Qualification

Requirements for the alignment of the assembled segmented target rods were such that only a few thousandths of an inch deviation from the center axis could be tolerated for the attachment of the end plugs to the cladding tubing. In order to meet this specification a TIG welding unit was attached to an optical bench, which was bolted to a surface ground steel channel, as shown in Figure 16. With this welder design the electrode revolves around the rod, which is held stationary in alignment fixtures. The entire assembly, including the fixtures for holding the cladding tube and end fitting, was aligned within 0.0015 in. over the span of the optical bench.

Additional specifications pertaining to welding techniques were (1) less than a 0.0015-in. rise on the weld zone, and (2) positively no abrasion of the weld. These conditions, which were quite strict for normal water reactor fuel pins, were imposed to guarantee the proper water flow through the thimbles containing the target assemblies and to prevent generation of cracks or stress concentrations after welding.

Parameters for welding, i.e., the best distance of the electrode to the piece, power setting, and rotational velocity of the electrode, were established through trials with appropriately machined end fittings and shortened tube sections. Each weld was sectioned and examined by standard

FIGURE 16. VIEW OF WELDING FIXTURE AS SET UP WITH A GLOVE BOX

metallographic techniques to determine the amount of penetration obtained with the power and rotational variations. Although the optimum weld parameters were quickly established, a slight misalignment from the center axis, sometimes as much as 0.009 in. was noted on the joined pieces. As the problem became better defined a decision was made to shim the end fittings and connectors slightly to compensate for shrinkage on cooling. This technique was quite successful in bringing the overall alignment of the welded section to within a few thousandths of an inch of the center axis, which was within the straightness of the stainless steel tubing.

Three test welds were then made under identical conditions to demonstrate repeatability of the operation. In all cases metallographic examination showed the required 100 percent penetration. A typical microstructure of a weld area is shown in Figure 17. These results completed qualification of the welding process; therefore, all appropriate fittings and connectors were joined to the cladding sections while the unit was outside the glove box. The eight circumferential welds were then examined by use of the postemulsifiable-penetrant inspection technique. This method is extremely sensitive to surface-connected discontinuities since the weld area is inspected with ultraviolet light. All welds appeared to be perfect except for two which were subsequently checked with a binocular microscope and found to have very slight surface imperfections. Although these welds were readily acceptable the sensitivity of the technique was also demonstrated to the extent that there was no question of the integrity of the welds as regards microcracking and surface defects.

At the end of this phase of the work the welding apparatus, as assembled on the alignment bench, was transferred into a glove box. Modifications were then made to the box to obtain a helium atmosphere and accommodate the electrical and gas feeds for the welding equipment. A test weld was then attempted under conditions identical to those used for qualification, but in the presence of a high-purity helium atmosphere. Metallographic examination of weld area showed that the amount of penetration was identical to that obtained by welding outside the glove box.

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FIGURE 17. TYPICAL MICROSTRUCTURE OF WELD ENCOMPASSING THE
TYPE 304 STAINLESS STEEL CLADDING-END FITTING INTERFACE

Encapsulation Procedures

Centerless ground pellets were wiped clean and visually examined for defects in accord with limits described in the pellet specifications. Following a thorough examination the pellets were placed on a "V" bar to obtain a stacking length measurement prior to loading. The bar used for this purpose was scribed with marks to accurately indicate the tolerances for the pellet stack lengths in each of the two target rod segment categories, i.e., 10.000 ± 0.125 and 43.000 ± 0.125 in. At this point pellets for chemistry determinations and archive storage were selected and placed in appropriately marked containers for identification. Dimensions and weights of several pellets typical of those to be loaded were measured and geometric or bulk densities were obtained from these figures. No effort was made to keep track of individual pellets throughout processing and loading; however, different batches of pellets were carefully identified as to position within the target rod segment.

Pellet stack lengths were adjusted within tolerances either by selection or grinding of the pellets. A properly dimensioned calcia-stabilized zirconia pellet was then inserted into the appropriate target rod tube and the neptunia pellets followed. Dimensions taken from the open end of the tube verified a flush fit between pellets. A second zirconia pellet was then ground to the length necessary to obtain the specified spring pressure of 1.0 and 2.5 lb for the short (10 in.) and long (43 in.) target rod segments, respectively. Spring deflections were checked under loads of 1.1 and 2.2 lb to insure conformance to specifications.

All welds were performed with a qualified operator according to procedures and parameters established earlier in the program. The glove box, which normally contained high-purity nitrogen, was switched over to helium flow and flushed thoroughly for several hours before initiation of the pellet loading and end fitting weld operations.

Extreme care was taken to keep the open end of the tube and the end fitting in the vicinity of the weld free of contamination. The end fittings were held securely but slightly shimmed to compensate for shrinkage during cooling. Visual and dimensional examination of the welds indicated that no defects were present and the total diametrical rise did not exceed 0.002 in. Deviation of the end fittings from the center axis of the target segment was less than 0.008 in. per ft. Qualification welds made before and after a series of welds were

examined metallographically and in all cases full penetration, i.e., 100 percent of the wall thickness, was observed.

Fabrication data for each target segment are summarized in Table 13. Original design specifications are also included in this table for comparison. Generally, the as-fabricated neptunium concentrations were exceedingly close to those initially specified except in case of the Segment A values. The reason for this discrepancy was pointed out earlier during the discussion of the sintering data since it relates to the very high density obtained on the 77.22 w/o NpO_2 pellets. A decision was made to shorten the stack lengths of the "A" segments by one pellet to provide sufficient archive samples since material of this composition was limited. Average pellet diameters were generally within a few ten thousandths of an inch of the values shown. This pellet diameter of 0.383+ in. fixed the pellet-cladding gap in the range between 0.003 and 0.004 in.

Cleaning and Inspection

All rod segments were decontaminated by standard techniques, i.e., cleaning with various detergent solutions followed by several rinses with ethyl alcohol. Smear counts taken after cleaning showed that no loose contamination remained on the surface. Direct counting of the surface as well as the weld areas verified the absence of contamination on the entire surface of every target segment.

A visual check was subsequently performed on the various segments in accordance with quality assurance procedures. These were found to be free of surface defects and were approved accordingly.

Following decontamination, each rod segment was immediately subjected to a helium leak check in the following manner. Several rods, or a single one if this was all that was available at the time, were loaded into a chamber which was pressurized overnight to 150 psi with helium. A thorough calibration of the leak detector with a standard leak of $7.3 \times 10^{-7} \text{ cm}^3$ per sec was initiated concurrent with this operation to assure smooth sequential movement of the segments from one step to the next. Individual rods were then rapidly moved to a chamber attached to the leak detector and evacuated. Meter readings significant of the helium present in the chamber were taken at 5 min-intervals for a period of approximately 20 min. The rate of change of the detector with the target rod present was then compared to the rate observed under identical

TABLE 13. NpO_2 TARGET SEGMENT EXPERIMENTAL AND DESIGN DATA

Segment	NpO_2 Concentration, w/o	Stack Length, in.	Average Pellet Diameter, in.	Total Target Volume, cm^3	Total Target Weight, g	Average Segment Density g per cm^3	NpO_2 Mass, g	Neptunium Mass, g		Neptunium Content per Total Target Volume, g per cm^3	
								Actual	Specified	Actual	Specified
1A	77.22	9.468	0.3835	17.92	152.62	8.52	117.85	103.83	102.69	5.79	5.44
2A	77.22	9.406	0.3835	17.80	152.33	8.56	117.63	103.64	102.69	5.82	5.44
1B	48.76	9.937	0.3835	18.81	116.14	6.18	56.63	49.89	51.35	2.65	2.72
2B	48.76	9.937	0.3837	18.83	116.84	6.20	56.97	50.19	51.35	2.67	2.72
1C	28.06	9.906	0.3834	18.74	100.53	5.36	28.21	24.85	25.67	1.33	1.36
2C	28.06	9.906	0.3838	18.78	101.00	5.38	28.34	24.97	25.67	1.33	1.36
1D	15.18	43.030	0.3834	81.41	412.85	5.07	62.67	55.21	55.20	0.68	0.68
2D	15.18	43.046	0.3835	81.48	410.90	5.04	62.37	54.95	55.20	0.67	0.68

conditions with the chamber empty and the blank rate after pumping for a period of several hours which was usually about $1.7 \times 10^{-8} \text{ cm}^3$ per sec. Analysis of the data indicated that the rate of helium dissipation found for the various rod segments was almost identical to that for the empty chamber and that readings less than the standard leak rate were attained within several minutes after the start of pumpdown.

Radiography of the target segments was divided into two objectives: (1) to obtain a full view or composite shot to verify close spacing of the pellets within the cladding and (2) to verify full penetration of the circumferential welds in the vicinity of the end fittings. The latter was accomplished by taking radiographs of both sides of the weld at 0-, 60-, and 120-deg rotations. This approach provided a total of six views of the weld, which was considered ample to detect gross defects. This reasoning was also predicated on the performance of a continuous and uniform weld, which was a necessary criterion invoked in the quality assurance procedure.

To satisfy the first objective radiographs were taken at a fairly low power setting with brass bars located adjacent to the cladding to reduce scatter. Some of these shots were also acceptable for weld examination; however, in most instances a different technique was needed to obtain a clear delineation of the weld zone and void at the fitting-cladding interface. This technique consisted of placing stainless steel shape corrections, machined to closely fit the contour of the rod, in the weld zone to equalize the beam penetration and reduce scatter. With this arrangement power settings were increased to produce a dark film which was examined with a high-intensity arc light source. Resolution of the weld zone was substantially increased with this procedure; therefore, all subsequent radiographs were taken in an identical manner.

The detection limit, or penetration resolution, was judged to be less than 0.002 in. with the latter technique, and this value was somewhat higher initially. These figures are based for the most part on examinations of penetrometer holes and visibility of the void between the end fitting and cladding wall which extended into the cladding about 0.7 in. All welds were judged to be free of defects and of 100 percent penetration within the limits of detection.

SHIPMENT AND ASSEMBLY

Early in the program a decision was made to ship the target rods to the reactor site in a total of four segments (two for each rod) and to carry out final assembly in the pool side area. A bench consisting of closely aligned plywood standoffs on a 10-ft-long steel channel was constructed to facilitate final joining of the rod sections and loading into a reactor fuel assembly. The entire unit comprising the eight segments and flow mixer was then assembled at BCL prior to shipment.

The three lower segments of each rod, i.e., Segments A, B, and C, were joined according to plan at the laboratory. This operation involved the following steps: (1) use of a torque wrench to tighten adjoining segments, (2) drilling and reaming of a hole through the assembled fittings, (3) pin insertion, and (4) welding of the peripheral surface of the pin to the fitting. A photograph of the assembled target rods fastened to the bench is shown in Figure 18. Note the modified flow mixer assembly at the far end of the target rods.

The two rods were then disassembled into the four remaining segments and transported to Connecticut Yankee Reactor together with the flow mixer, alignment bench, and other tools needed to complete the assembly operation. The rods segments were joined at the reactor pool area without difficulty and loaded into an appropriate fuel assembly for storage until reactor reloading.

The fuel assembly containing the neptunium target rods was loaded into Connecticut Yankee Reactor on May 8, 1971. These targets will undergo continuous irradiation until June, 1972, at which time they will be removed for cooling and subsequent examination at BCL.

DISCUSSION AND CONCLUSIONS

As a result of the studies conducted on this program for the preparation and characterization of $\text{NpO}_2\text{-CaO-ZrO}_2$ target rods for Connecticut Yankee Reactor, information and data have been generated in a variety of areas.

Wet ball milling, used to blend the NpO_2 and calcia-stabilized ZrO_2 powders, was found to be most suitable for mixing these powders of widely different densities.

FIGURE 18. NEPTUNIUM TARGET RODS ASSEMBLED AND FASTENED TO BENCH
Note modified flow mixer (far right) attached to the
top end of the rods.

A sintering study conducted with pellets cold pressed from wet-milled, dry-blended, and as-received powders demonstrated the greater activation of the wet-milled powder and enhanced densification through sintering that could be obtained through particle reduction. A 2-hr sinter in high-purity nitrogen at 1675 C was found to give satisfactory densities for the 15.18, 28.06, and 48.76 w/o NpO_2 compositions; a temperature of 1600 C was used for the 77.22 w/o NpO_2 pellets.

Dry centerless grinding of the sintered pellets was incorporated into the fabrication process to insure uniform clearance between the pellets and the cladding wall.

Chemical analysis studies performed on selected pellets showed that total gas, moisture, and hydrogen contents were considerably less than specified tolerances.

Metallographic examination revealed that the grain size for various batches of pellets was quite uniform, considering the wide range of compositions prepared. Average values determined from the photomicrographs varied from 8 to 10 μ . This factor, in conjunction with the uniformity of observed porosity in all specimens, led to the conclusion that the distribution of the neptunia and calcia-stabilized zirconia was homogeneous. Autoradiographs were taken that generally verified the metallographic observations, providing further evidence of the homogeneous nature of all the pellets.

The linear thermal expansion coefficient of the 15.18 w/o NpO_2 material was found to be 8.2×10^{-6} per C. Thermal cycling tests performed on various pellets confirmed the conformance of the materials to design specifications and their stability to fracture during irradiation.

A document was written detailing complete specifications for the neptunia-zirconia target pellets.

During the course of the program, full quality assurance procedures were developed and conducted for cladding examination, pellet fabrication, pellet characterization, some physical property measurements, rod segment welding, shipping, and final assembly and welding at the reactor site.

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