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ABSTRACT

Bench scale roasting and dissolution of ThO_2 and ThO_2/UO_2 reactor-grade ceramic pellets were studied at the Savannah River Laboratory to define the key parameters affecting dissolution. Pellet breakup, and subsequent dissolution rates, were determined for ThO_2 and ThO_2/UO_2 pellets roasted in air or in oxygen.

Roasting ThO_2/UO_2 pellets in air at temperatures from 400 to 900°C caused the pellets to crack but not fragment. Roasting whole pellets or fine powdered materials decreased the rate of dissolution in a nitric acid solution containing a fluoride catalyst. Roasting 100% ThO_2 pellets did not cause cracking or affect the subsequent dissolution rate. Mixed ThO_2/UO_2 ceramic pellets dissolved at a faster rate than the 100% ThO_2 pellets.

The effect of MgO and CaO on dissolution rate was determined. MgO (~1.0 wt %) increased the dissolution rate of ThO_2 pellets, an effect which was similar to that obtained by the addition of 20% UO_2 to the ThO_2 pellets. The combination of 1% MgO and 20% UO_2 did not result in an additional increase in dissolution rate. However, the addition of 0.25 to 0.50 wt % CaO did increase the dissolution rate of 80% ThO_2/UO_2 ceramic pellets. High temperatures (and pressure) were ineffective in dissolving thoria-based fuels in HNO_3 in the absence of a fluoride catalyst. A process flowsheet outlining the required head end steps for the reprocessing of thoria-based fuels was developed.

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ROASTING AND DISSOLUTION STUDIES ON NONIRRADIATED THORIUM DIOXIDE/URANIUM DIOXIDE FUEL PELLETS

INTRODUCTION

In 1975, a Light Water Reactor (LWR) Fuel Cycle Program was initiated to study the recovery of uranium and plutonium for subsequent recycle in LWRs or breeder reactors.[1] In 1977, the national energy policy was modified to defer the separate recycling of plutonium and to focus on the development of fuel recycle systems which reduce the risk of nuclear weapons proliferation. The Alternative Fuel Cycle Technologies (AFCT) Program was extended to include an evaluation of fuel cycles in which thorium was used in the Thorium Fuel Cycle Technologies (TFCT) Program. The primary goal of the AFCT/TFCT programs was to develop the technical information required to support the establishment of fuel recycle facilities.

A reference case thorium fuel cycle was defined[2] in 1977 to serve as a common basis for development work among the participating national laboratories, universities, and commercial facilities. Final selection of a thorium fuel cycle would depend on evaluation of proliferation resistance, environmental effects, and economic evaluation of the total system.

The characteristics of the reference fuel cycle for the TFCT Program were as follows:

- Fissile uranium would be denatured by mixing with ^{238}U.
- Chemical processing plant design would be based on the assumption that plants would be located in secure areas.
- Plutonium would be recycled within these secure areas.
- Thorium would be recycled with recovered uranium and plutonium.
- The head end of the chemical processing plant would handle a variety of core and blanket fuel assembly designs for light water reactors (LWRs) and heavy water reactors (HWRs).
- The fuel form would be a homogeneous mixture of uranium and thorium oxide powders pressed into pellets.

- Fuel cladding would be Zircaloy.
- MgO would be added to the fuel to improve the thorium-dissolving characteristics.

Thorium was considered to be the fertile component (vs. ^{238}U) of nuclear reactor fuel because it provided increased proliferation resistance. ^{235}U (which constituted the initial fissile content) and ^{233}U (which was produced from thorium during the irradiation) could be denatured or made unusable for feasible explosive devices by mixing with ^{238}U. The amount of plutonium — which could not be denatured — produced during irradiation was reduced by replacing the fertile ^{238}U with thorium. Only 20 to 30% of the fuel material consisted of ^{238}U (to denature the ^{235}U and the ^{233}U); therefore, the amount of plutonium produced would be reduced to 1/3 to 1/4 of a standard uranium-based LWR fuel.

PURPOSE OF SRL PROGRAM

The purpose of the roasting and dissolution program at Savannah River Laboratory (SRL) was to study the head end steps of the proposed thorium fuel cycle by using *nonirradiated* ThO_2 and ThO_2/UO_2 ceramic pellets. The program objectives were to define the specific process conditions and equipment required to reprocess the thorium fuel materials. The effects of pellet fabrication parameters, including uranium content and other additives, were to be studied.

The SRL studies emphasized steps prior to dissolution (fuel rod shearing, separation of cladding and fuel materials, and tritium removal) and during dissolution (including optimization of the fluoride-catalyzed acid dissolution process and characterization of the insoluble dissolution residues).

RESULTS

Material Description

Unirradiated ThO_2 and ThO_2/UO_2 were procured for cold laboratory studies preceding hot cell studies of tritium removal and dissolution. These ceramic pellets were intended to be as close to reactor-grade quality as possible, considering properties such as density, grain and pore size, impurity levels, and homogeneity. The materials are described below.

Nuclear Fuel Services (NFS) Pellets

Approximately five kg of 100% ThO_2 reactor-grade "reflector" pellets were obtained from Nuclear Fuel Services, Inc., Erwin, Tennessee. These pellets were prepared for the original light water breeder reactor program in the early 1960's. The pellets were 0.72 inch diameter by 0.75 inch long with ~98% theoretical density. The pellet production steps were[3]

- Thorium nitrate source: Ferndale, Ohio
- Oxalate precipitation [oxalic acid addition to $Th(NO_3)_4$]
- Thorium oxalate heated to thorium dioxide
- ThO_2 micronized and dry screened
- Steratex binder added and powder pressed to green pellets
- Green pellets calcined to remove binder
- Pellets sintered under hydrogen atmosphere

General Electric of Canada (GEC) Pellets

Six types of ThO_2 and ThO_2/UO_2 fuel pellets were fabricated for SRL by the Canadian General Electric Co., Ltd. (GEC), Peterborough, Ontario, Canada. The samples (Table 1) included a range of urania content and samples with MgO and CaO additives to test their effects on dissolution. The pellets were 0.55 inch diameter by 0.55 inch long, and all samples were reactor-grade quality, except for those pellets containing CaO, which had low density and poor mechanical integrity.

The GEC pellets were made by the process used to fabricate fuels for (CANDU) reactors.[4]

TABLE 1

Unirradiated Ceramic Materials from GEC

Samples, Wt%					% Theoretical*
ThO_2	UO_2	MgO	CaO	Amount, kg	Density
80	20	-	-	11.9	93.4
70	30	-	-	5.7	94.0
79	20	1	-	5.7	93.9
78.6	20	-	1.4	6.0	**
99	1	-	-	5.0	96.3
100	-	-	-	4.8	96.9

---

* UO_2 theoretical density = 10.88 g/cm^3.
ThO_2 theoretical density = 10.03 g/cm^3.
MgO theoretical density = 3.58 g/cm^3.

** Pellets are not reactor-grade quality.

- The ThO_2 was obtained from Tennessee Nuclear Specialties, Jonesborough, Tennessee. It had been prepared by calcining thorium oxalate at 1,000°C [the $Th(C_2O_4)_2$ was precipitated from $Th(NO_3)_4$].
- The UO_2 was obtained from Eldorado Nuclear Ltd., Ontario, Canada (depleted uranium, 0.52% ^{235}U).
- The ThO_2 and UO_2 powders were blended and reduced in particle size by high-energy wet attrition milling. The resulting slurry was dried and granulated with a zinc stearate binder, and a dissolution aid (MgO or CaO) was added.
- The granules were cold pressed into pellets and sintered in a hydrogen atmosphere at 1680°C.

General Atomic Company (GA) Microspheres

Although the primary interest of the program is for fuel in the form of ceramic pellets, about five kg of ThO_2 microspheres was obtained from the General Atomic Company (GA), San Diego, California. The spheres have a nominal diameter of 540 µm.

Westinghouse-Bettis Atomic Power Laboratory (Bettis) Pellets

Two kg each of four types of 100% ThO_2 fuel pellets of different sizes and pore structures were obtained from the Westinghouse Electric Corp., Bettis Atomic Power Laboratory, West Mifflin, Pennsylvania. Bettis had prepared a variety of ThO_2 pellets for the Department of Energy (DOE) Division of Naval Reactors (DNR). In mid-1978, materials in excess of the DNR needs became available to other DOE laboratories.[5] Details of the pellet characteristics (dimensions, density, impurities, grain and pore size, cracks, and internal inclusions) are given in Appendix A.

Battelle-Pacific Northwest Laboratories (PNL) Pellets

Four samples of 80% ThO_2/20% UO_2 reactor-grade ceramic pellets containing different levels of CaO were prepared by PNL for dissolution tests at SRL.[6] The initial three lots of PNL pellets contained 0, 0.33, and 0.66% CaO. The CaO addition appeared to increase cracking of the pellets and also modified the grain structure. Islands of coarse grains surrounded by regions of very fine grains were evident in the pellets containing CaO. A fourth sample containing 0.50% CaO was prepared subsequently with a different lot of UO_2 powder. The pellets in this sample did not exhibit the cracking of the previous samples, but the inhomogeneous grain structure, attributed to the CaO, was still present. Details of pellet fabrication and microstructural data were supplied by PNL. Scanning electron microprobe and x-ray techniques were used by SRL to analyze further the pellets. The results showed that the PNL control pellets (0% CaO, 80% ThO_2, and 20% UO_2) had a more inhomogeneous mixing of ThO_2 and UO_2 than the 80/20 ThO_2/UO_2 pellets from GEC. The addition of CaO (0.33 or 0.66%) improved the ThO_2/UO_2 homogeneity of the PNL pellets. Details of these analyses are given in Appendix A.

Oxidation of ThO_2/UO_2 Pellets

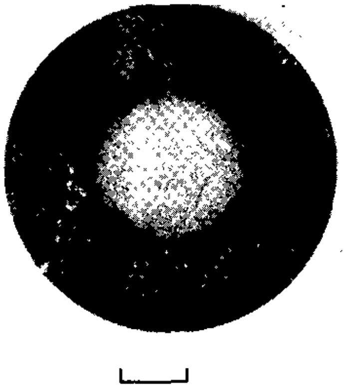
When uranium oxide pellets designed for current light water commercial power reactors were heated (450-600°C) in air or oxygen, the UO_2 was oxidized to U_3O_8. The change from face-centered cubic UO_2 to orthorhombic U_3O_8 caused the pellet to disintegrate into a fine powder. In the case of irradiated UO_2 fuel materials, the phase change allowed tritium to diffuse out, and a large fraction of the tritium was removed before dissolution.

Although no analogous oxidation reaction and phase change occurred with ThO_2, pellets with a high percentage of UO_2 (20 to 30%) were studied to determine if physical changes, such as cracking or fracturing, would occur under oxidizing conditions.

Oxidation experiments with the NFS and GEC materials were performed by heating the pellets inside a 1-1/4-inch-diameter ceramic cylinder in a clam shell furnace with air flowing at 30 cc/min through the cylinder.

The experiments confirmed that the 100% ThO_2 pellets were not affected by air oxidation: no weight gain or dimensional changes were observed, and the subsequent rate of dissolution in Thorex dissolving solution was not affected. [Thorex solution is 12M HNO_3, 0.05M HF, and 0.1M $Al(NO_3)_3$].

However, in the case of the GEC pellets which contain 20 or 30% UO_2, oxidation of the UO_2 was observed. The periphery of the pellets changed color (from light yellow-green to black) as roasting continued. A network of small cracks developed in the oxidized portion, but fracturing or powdering did not occur. An example of a partially oxidized pellet is shown in Figure 1, with the center of the pellet consisting of nonoxidized material.



(3.2X Magnification)

FIGURE 1. Photograph of Cross Section of Oxidized ThO_2/UO_2 Pellet (GEC Type II, 70% ThO_2/30% UO_2) Air Roasted at 900° for 16 Hours.

The GEC-mixed ThO_2/UO_2 pellets were single phase, homogeneous, solid solutions, with a face-centered-cubic crystal structure. The oxygen-to-metal ratio of the oxidized portion of each pellet was determined over a wide range of roasting temperatures (500 to 900°C), and heating times (16 to 96 hours) for three of the GEC pellet types (80/20 ThO_2/UO_2, 70/30 ThO_2/UO_2 and 79/20 ThO_2/UO_2 + 1% MgO). The UO_2 in the pellet was oxidized to a relatively constant oxygen-to-metal ratio ($UO_{2.50} \pm_{0.05}$) for all conditions tested. The oxygen-to-metal ratio of the UO_2 was determined by 1) cross sectioning each roasted pellet to determine what fraction had oxidized, 2) determining the weight gain of each pellet, and 3) calculating the oxygen-to-metal ratio of the oxidized UO_2. The results of these experiments and calculations are shown in Table 2.

The oxidation of UO_2 increased with time, and the rate of oxidation increased with temperature (Figure 2). Changing from air to 100% oxygen atmosphere did not affect the oxidation rate significantly. These results suggested that the oxidation of the uranium in the ThO_2/UO_2 pellets was diffusion controlled and that the oxidation mechanism is similar throughout the range of temperatures studied.

Characterization of ThO_2/UO_2 Pellets from GEC

Several types of ThO_2/UO_2 fuel pellets made by GEC (Table 1: Types I, II, III, and IV) were characterized by x-ray diffractometry, scanning electron microscopy, electron microprobe analysis, thermal analysis, and metallography. The pellets were studied both as received from the manufacturer and after heating in air.

Characterization of ThO_2/UO_2 pellets made by GEC showed homogeneous solid-solution $(Th/U)O_{2.00}$. MgO, added to aid dissolution, was present as a distinct phase. CaO, another additive to aid dissolution, formed a solid solution with $(Th/U)O_2$. Oxidation of $(Th/U)O_2$ at 500 to 900°C contracted the face-centered-cubic (fcc) cell and caused the pellets to fracture but not pulverize. A crystallographic structure change that would release tritium did not occur when ThO_2 containing 20 to 30 wt % UO_2 was heated.

80% ThO_2/20% UO_2 Pellets

These pellets consisted of a single-phase, solid-solution oxide with an fcc crystal structure having a lattice constant a = 5.5739 ±0.0002 Å. Electron microprobe analysis showed the solid-solution oxide to contain 79.7 ±1.0 wt % ThO_2 and 20.3 ±1 wt % UO_2, corresponding to a composition of $Th_{0.801}U_{0.199}O_{2.00}$. The yellow-green color of the oxide also indicated a stoichiometric mixture, i.e., $O/(Th+U) = 2.00$. The pellet density of 9.53 g/cm^3 was 93.7%

TABLE 2

Oxidation Results with General Electric of Canada Pellets

Pellet Type Temperature, °C	Hours Heated	GECI 80/20 ThO_2/UO_2				GECII 70/30 ThO_2/UO_2				GECIII 80/20 ThO_2+1%MgO				GECIV* 80/20 ThO_2/UO_2+1.4% CaO		Average** O/U Ratio
		Pellet*** Weight, g	Weight† gain, g	% †† Oxidized	O/U ¶ Ratio	Pellet Weight, g	Weight gain, g	% Oxidized	O/U Ratio	Pellet Weight, g	Weight gain, g	% Oxidized	O/U Ratio	Pellet Weight, g	Weight gain, g	
900	24									87.4	0.492	98.6	2.48			2.47
	16	89.05	0.440	89.4	2.46	88.15	0.725	93.9	2.49							
	16	88.06	0.451	91.0	2.47											
	8	89.09	0.350	70.4	2.48	88.37	0.599	87.9	2.43							
800	96	89.24	0.572	100	2.49											2.52
	24	88.17	0.485	85.8	2.54											
	20	89.68	0.456	85.4	2.49											
	16					89.63	0.692	83.1	2.52	88.20	0.420	77.8	2.52			
	8	87.80	0.323	55.9	2.56	88.85	0.550	66.0	2.52					86.15	0.439	
700	64	88.96	0.585	~90	~2.62											2.55
	26									88.40	0.414	72.3	2.55			
	20	89.50	0.280	78.6	2.33	88.30	0.654	73.0	2.57					80.65	0.379	
	8					89.40	0.497	56.7	2.55							
	8	85.50	0.260	47.9	2.52	87.96	0.462	50.1	2.59							
600	72					89.35	0.854	93.8	2.57							2.56
	64	89.10	0.212	74.6	2.26									81.0	0.482	
	24									22.0	0.05	38.6	2.49	22.0	0.114	
	16	89.47	0.188	28.5	2.61	89.07	0.549	62.1	2.56	88.71	0.240	40.3	2.57			
	8	88.25	0.137	23.8	2.59	89.75	0.403	46.0	2.56							
500¶¶	24	88.67	0.068	15.3	2.44											2.51
	16					89.35	0.398	45.7	2.56	88.10	0.049	-	-	80.48	0.323	
	8	44.62	0.013	~5.0	~2.0	46.30	0.151	34.5	2.53							
	8	22.42	0.006			21.56	0.060	-	-							
400¶¶	16					88.57	0.059	13.3	2.31							-
	8					88.29	0.035	-	-							

---

* % oxidation and O/U ratio not determined because pellets were a dark color initially; no color change discerned on oxidation.

** Average O/U Ratio: The average over time and pellet type at each different temperature.

*** Weight of pellets before roasting; individual pellet weight of ~22 grams.

† Total weight gain of the roasted pellets.

†† % Oxidized; determined by cross sectioning the roasted pellet and calculating the % oxidized vs. nonoxidized as indicated by the change in color.

¶ O/U Ratio, oxygen to uranium ratio; calculated by assuming a homogeneous mixture of U throughout the pellet, and by assuming the absorbed oxygen is associated with the uranium ion.

¶¶ % oxidation at low temperature/time combinations difficult to determine accurately, as only a small portion of the outer surface was oxidized.

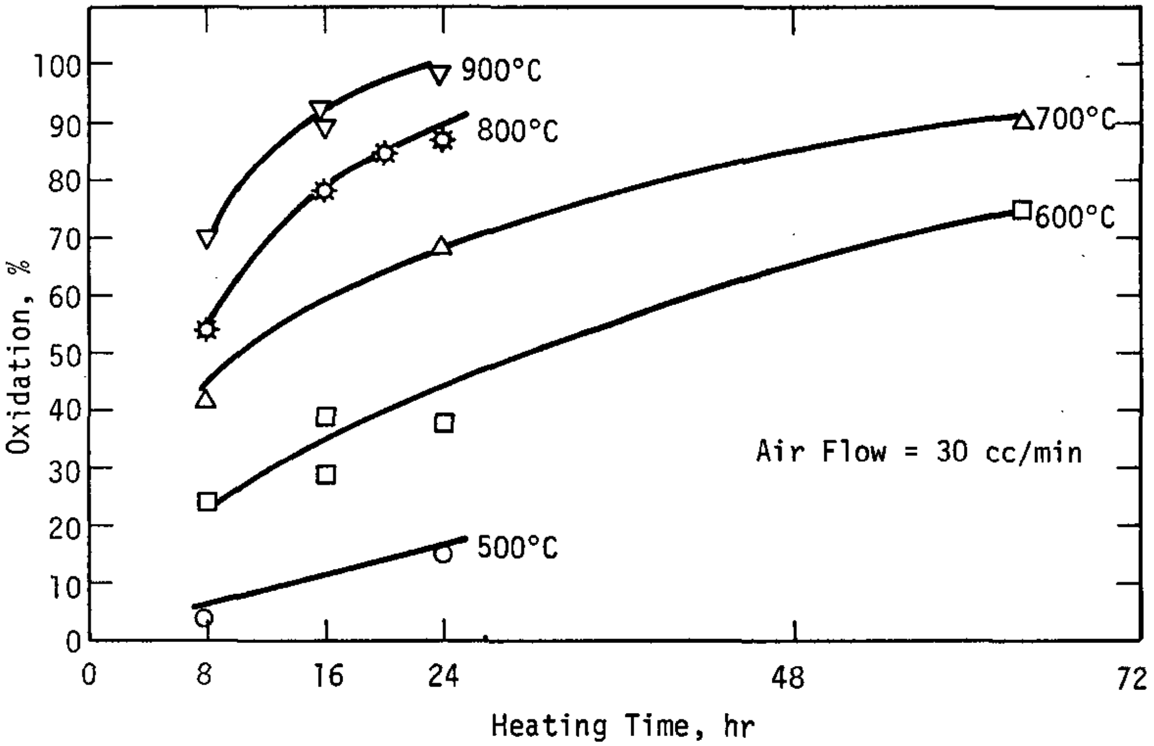


FIGURE 2. Oxidation vs Heating Time and Temperature - GEC ThO_2/UO_2 (80%/20%) Pellets.

of the x-ray density of the oxide (10.17 g/cm^3). A microstructural examination of a polished pellet showed the presence of round pores about one micrometer in diameter.

Heating $Th_{0.801}U_{0.199}O_{2.00}$ powder at 800°C for 16 hours in air oxidized it to O/(Th+U) = 2.113 (0.683% weight gain) and contracted the fcc cell to a = 5.5681 ±0.0003 Å. The x-ray density increased to 10.27 g/cm^3. Black layers of the same composition formed on the exterior of pellets heated at 500 to 900°C. Tension introduced by contraction of the fcc cell on oxidation caused cracking in the outer layer.

70% Thoria/30% Urania Pellets

These pellets also consisted of a single-phase, solid-solution oxide with an fcc crystal structure; but the lattice constant a = 5.5617 ±0.0003 Å was slightly smaller than that of $Th_{0.801}U_{0.199}O_{2.00}$. Electron microprobe analysis showed the solid-solution oxide to contain 70.0 ±1.8 wt% ThO_2 and 30.0 ±1.8 wt % UO_2, corresponding to a composition of $Th_{0.705}U_{0.295}O_{2.00}$. The yellow-green color indicated the oxide to be stoichiometric. The pellet density of 9.67 g/cm^3 was 94.0% of the x-ray density (10.26 g/cm^3). The microstructure was the same as observed for the 80 wt % UO_2 pellet.

Heating $Th_{0.705}U_{0.295}O_{2.00}$ powder at 800°C for 16 hours in air oxidized it to O/(Th+U) = 2.173 (1.041% weight gain) and contracted the fcc cell to a = 5.5527 ±0.0005 Å. The x-ray density increased to 10.42 g/cm^3. Oxide with the same structure formed on the exterior of pellets heated at 500 to 900°C. The contraction of the fcc cell of $Th_{0.705}U_{0.195}O_{2.173}$ was greater than that for $Th_{0.801}U_{0.199}O_{2.113}$ and caused more cracking of the oxidized layer. The difference between the cracking pattern at the circumference and at the ends suggests that cracking relieved residual fabrication stresses as well as the tension from the cell contraction.

79% Thoria/20% Urania Pellets, with 1.0% MgO

These pellets consisted of a solid-solution, fcc oxide with a = 5.5736 ±0.0005 Å, and traces of MgO (fcc, a = 4.213 Å). Electron microprobe analysis showed that the solid-solution oxide contained no MgO; the composition was 78.9 ±0.9 wt % ThO_2 and 21.1 ±0.9 wt % UO_2, corresponding to $Th_{0.793}U_{0.207}O_{2.00}$. X-ray densities were 10.18 g/cm^3 for $Th_{0.793}U_{0.207}O_{2.00}$ and 3.58 g/cm^3 for MgO for an overall density of 10.00 g/cm^3; the observed pellet density was 9.52 g/cm^3, 95.2% of the x-ray density.

The microstructure of the solid-solution oxide phase was similar to those observed for 80 wt % ThO_2-20 wt % UO_2 and 70 wt % ThO_2-30 wt % UO_2 pellets.

The MgO was present as particles about one micrometer in diameter at the boundaries of the larger particles (about 300 micrometers in diameter) of $Th_{0.793}U_{0.207}O_{2.00}$. This distribution is expected for the fabrication process in which MgO is blended with granules of the mixed ThO_2 and UO_2. Sintering in hydrogen produces stoichiometric oxide (O/Metal = 2.00), and MgO does not form solid solutions with $UO_{2.00}$.[7] However, MgO does form solid solutions containing up to 40 mole % MgO with UO_{2+x}. MgO would probably aid dissolution of $(Th,U)O_2$ better if it were in solid solution rather than present as a separate phase. MgO in solid solution might be prepared by sintering under nonreducing conditions to allow O/(Th+U) to exceed 2.00.

Heating 79 wt % ThO_2/20 wt % UO_2/1 wt % MgO pellets at 500 to 900°C in air oxidized the exterior of the pellets to layers of black oxide similar to those observed with $Th_{0.801}U_{0.199}O_{2.00}$ and $Th_{0.705}U_{0.295}O_{2.00}$. The exterior oxide had an fcc structure with a = 5.5667 ±0.0002 Å. This contraction (from a = 5.5736 ±0.0005 Å) in the fcc cell corresponds to an increase in O/(Th+U) from 2.00 to 2.126. Cracking of the exterior oxide caused by the fcc cell contraction appeared slightly more extensive than observed for $Th_{0.801}U_{0.199}O_{2.00}$. The cracking did not follow the MgO distribution.

78.6% Thoria/20% Urania Pellets, with 1.4% CaO

These pellets consisted primarily of a solid-solution fcc oxide with a = 5.5707 ±0.0004 Å. Formation of a solid solution between CaO and $(Th/U)_{2.00}$ during pellet fabrication was expected.[8] Microprobe analysis showed grains of solid-solution oxide about 300 micrometers in diameter containing 79.6 ±2.7 wt % ThO_2, 19.9 ±2.7 wt % UO_2, and 0.5 ±0.1 wt % CaO, as well as CaO or $CaO \cdot XH_2O$ inclusions at the grain boundaries. Pores in the solid-solution oxide were faceted rather than rounded. The composition of the solid-solution oxide corresponded to $Th_{0.786}U_{0.192}Ca_{0.022}O_{1.978}$. Its black color was caused by defects from the CaO in the fcc lattice. The x-ray density was 10.15 g/cm^3, but the pellets were too poorly formed to measure their densities accurately. The pellets also deteriorated with time, apparently because of reaction of the CaO inclusions with atmospheric moisture. Although the presence of CaO in solid solution aids dissolution, the total amount should be less than 0.5 wt % to avoid formation of CaO inclusions.

Heating the pellet for 64 hours at 600°C caused complete oxidation. The fcc cell of the solid-solution oxide contracted to a = 5.5619 ±0.0006 Å, corresponding to an increase in O/(Th+U+Ca) to 2.142. There was no cracking of the pellet when it was oxidized.

Dissolution Studies of Oxidized Thoria/Urania Pellets

Dissolution results with the nonirradiated GEC thoria/urania pellets which had been oxidized indicated that increasing the roasting temperature above 600°C reduced the subsequent rate of dissolution (Table 3). Dissolution rate of the oxidized 80/20 ThO_2/UO_2 material was also found to decrease as the % oxidation increased (as exposure time at 800°C increased) (Table 4). However, if tritium removal from irradiated thoria/urania materials is related to the oxidation of the UO_2, oxidation of the UO_2 may be required to disrupt the crystalline structure and allow tritium to diffuse out.

Dissolution results suggest that the greater the oxidation level, the slower the subsequent dissolution. One approach to eliminate this contradiction would be to grind the thoria/urania to a small particle size, allowing faster oxidation and subsequent dissolution. To obtain 99+% dissolution in Thorex in six hours and to obtain about 99% oxidation in 4 to 6 hours, the 80% thoria/20% urania (GEC I) pellets must be pulverized to less than 1000 μ (Table 5).

Effect of Additives on Dissolution of Thoria and Thoria/Urania Pellets

Results with GEC Materials

Dissolution results with GEC pellets showed that the addition of MgO (Reference 9) or UO_2 to ThO_2 increased the dissolution rate in refluxing Thorex solution (Table 6 and Figure 3). The addition of 1% MgO to the 80/20 ThO_2/UO_2 formula did not increase dissolution rate vs. the 80/20 ThO_2/UO_2 sample without MgO. Although the pellets with 1.4% calcium oxide were not of reactor quality (low density and mechanical integrity), these pellets were completely soluble in Thorex. X-ray characterization of the 1.4% CaO pellets showed that about 0.5% of the CaO formed a solid-solution with the ThO_2 and UO_2, with the remaining 0.9% present as inclusions at grain boundaries. Possibly, the "excess" CaO caused poor pellet formation, but a lower content (about 0.5%) could yield acceptable pellet quality.

TABLE 3

% Oxidation/% Dissolution* OF GEC 80% ThO_2/30% UO_2 Pellets

Oxidation Temperature, °C	Heating Time, hr			
	0	8	16	64
25	0/46			
500		~5/42		
600		24/**	29/60	75/65
700				90/53
800				100/41

---

* % Dissolution in 6 hours in refluxing "Thorex" solution.

** Not measured.

TABLE 4

Effect of Oxidation at 800°C on Dissolution of GEC 80% ThO_2/20% UO_2

Material Size	% Oxidation/% Thorex Dissolution, 6-hr Reflux
Pellets (0.53 inch)	0/45 100/41
Powder (100% less than 1/4 inch)	0/99+ 82/91 87/83 97/78

TABLE 5

Effect of Particle Size on % Oxidation and % Dissolution of GEC 80% ThO_2/20% UO_2

Particle Size	% Oxidation	% Dissolution*
Pellet (0.55 inch)	29	60
Powder (100% less than 1/4 inch)	80	99+
Powder (100% less than 1000 μ)	97	99+

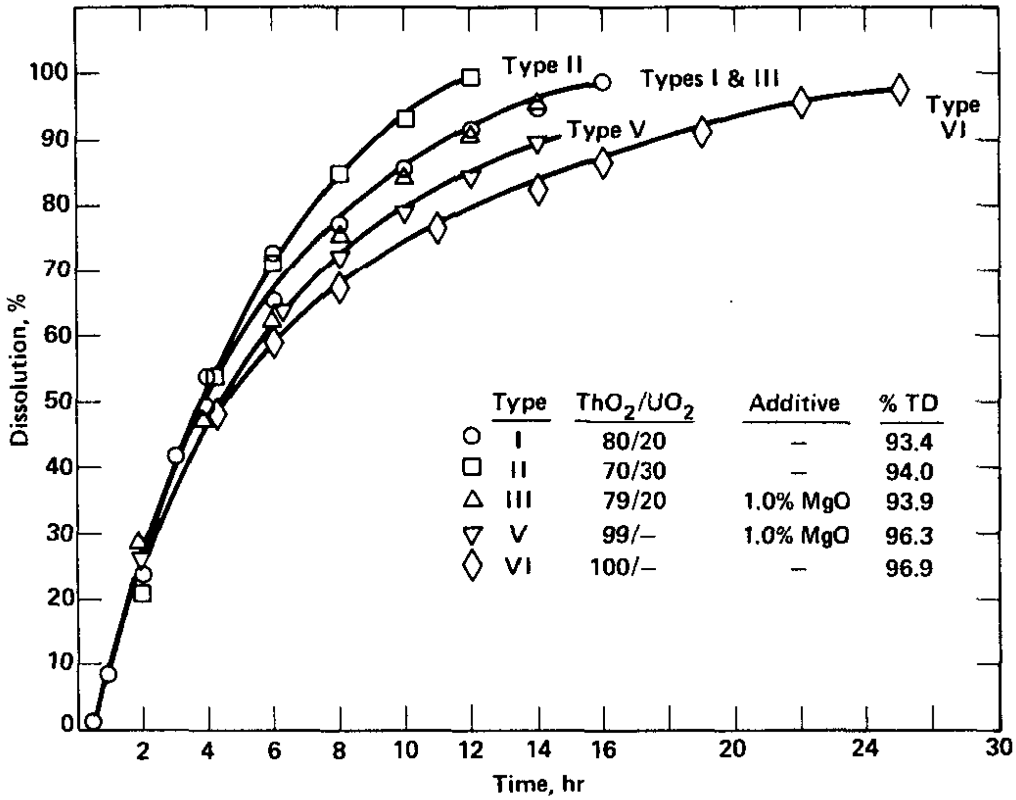
---

* % Dissolution in six hours in refluxing Thorex solution.

TABLE 6

Effect of Additives on GEC ThO_2 Pellet Dissolution

Pellet Type				% Dissolution in Thorex Solution, 6 hrs	
ThO_2	UO_2	MgO	CaO	0.025M HF	0.050M HF
100	-	-	-	42	58
99	-	1	-	48	63
80	20	-	-	46	67
79	20	1	-	47	67
70	30	-	-	58	72
78.6	20	-	1.4	100	-



	Type	ThO_2/UO_2	Additive	% TD
○	I	80/20	–	93.4
□	II	70/30	–	94.0
△	III	79/20	1.0% MgO	93.9
▽	V	99/–	1.0% MgO	96.3
◇	VI	100/–	–	96.9

FIGURE 3. Dissolution Rate of GEC Pellets in "Thorex" Solution.

- *whole ceramic pellets*
- 0.050M HF Thorex solution

Results with PNL Materials

Battelle-Pacific Northwest Laboratory was asked to prepare reactor-grade 80/20 ThO_2/UO_2 ceramic pellets with various levels of CaO to be used in studies of the effect of CaO as a dissolution aid. Battelle prepared samples with 0, 0.33, 0.50, and 0.66% CaO (80/20 ThO_2/UO_2), which were of reactor-grade quality. The CaO in the PNL pellets formed a homogeneous solid solution with the ThO_2/UO_2 crystal structure and was not present at grain boundaries (as was the case with the GEC Type IV pellets).

The dissolution data shown in Figures 4 and 5 and Table 7 indicate that the addition of CaO significantly increased the dissolution rate of the ceramic pellets. The change in dissolution rate due to the addition of calcium oxide was more apparent when a lower concentration of fluoride ion was used in the dissolvant (Table 7). The use of CaO, therefore, might allow the use of a lower fluoride ion concentration during the dissolving stage of a reprocessing cycle, which would significantly reduce the corrosive properties of the Thorex dissolvant.

The data in Figure 6 indicate that dissolution rate drops significantly when the fluoride ion concentration is reduced to less than 0.020 molar. The % dissolution of 80/20 ThO_2/UO_2 CaO (PNL) pellets at six hours was 95 ±1%, at 0.050, 0.025 and 0.020 HF concentrations. With 0.015 MHF, the % dissolution dropped to ~78%.

Effect of HF Concentration on Dissolution of GEC Pellets

The effect of 0.025 and 0.050 HF concentration on the dissolution rate of GEC Types I, III, and V is shown in Figures 7, 8, and 9, respectively. The effect of breaking the 0.55 x 0.55-inch GEC pellets into smaller pieces (approximately the size of the PNL pellets (0.37 inch diameter x 0.30 inches long) is also shown in Figures 7, 8, and 9. The GEC pellets were broken into smaller pieces so that the dissolution rate of the GEC and PNL materials could be directly compared. The broken GEC pellets dissolved faster than the unbroken pellets.

Induction Period During Dissolution of GEC Pellets

The data in Figures 7 and 8 also depict the presence of an induction period during the dissolution of the Type I and VI GEC pellets (80/20 ThO_2/UO_2 and 100% ThO_2, respectively). In 0.025 MHF, the induction period took about 1.5 hours with the Type I pellets and about 0.5 hour with the Type VI pellets. The induction time was shorter at higher (0.050M) HF concentration.

TABLE 7

Effect of CaO on Dissolution Rate of 80/20 ThO_2/UO_2 PNL Pellets

Pellet Type	% CaO	% Dissolution at 6 Hours in Refluxing Thorex 0.025M HF	 0.050M H
PNL	0	73.6	87.2
PNL	0.33	96.6	96.8
PNL	0.50	93.3	94.5
PNL	0.66	98.0	98.2
GEC I	0	73.0	91.5

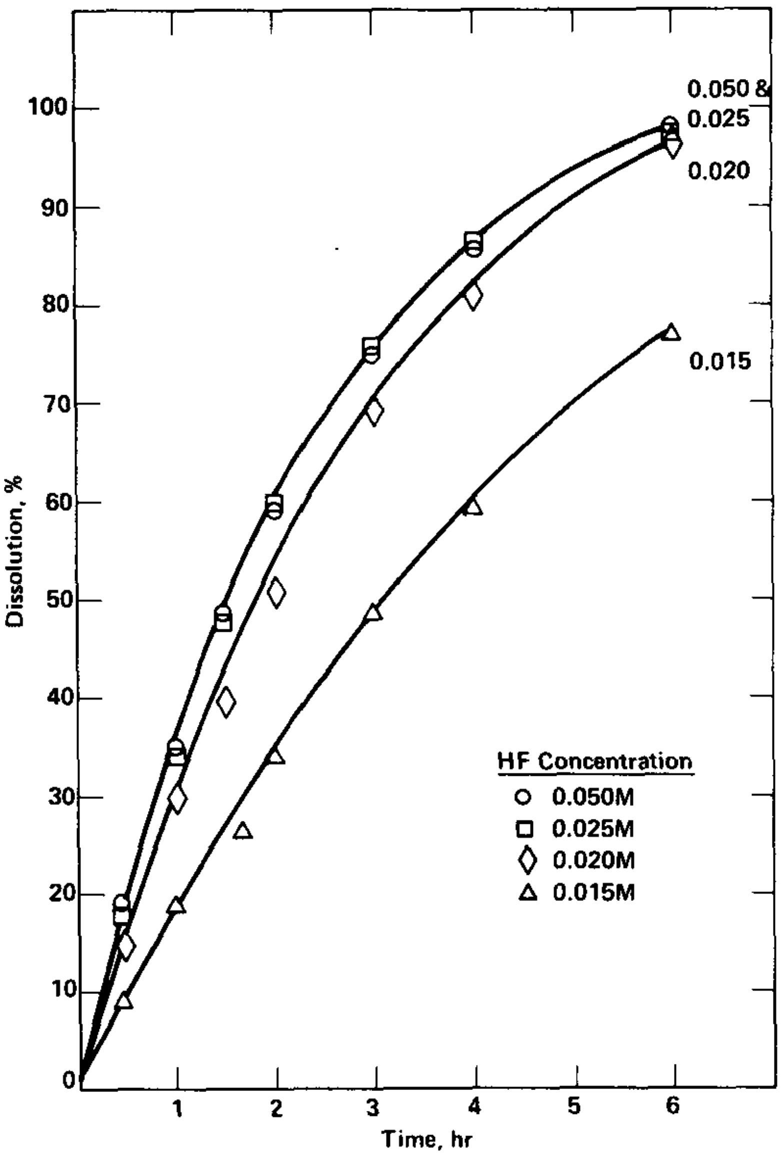


FIGURE 6. Dissolution Rate of PNL Pellets vs HF Concentration.

- 0.33% CaO pellets

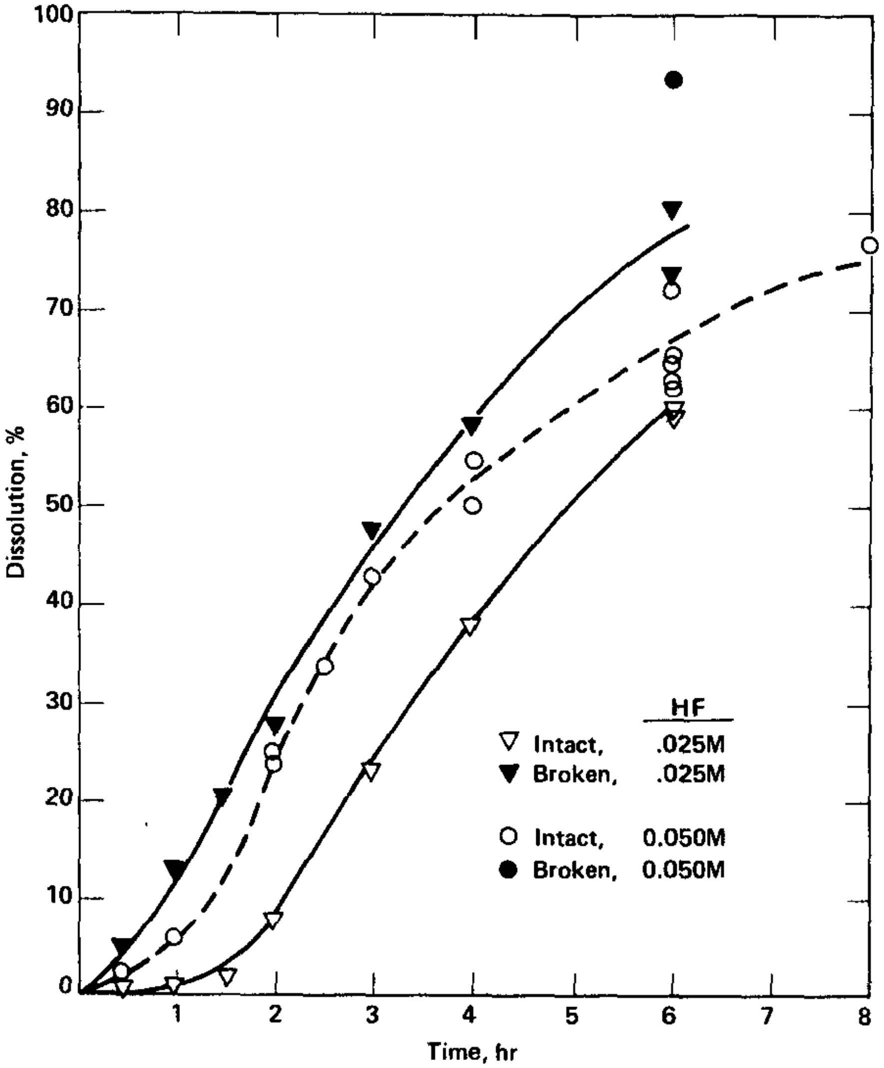


FIGURE 7. Dissolution Rate of GEC Pellets, Type I (80/20 ThO_2/UO_2), 0.025 vs 0.050M HF.

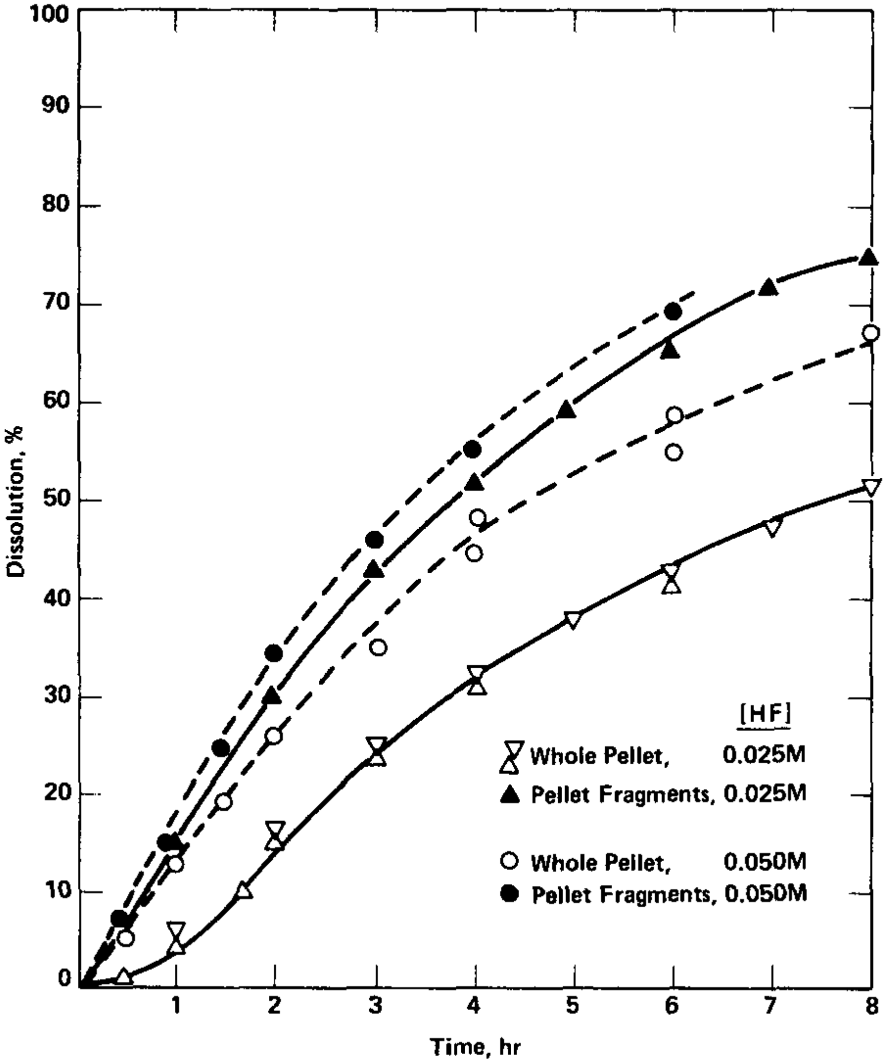


FIGURE 8. Dissolution Rate of GEC Pellets Type VI (100% ThO_2), 0.025 vs 0.050M HF.

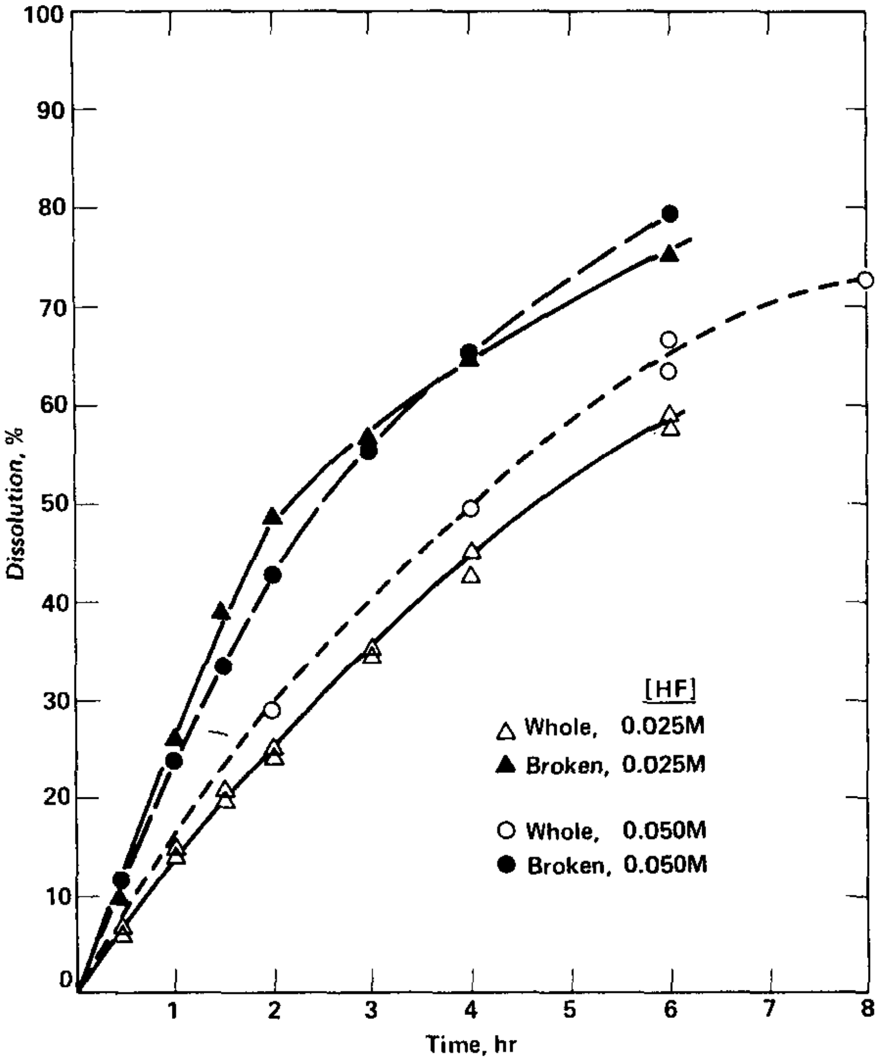


FIGURE 9. Dissolution Rate of GEC Pellets, Type V (99% ThO_2, 1% MgO), 0.025 vs 0.050M HF.

A GEC Type I pellet was analyzed by scanning electron microprobe (SEM) to determine the cause of the induction period. The analyses showed the outer surface (~150 μm) of the GEC Type I pellet to have a different structure than the bulk of the material. The surface layer also contained Ca, Fe, S, Na, Mg, Al, and Si which were not present in the interior of the pellet. The PNL 80/20 ThO_2/UO_2 pellets did not exhibit a similar induction period and did not have a surface layer different from the interior. Details of the SEM analysis are given in Appendix D.

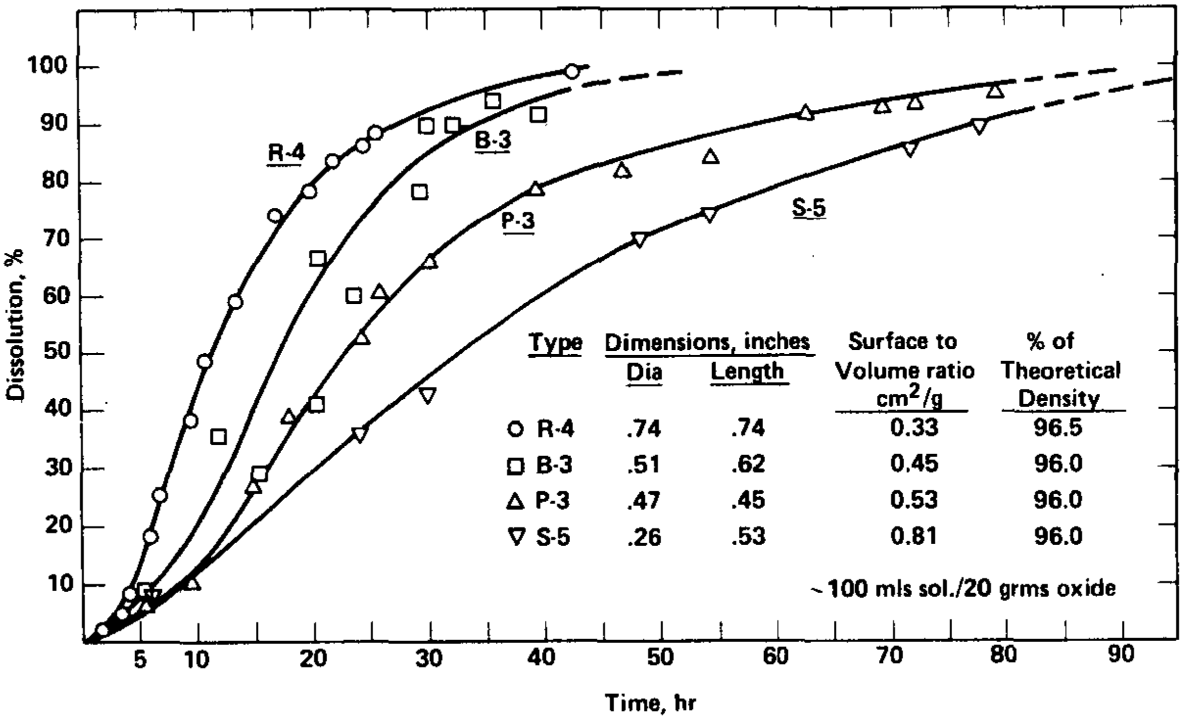
When the GEC Types I and VI pellets were broken into small fragments (the broken pieces were approximately the same size as the smaller PNL pellets), the dissolution induction period was essentially eliminated. This confirmed that the interior of the GEC Types I and VI pellets dissolved at a faster rate than the exterior surface of the pellets.

The possibility of an induction period during dissolution lends additional support to the concept that a crushing or grinding step will be required when reprocessing ThO_2-based fuels.

Effect of Pellet Size, Density, and Structure on Dissolution Rate of 100% Thoria Pellets

Four samples of 100% ThO_2 pellets with very similar physical characteristics, except for pellet size, were obtained from Westinghouse-Bettis to investigate the effect of pellet size on dissolution rate. The dissolution rate results are shown in Figure 10. The smaller pellets, with a greater surface area-to-volume ratio were expected to dissolve faster; however, the opposite effect was found. The data in Table 8 and Figure 10 indicate that those pellets with larger pore size, larger cracks, and larger inclusions dissolved faster. The % of theoretical density was the same for all four samples. This leads to the conclusion that microstructural characteristics can be more important than pellet size with respect to dissolution rate.

Additional data which support the conclusion that pellet size is not the critical parameter with respect to dissolution rate (in the range studied) are shown in Figure 11. In these examples, the Bettis Type R-4 and NFS "Reflector" pellets — both of similar size — dissolved at significantly different rates. The slower dissolution rate of the NFS pellets may be related to its higher density (vs. the Bettis R-4 pellets). However, fabrication procedures,



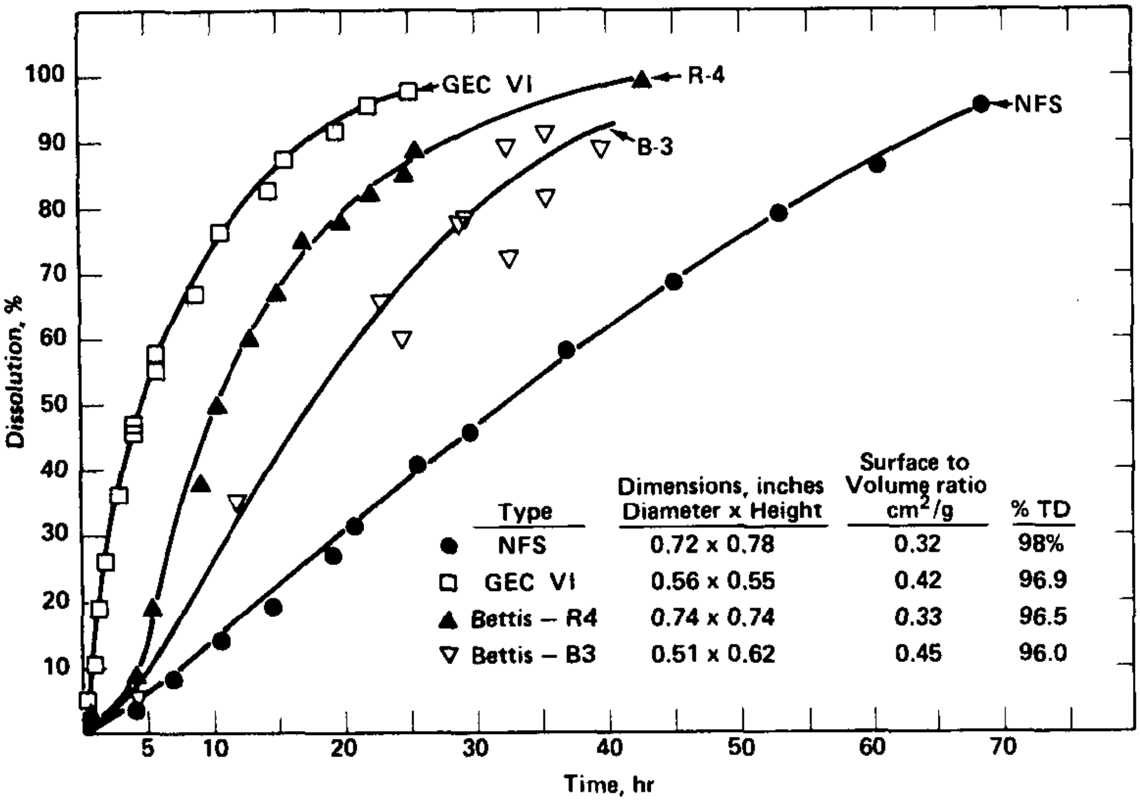
Type	Dimensions, inches Dia	 Length	Surface to Volume ratio cm^2/g	% of Theoretical Density
○ R-4	.74	.74	0.33	96.5
□ B-3	.51	.62	0.45	96.0
△ P-3	.47	.45	0.53	96.0
▽ S-5	.26	.53	0.81	96.0

FIGURE 10. Dissolution Rate of Bettis Pellets (100% ThO_2) 0.050M HF

TABLE 8

Key Characteristics of the Westinghouse-Bettis 100% ThO_2 Pellets

	Pellet Designation			
	R-4	B-3	P-3	S-5
Pellet Dimensions, inches				
● Diameter	0.74	0.51	0.47	0.26
● Height	0.74	0.62	0.45	0.53
Surface to Volume Ratio				
cm^2/gm	0.33	0.45	0.53	0.81
% of Theoretical Density	96.5	96.0	96.0	96.0
Grain Size	13	13	13	13
Pore Size				
● max area of pore ($in.^2$)	0.0043	0.002	0.002	0.002
● max diameter (in.)	0.074	0.056	0.056	0.050
Internal Cracks				
● max crack area ($in.^2$)	0.0012	0.0008	0.0008	0.0004
Foreign Inclusions				
● max diameter (in.)	0.037	0.023	0.023	0.012



Type	Dimensions, inches Diameter x Height	Surface to Volume ratio cm^2/g	% TD
● NFS	0.72 x 0.78	0.32	98%
□ GEC VI	0.56 x 0.55	0.42	96.9
▲ Bettis – R4	0.74 x 0.74	0.33	96.5
▽ Bettis – B3	0.51 x 0.62	0.45	96.0

FIGURE 11. Dissolution Rate of 100% ThO_2 Pellets 0.050M HF.

● 100 m/s solvent/20 g ThO_2

all conditions tested, no reaction was observed between the SO_2 and ThO_2-20% UO_2. Tests with stronger Lewis acids such as SO_3 are recommended to determine whether this thermodynamically favored reaction will occur.

Alternative Complexing Agents

Tests indicate that use of a complexing agent other than aluminum is feasible and compatible with the process (e.g., solvent extraction or waste management). Comparison of pellet dissolutions of ThO_2, ThO_2-20% UO_2, and ThO_2-30% UO_2 shows that increasing the uranium content to meet nonproliferation guidelines increases the dissolution rate of pellets regardless of which complexing agent is used.

The amount of dissolution that occurred during six hours of reflux was used to test the relative effect of various complexing agents on dissolution rather than attempting complete dissolution. Greater than 90% of ThO_2 sol-gel powders dissolve during six hours of reflux in dissolver reagent initially consisting of 13M HNO_3, 0.025M HF and 0.1M $Al(NO_3)_3$.

Test results show that the use of 0.1M aluminum nitrate or 0.1M calcium nitrate to complex fluoride does not change significantly the effectiveness of fluoride-catalyzed (0.05M HF - 12M HNO_3) dissolution of pellets. The use of 0.1M thorium nitrate as complexant does reduce the rate of dissolution (Table 10).

Effect of Bulk Zircaloy on Dissolution of Unirradiated Thoria

Tests show that Zircaloy cladding will be compatible with a shear/leach process for thoria fuels because a protective oxide coating on the cladding surface retards attack by the fluoride-catalyzed dissolver solution 13M HNO_3-0.025M HF-0.1M $Al(NO_3)_3$. In the TFCT reference fuel cycle, it is assumed that Zircaloy cladding will be used to achieve neutron economy and that spent fuel clad in Zircaloy can be easily reprocessed.

In one test, a 1-inch segment of bulk cladding and 25 grams of thoria powder were refluxed for eight hours in 150 mL of dissolver solution. Only 0.10% of the cladding dissolved, but the thoria completely dissolved in less than four hours. Thoria alone also dissolved completely in less than four hours. In a separate test, cladding was refluxed with 150 mL of dissolver solution for eight hours with no thoria present; 0.38% of the cladding dissolved, which shows that thoria powder retards the dissolution of cladding.

TABLE 10

Effect of Complexing Agents on Dissolution of Pellets in 12M HNO_3-0.05M HF

Complexing Agent	% Dissolution After 6 hours of Reflux		
	ThO_2	ThO_2-20% UO_2	ThO_2-30% UO_2
None	52	65	-
0.1M $Al(NO_3)_3$	50	62	62
0.1M $Th(NO_3)_4$	38	53	56
0.1M $Ca(NO_3)_2$	50	68	-

To confirm that the blue-black oxide coating on the Zircaloy retarded dissolution of the cladding, the exterior surface of a cladding segment was mechanically polished before reflux. During eight-hour reflux, 3.38% of the polished cladding segment dissolved in 150 mL of dissolver solution. Freshly sheared fuel elements would have unoxidized edges and could dissolve to the extent observed with the polished cladding (3 to 4%). If a heating cycle in air is used to remove tritium from these thoria-based fuels, the raw metal edges should be sufficiently oxidized to retard Zircaloy dissolution.

Head End Process Flowsheet

A preliminary head end flow sheet was defined, based on the laboratory testing of the unirradiated thoria/urania pellets:

1. Shear Zircaloy rods.

2. Declad oxide fragments and separate hulls.

3. Grind fuel fragments to 100% less than 1000 microns.

4. Remove tritium from powdered material by either air roasting or vacuum treatment.

5. Dissolve powder in Thorex $[12M\ (HNO_3)_3,\ 0.05M\ HF,\ 0.1M\ Al(NO_3)_3]$

6. Heat treat zirconium hulls to remove tritium and to minimize pyrophoric nature of zirconium fines.

7. Leach Zircaloy hulls.

8. Denitrate combined dissolver solution and leach solution.

9. Clarify and adjust feed solution for solvent extraction.

Continuing study. Laboratory studies of unirradiated fuels will be continued. Hot cell studies of irradiated fuels will be initiated to further study the tritium removal and dissolution processes.

CONCLUSIONS

The roasting and dissolution experiments conducted with nonirradiated ThO_2 and ThO_2/UO_2 ceramic pellets gave the following conclusions:

- Roasting of ceramic pellets of ThO_2 or ThO_2/UO_2 with up to 30% UO_2 in air did not cause the pellets to break up or fragment into fine powder as did UO_2 roasted in air. Ceramic pellets with 20 or 30% UO_2 were oxidized, but the pellets retained their integrity and did not fragment.
- The addition of 20 or 30% UO_2 to ThO_2 ceramic pellets increased the dissolution rate vs. that of 100% ThO_2 pellets (in Thorex solution).
- Calcium oxide was found to significantly increase the dissolution rate in 80% ThO_2/20% UO_2 ceramic pellets. MgO did not affect the dissolution rate significantly when added to 80/20 ThO_2/UO_2 pellets.
- High-temperature and pressure-dissolution conditions did not eliminate the need for fluoride in the solvent.
- Pretreatment of ThO_2 with SO_2 gas did not improve the dissolution rate.
- Zircaloy cladding would be compatible with a shear-leach process for thoria fuels, because a protective oxide coating on the cladding surface retarded attack by the fluoride catalyzed dissolver solution and minimized the amount of zirconium dissolved in the dissolution step.

A preliminary head end process flow sheet for thoria/urania ceramic pellets was defined based on the laboratory testing of the nonirradiated materials.

APPENDIX A

DESCRIPTION OF WESTINGHOUSE-BETTIS 100% ThO_2 PELLETS

These pellets were prepared under the Naval Reactors (NR) Water-Cooled Breeder Reactor program. The pellets were declared excess for the NR program[5] and were made available for use by other DOE organizations.

The special attributes of the pellets used at SRL are given in Tables A-1 and A-2.

TABLE A-1

Chemistry

A. Thorium Composition 87.6 - 88.4 w/o

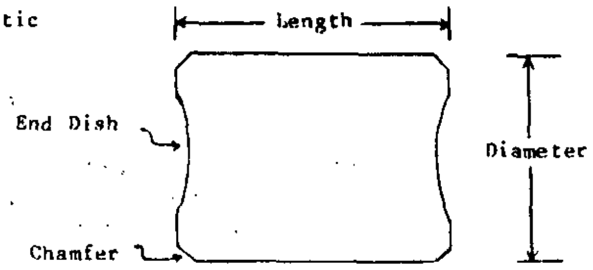
B. Impurities

Impurity	Maximum Limit, ppm
Al	500
B	1
C	200
Ca	150
Cl-Br	15
Co	10
Cr	100
Cu	40
F	20
Fe	300
Hg	2
Mg	100
Mn	10
Mo	100
N	25
Ni	200
Si	300
Ti	20
U	25
V	25
Dy	1.6
Eu	0.71
Gd	3.1
Sm	2.4

TABLE A-2

Physical and Metallographic Attributes

A. Pellet Schematic



Typical Pellet (not to scale)

B. Dimensions (All Values in Inches)

Pellet Types

Pellet Identification	S5		P3		B3		R4	
Diameter	0.2555	±0.0005	0.4695	±0.0005	0.5105	±0.0005	0.7415	±0.0005
Length	0.530	±0.020	0.445	±0.020	0.615	±0.020	0.740	±0.060
End Dish Configuration Spherical Radius (ref)	0.298		1.160		0.1439		3.152	
Dish Depth	0.009	±0.003	0.014	±0.004	0.014	±0.004	0.014	±0.004
Dish land width (min)	0.030		0.037		0.037		0.074	
Chamfer	0.015	±0.005	0.006	±0.004	0.006	±0.004	None	
Perpendicularity (max)	0.0016		0.0037		0.0029		0.0035	

C. Density (Theoretical Density 10.00 g/cc)

Individual Pellets (max)	100	100	100	100
Individual Pellets (min)	94	93	93	93
Individual Blend avg (min)	96.0	96.0	96.0	96.5

D. Metallographic Attributes

1. Grain Size (ASTM No.)

(min)	13	13	13	13
(max)	3	3	3	3

TABLE A-2 (continued)

D. Metallographic Attributes (continued)

	Pellet Types			
	S5	P3	B3	R4
2. Pore Size				
Max area of pore (in.^{2})	0.002	0.002	0.002	0.0043
Max diameter of pore (in.)	0.050	0.056	0.056	0.074
3. Internal Cracks				
Max crack area (in.^{2})	0.0004	0.0008	0.0008	0.0012
4. Foreign Inclusions				
Max diam of single inclusion (in.)	0.012	0.023	0.023	0.037
Max avg diam of five inclusions (in.)	0.006	0.011	0.011	0.018

APPENDIX B

DESCRIPTION OF PNL PELLETS

Four types of ThO_2/UO_2 pellets containing various levels of CaO were prepared at PNL and shipped to SRL (Tables B-1 and B-2).

TABLE B-1

ThO_2/20 wt % UO_2 with 0, 0.33, and 0.66 wt % CaO

Preparation Steps

- Dry co-ball mill the UO_2 and ThO_2 powders 4 hours
- Cold press at 76 mPa
- Granulate to <850 μm
- Add 0.2% zinc stearate (die lubricant)
- Press at 303 mPa to an average green density of 60% TD
- Sinter at 1700°C in Ar-4% H_2 for 4 hours

Pellet Properties

Batch Number	Composition	Net wt, g	Average Density* ±2, % TD	Open Porosity,* vol %	No. of Intact Pellets	No. of Pellets with External Cracks
TB-3-14-2	ThO_2-20 wt % UO_2	349	95.9 ±0.4	0.14	37	15
TB-3-12-2	ThO_2-20 wt % UO_2 + 0.33 wt % CaO	338	95.7 ±0.4	0.03	32	20
TB-3-13-2	ThO_2-20 wt % UO_2 + 0.66 wt % CaO	336	94.9 ±1.0	0.10	27	26

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* The pellet densities and open porosities were measured by using an immersion technique which is a modification of ASTM Standard C-373-72.

The data in the Table B-1 indicated that the addition of CaO increased the amount of pellet cracking, thereby reducing the sintered density.

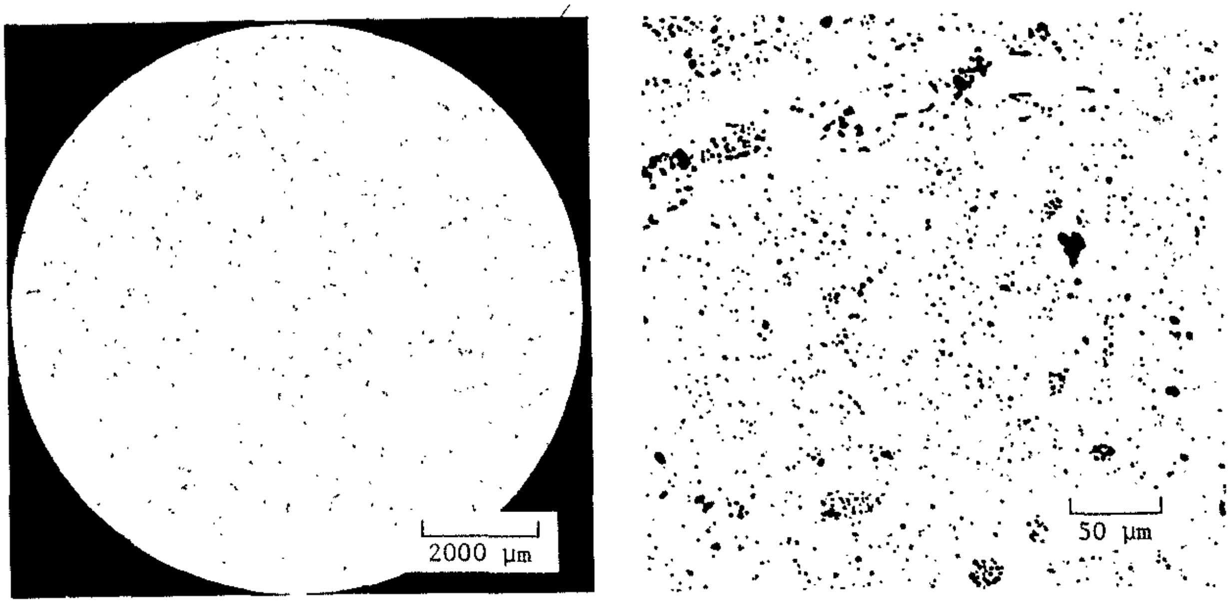
The microstructures shown in Figures B-1, B-2, and B-3 show that the CaO additions also modify grain structure. Islands of coarse grains surrounded by regions of very fine grains appear in the samples containing 0.33 and 0.66 wt % CaO.

The fourth pellet type was fabricated similarly to the three listed above, except that a different source of UO_2 powder was used (Table B-2). This made the slugging and granulation steps unnecessary. These pellets (with 0.50% CaO) did not exhibit the cracking problems experienced with the initial three types.

TABLE B-2

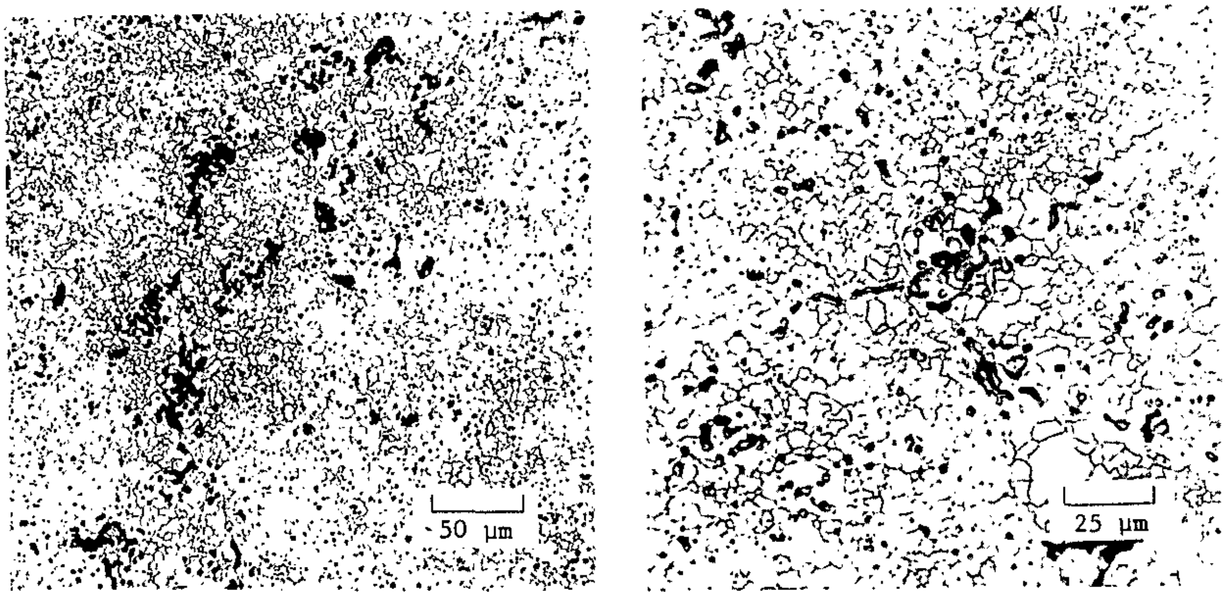
ThO_2/20 wt % UO_2 with 0.50 wt % CaO

Net wt., g	Average Density ±2, % TD	Open Porosity, vol %	No. of Intact Pellets
208	95.1 ±0.2	0.007	31



a. 10X Enlargement of TB-3-14-2 Pellet

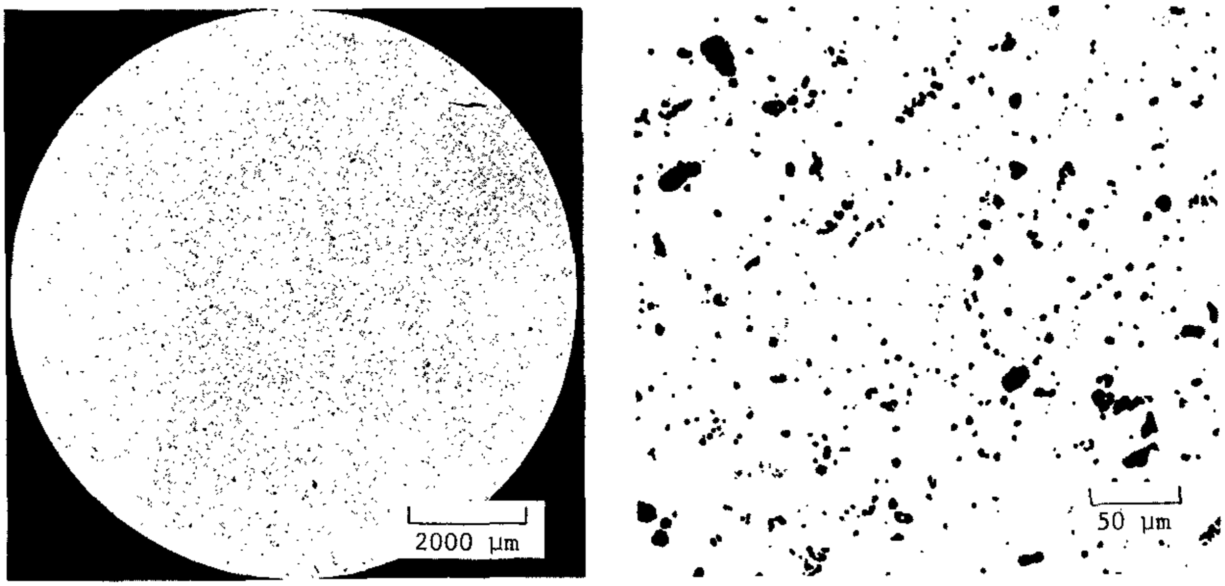
b. Enlarged SEM Photograph of TB-3-14-2 Pellet



c. Enlargement of Etched TB-3-14-2 Pellet

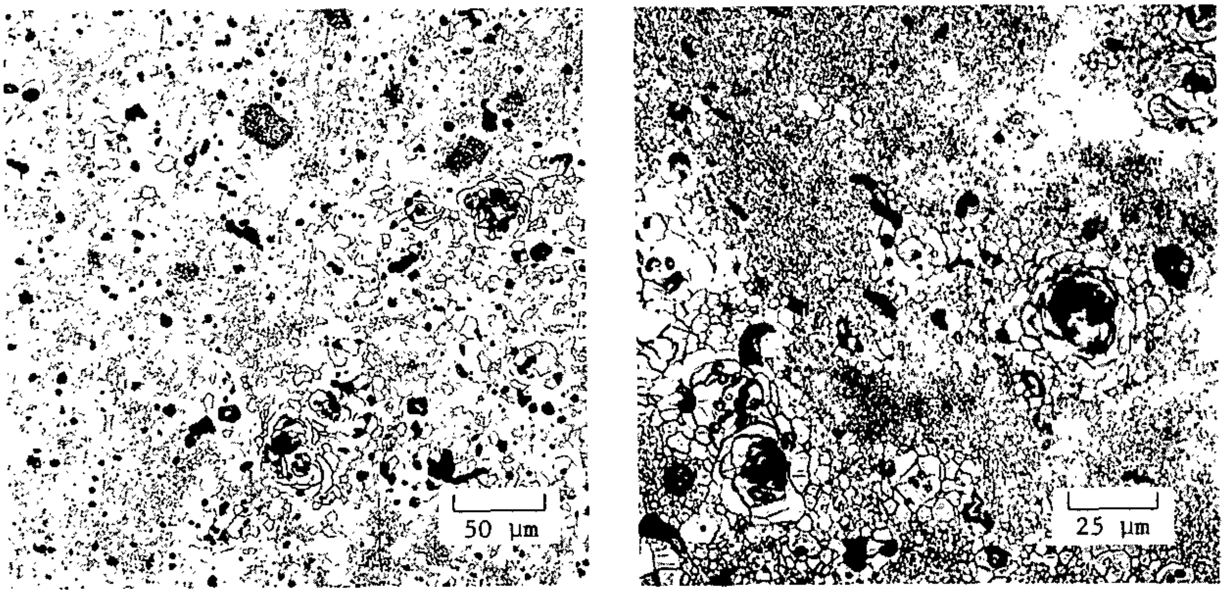
d. Different Section of Etched TB-3-14-2 Pellet

FIGURE B-1. Photographs of TB-3-14-2 Pellet: 80% ThO_2 - 20% UO_2



a. 10X Enlargement of TB-12-2 Pellet

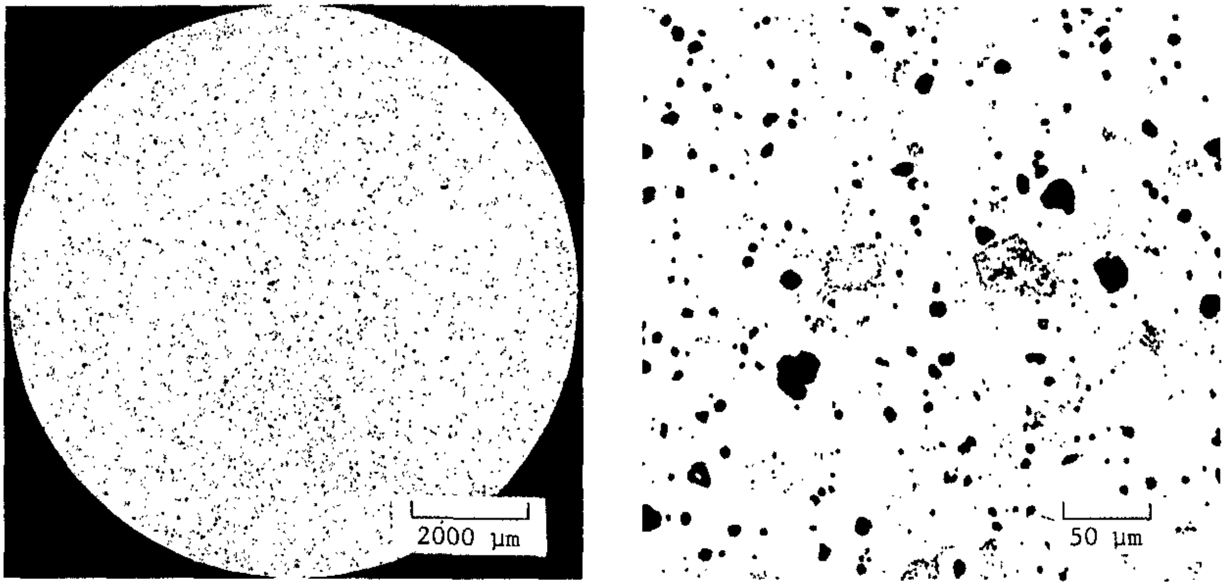
b. Enlarged SEM Photograph of TB-3-12-2 Pellet



c. Enlargement of Etched TB-12-2 Pellet

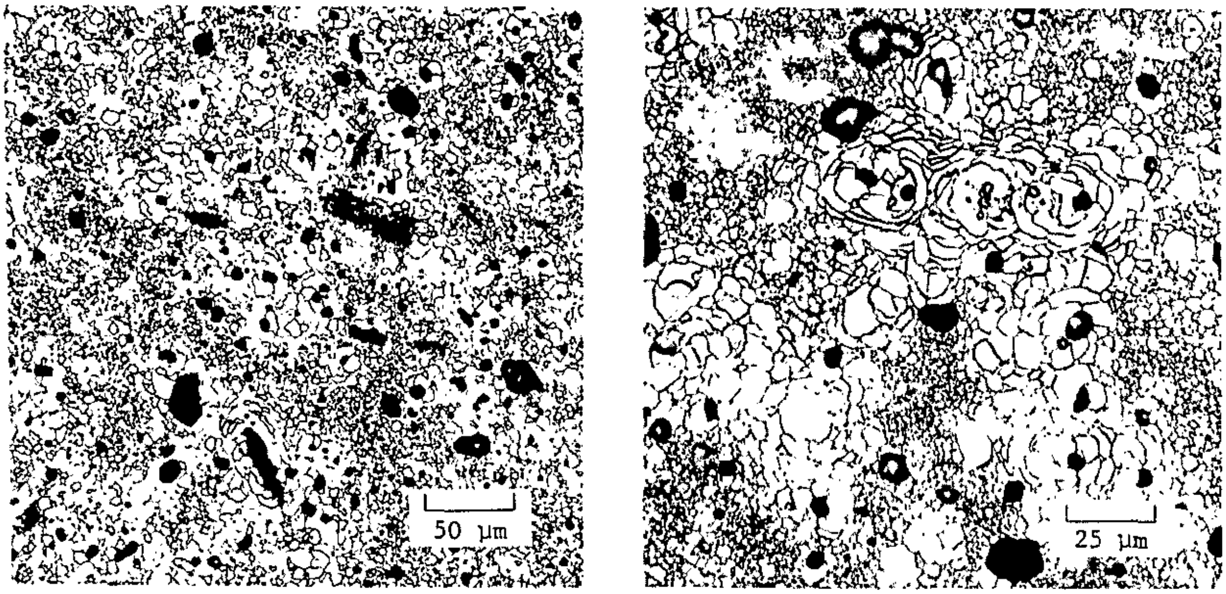
d. Different Section of Etched TB-3-12-2 Pellet

FIGURE B-2. Photographs of TB-3-12-2 Pellet: ThO_2 - 20 wt% UO_2 + 0.66 wt% CaO



a. 10X Enlargement of TB-3-13-2 Pellet

b. Enlarged SEM Photograph of TB-3-13-2 Pellet



c. Enlargement of Etched TB-3-13-2 Pellet

d. Different Section of Etched TB-3-13-2 Pellet

FIGURE B-3. **Photographs of TB-3-13-2 Pellet: ThO_2 - 20 wt% UO_2 + 0.66 wt% CaO**

APPENDIX C

SRL MICROSCOPY RESULTS ON PNL PELLETS

Three ThO_2/UO_2 ceramic pellets prepared by PNL were examined by Scanning Electron Microscopy at SRL (Table C-1).

The three pellets were

Identification	Composition
TB-3-14-2	ThO_2-20 wt % UO_2
TB-3-12-2	ThO_2-20 wt % UO_2-0.33 wt % CaO
TB-3-13-2	ThO_2-20 wt % UO_2-0.66 wt % CaO

TABLE C-1

Analysis of PNL Pellets

	Pellet Type		
	14-2	12-2	13-2
Wt % Range ThO_2	74.0-99.2	79.6-85.2	77.3-80.1
UO_2	26.0-0.85	20.2-14.6	22.2-19.5
CaO	-	0.21-0.64	0.34-0.75
Average wt % ThO_2	83.5	81.4	79.0
UO_2	16.5	18.3	20.5
CaO	-	0.31	0.5
% Variance (1σ) ThO_2	7.0	1.9	0.50
UO_2	7.0	1.8	0.8
CaO	-	1.12	0.12

The following conclusions with respect to these pellets were reached:

Type 14-2 (0% CaO)

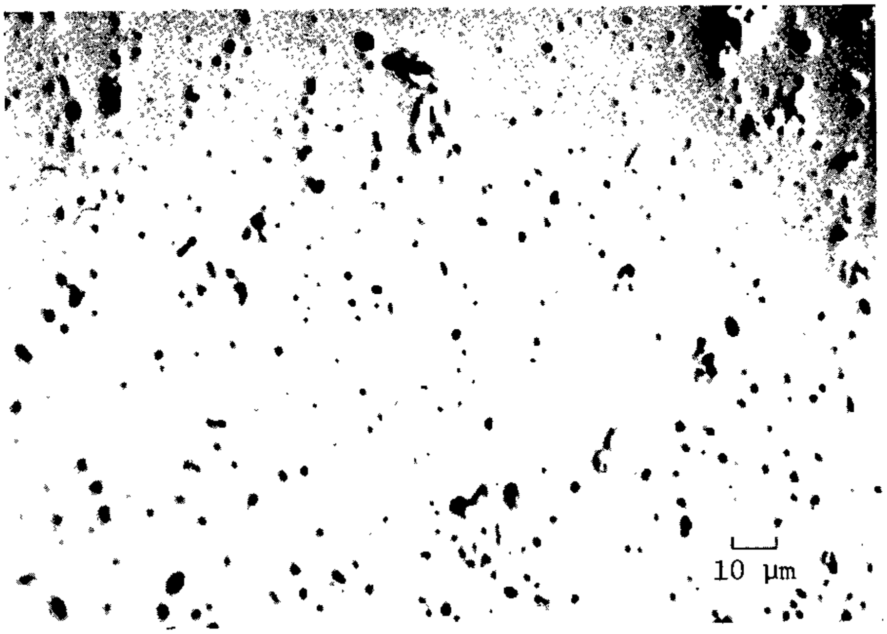
This pellet is more inhomogeneous than a similar type 80% ThO_2/20% UO_2 pellet produced by General Electric of Canada (see the section "80% ThO_2/20% UO_2 Pellets). The PNL pellet had larger grains than the GEC pellet (Photographs of the two types of pellets are compared in Figure C-1).

Type 12-2 (0.33% CaO)

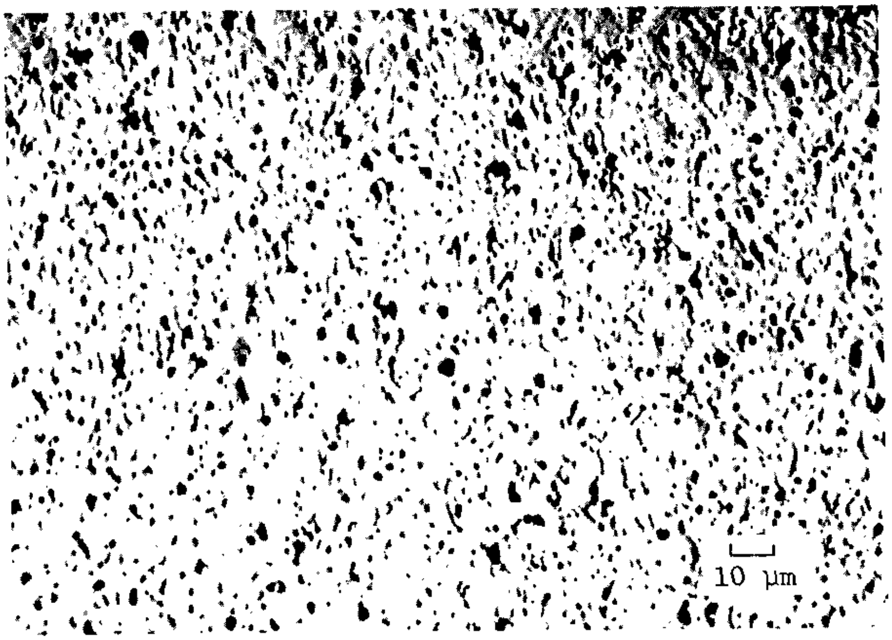
The pellet had some high Ca inclusions. Addition of the CaO improved the ThO_2-UO_2 homogeneity (Figure C-2).

Type 13-2 (0.66% CaO)

The 0.66% CaO pellet had more high - Ca inclusions than the 0.33% Ca pellet. The addition of more CaO continued the improvement in ThO_2-UO_2 homogeneity (Figure C-3).

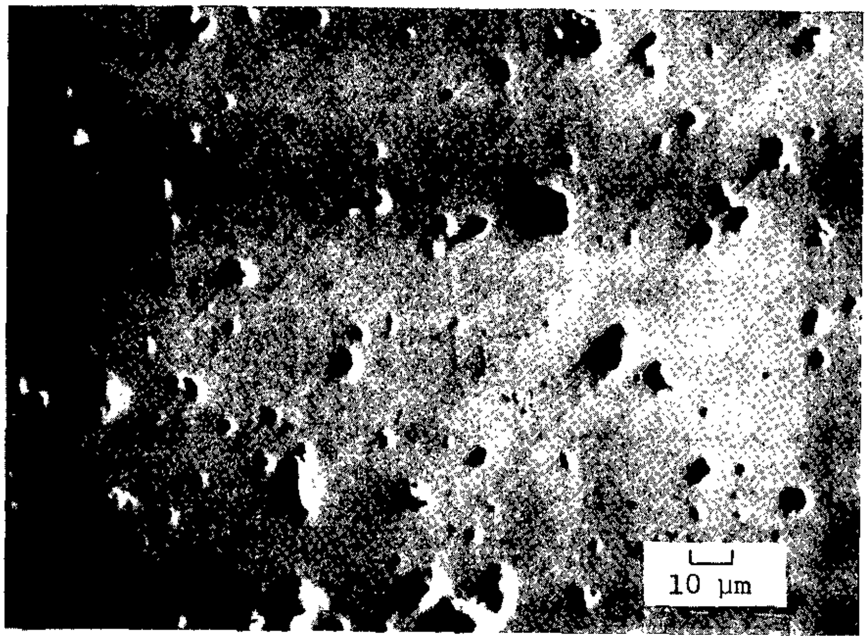


a. PNL Pellet 14-2 80 ThO_2 - 20 UO_2

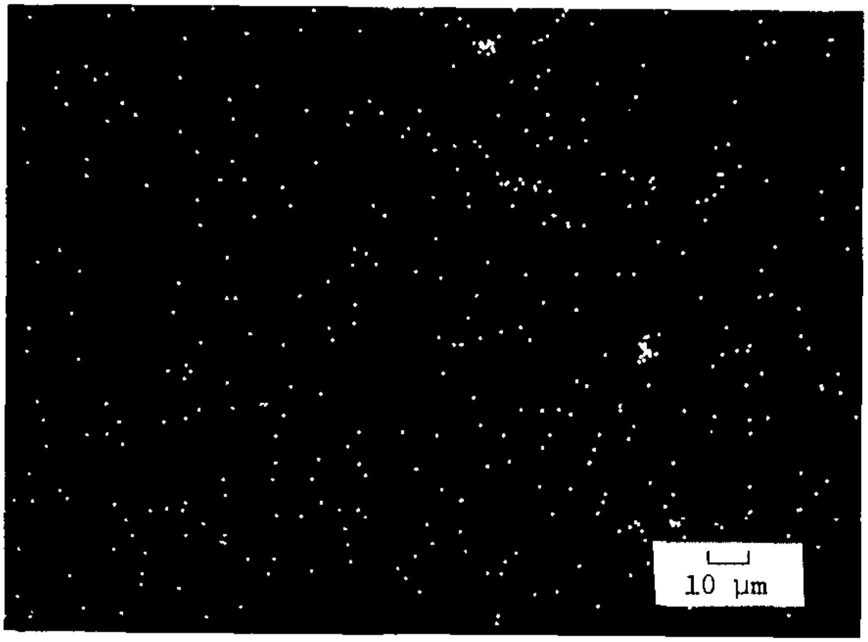


b. CGE Pellet 1A 80 ThO_2 - 20 UO_2

FIGURE C-1. Photographs of BSE Images of Polished Surfaces

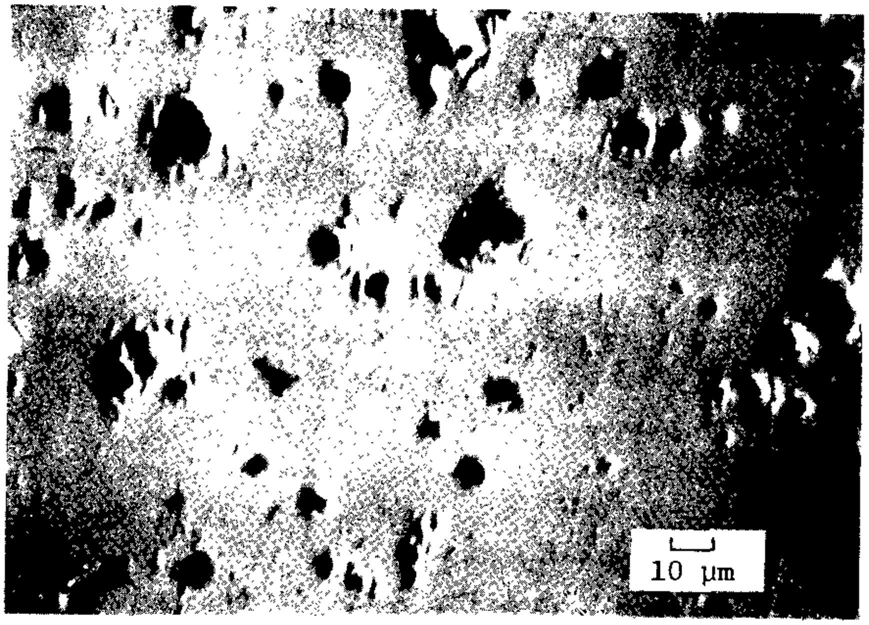


a. BSE Image of Polished Surface with 0.33% CaO

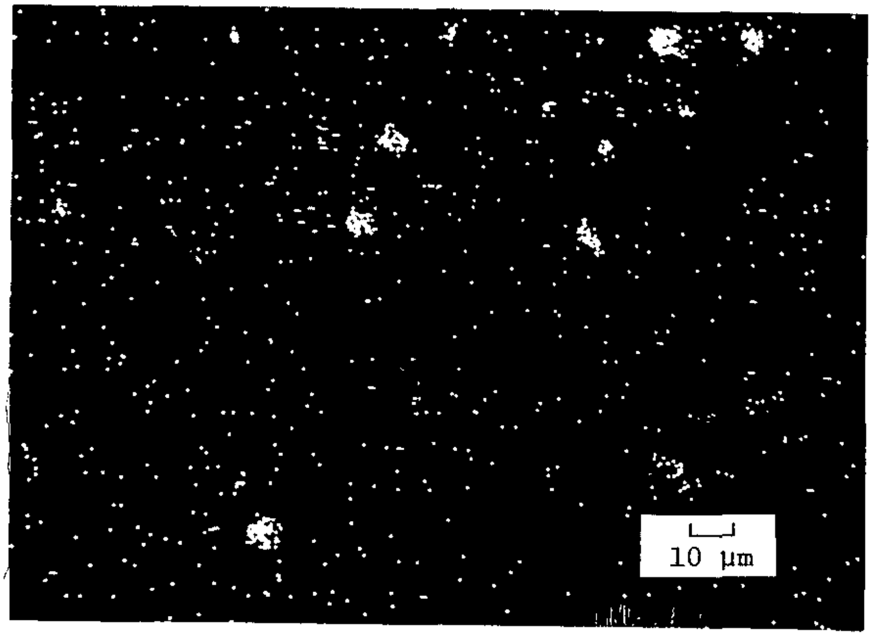


b. Ca X-Ray Image

FIGURE C-2. Characterization of PNL ThO_2/UO_2 Fuel Pellet - 12-2



a. BSE Image of Polished Surface with 0.66% CaO



b. Ca X-Ray Image

FIGURE C-3. Characterization of PNL ThO_2/UO_2 Fuel Pellet - 13-2

SRL MICROSCOPY STUDY ON GEC PELLETS TO DETERMINE THE CAUSE OF AN INDUCTION PERIOD DURING DISSOLUTION

The surfaces of a GEC Type I (80% ThO_2/20% UO_2) pellets were analyzed with the SEMQ (Table D-1) as received and after 30 minutes dissolution in Thorex reagent. A PNL pellet that did not exhibit a dissolution induction period was analyzed as a control (Table D-2).

The outer layer (about 150 microns deep) of the GEC pellet had a different structure than the bulk of the pellet (Figure D-1). The surface layer of the GEC pellet contained Ca, Fe, S, Na, Mg, Al, and Si, which were not detected in the bulk of the GEC pellet or in the PNL pellet (Figures D-2 and D-3).

It was concluded that the elemental impurities caused a modification of the oxide structure on the outer 150-micron layer of the pellet. It is assumed that the impurities were introduced into the surface during pellet fabrication. The modified oxide structure is apparently more resistant to dissolution, causing the induction period.

TABLE D-1

SEMQ Analyses of 80% ThO_2-20% UO_2 Pellet (GEC Type I) From the Canadian General Electric Ltd.

Oxide	Composition As Oxide Wt %									
	As Received		After 30 min in Thorex Reagent							
			Surface**						Interior**	
	Surface*	Interior*	No.							
			1	2	3	4	5	6	1	2
ThO_2	51.27 ±0.90	79.18 ±0.70	76.41	73.97	78.93	74.06	75.24	74.47	78.93	78.75
UO_2	48.73 ±0.90	20.82 ±0.70	20.63	20.26	21.07	19.53	19.56	19.65	21.07	21.25
CaO	-	-	0	0	0	0.11	0.13	0.19	0	0
FeO	-	-	0.15	0	0	0.12	0.20	0.19	0	0
SO_3	-	-	-	-	-	0.45	0.32	0.43	0	0
Na_2O	-	-	0.16	0	0	0	0	0.14	0	0
MgO	-	-	0	0	0	0	0.25	0.21	0	0
Al_2O_3	-	-	0.56	5.27	0	4.78	1.31	2.08	0	0
SiO_2	-	-	2.10	0.51	0	0.95	3.00	2.64	0	0

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* Analyzed only for Th, U, and Ca.

** Analyzed for 39 elements.

TABLE D-2

SEMQ Analyses of 80% ThO_2-20% UO_2 Pellet (PNL)
the Pacific Northwest Laboratories

Composition as Oxide Wt %

Oxide	Surface No. 1*	Surface No. 2*
ThO_2	76.65	76.64
UO_2	23.35	23.36
CaO	0	0
FeO	0	0
SO_3	0	0
Na_2O	0	0
MgO	0	0
Al_2O_3	0	0
SiO_2	0	0

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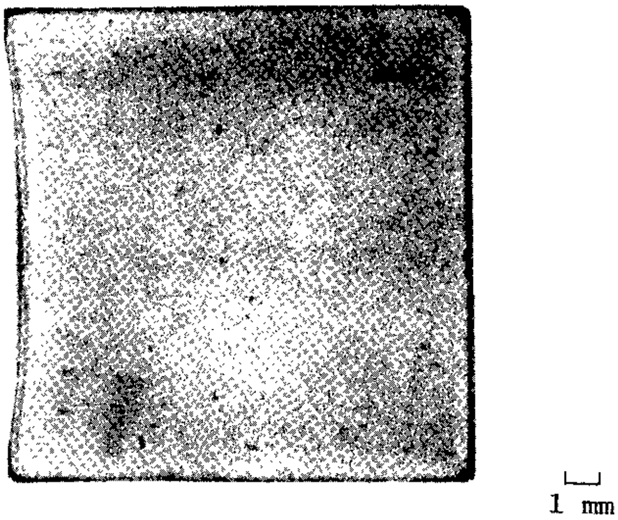
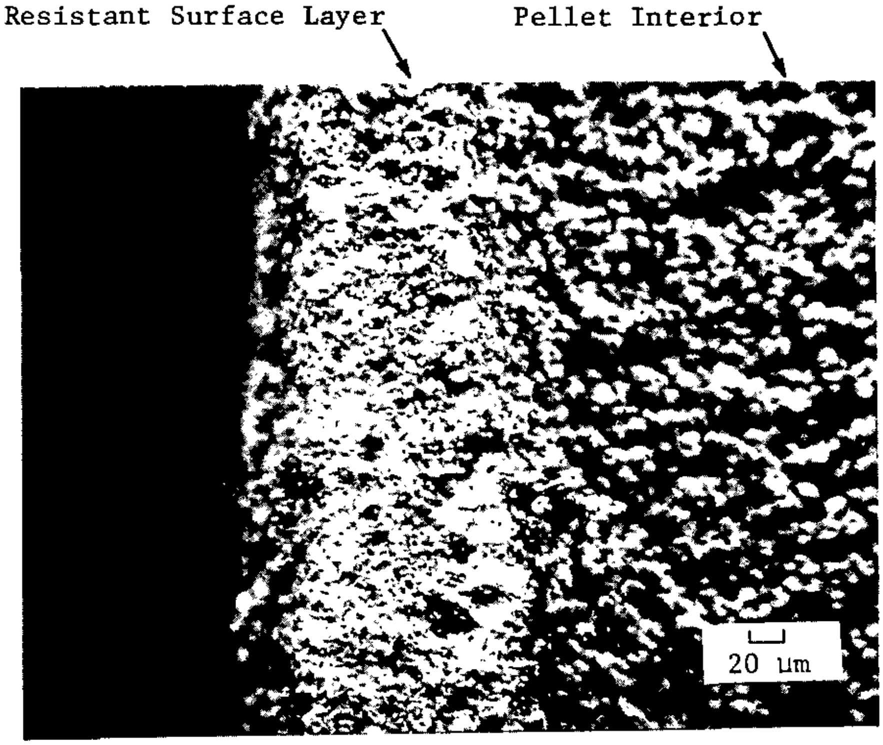
* Analyzed for 39 elements.



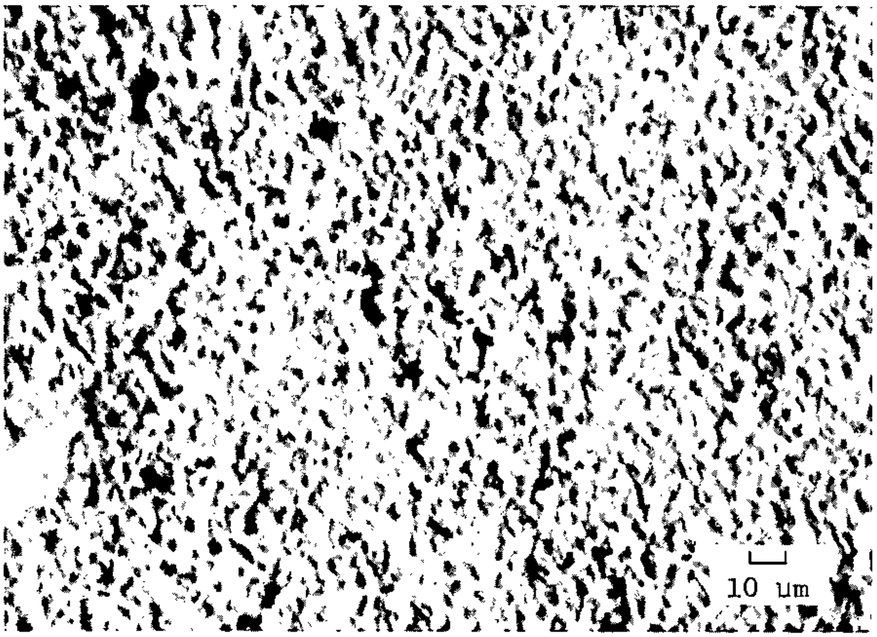
Dark Rim is
Chemically
Resistant Layer

a. Optical Image of Sectioned Pellet

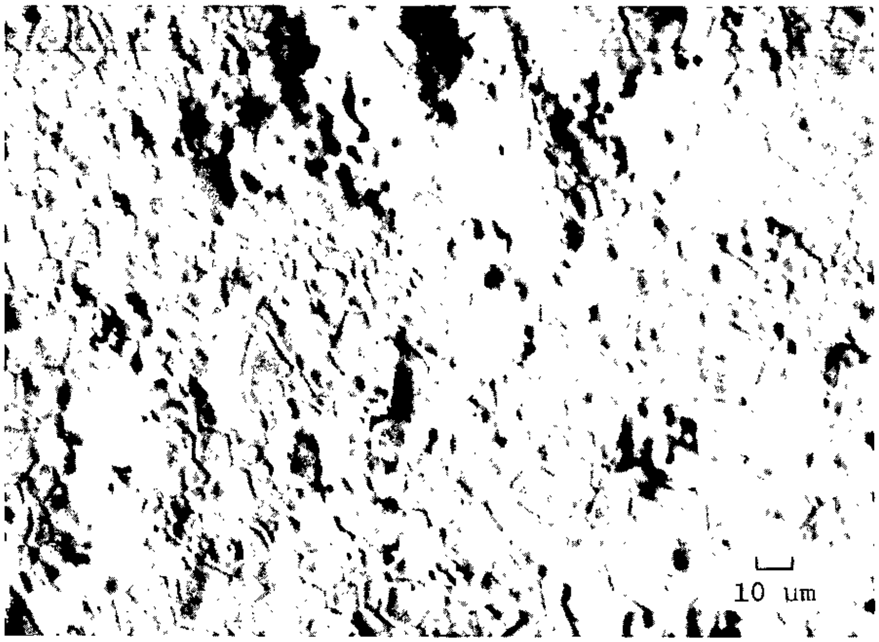


b. SEMQ Backscattered Electron Image. Sectioned CGEI Pellet After 30 Min in Thorex Reagent. The Outer ∿150 μm Is Resistant to Dissolution.

FIGURE D-1. Photographs of CGEI Pellets

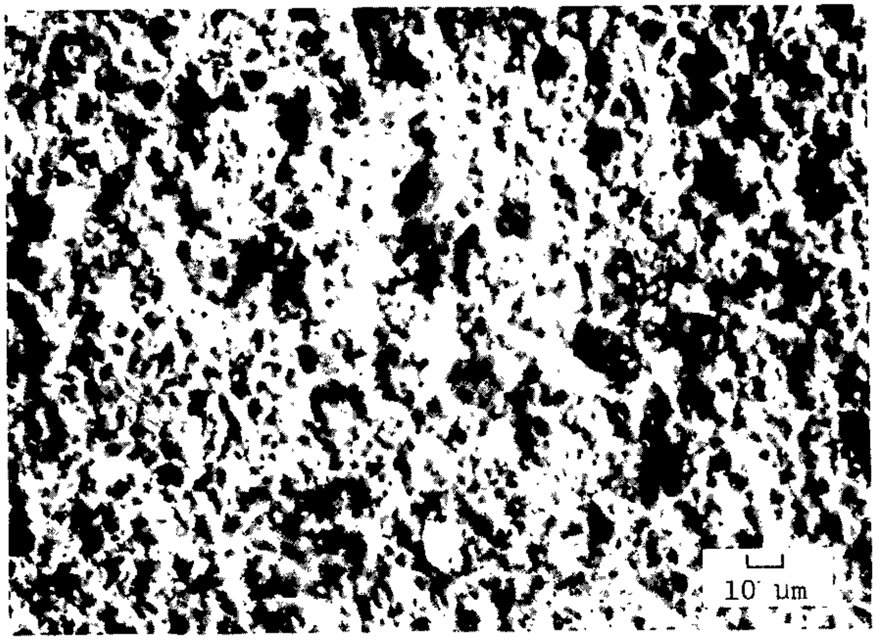


a. CGEI Pellet

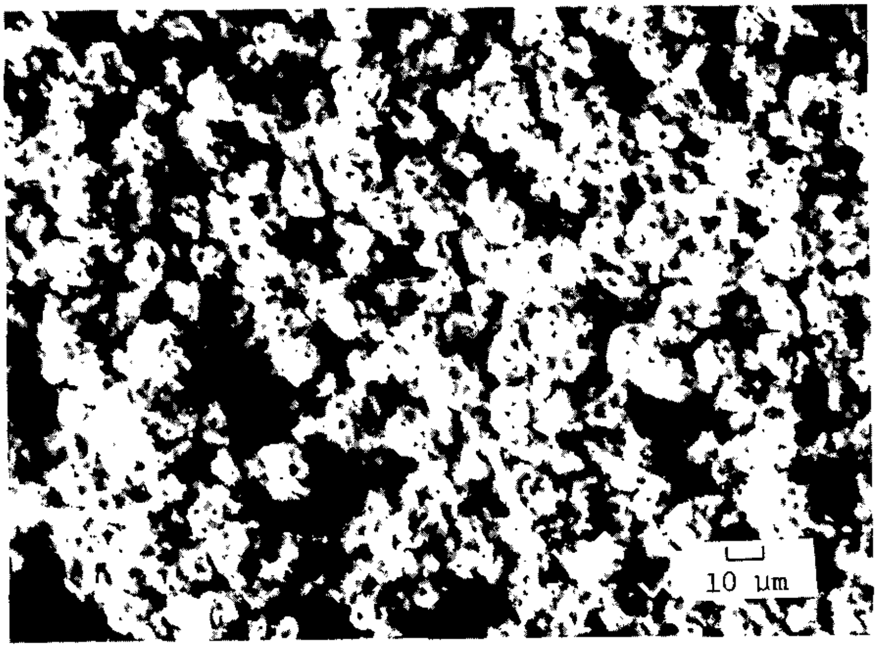


b. PNL Pellet

FIGURE D-2. Surfaces of As-received Pellets



a. Surface



b. Interior

FIGURE D-3. Sectioned CGEI Pellets After 30 Min in Thorex Reagent

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