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VOLOXIDATION - REMOVAL OF VOLATILE FISSION PRODUCTS
FROM SPENT LMFBR FUELS

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VOLOXIDATION – REMOVAL OF VOLATILE FISSION PRODUCTS FROM SPENT LMFBR FUELS

Compiled and edited by J. H. Goode

ABSTRACT

Results of studies of the voloxidation process by several ORNL groups are presented. In this process, sheared fuel is heated in air at 450 to 500°C to remove tritium, krypton, xenon, and iodine and, in the case of LMFBR fuel, to oxidize any "tramp" sodium prior to dissolution.

Data obtained in preliminary thermogravimetric studies of the oxidation of (U,Pu)O₂ pellets containing 20 and 25% PuO₂ showed that significant oxidation took place at temperatures higher than 350°C but that the conversion of UO₂ to U₃O₈, based on weight gain, was not always complete. The data also showed that some mechanically blended pellets disintegrated to a fine powder while others remained intact.

Detailed thermogravimetric and X-ray diffraction studies with pellet fragments showed that the oxidation of solid solution (U_{0.8}Pu_{0.2})O₂ was a two-stage process, which followed the ternary phase diagram of the U-Pu-O system. The first stage was rapid oxidation to a tetragonal M₃O₇ phase having an O/M ratio of approximately 2.35. The second stage, which resulted in disintegration of the fuel, occurred when the M₃O₇ phase converted to M₃O₈ + MO₂. The kinetics involved in the second stage were strongly dependent on temperature, fuel homogeneity, and other factors. At 550°C, the order of ease of oxidation in the second stage was: coprecipitated > sol-gel > mechanically blended pellets. Solid solution (U_{0.75}Pu_{0.25})O₂ also oxidized readily to an M₃O₇ or M₄O_{9+x} phase having an O/M of approximately 2.35, but proceeded to higher O/M ratios only with great difficulty; since entry into the M₃O₈ + MO₂ phase was not made, the fuel did not pulverize. The behavior of a nonhomogeneous mixture consisting of plutonium-rich regions in a UO₂ matrix was similar to that of UO₂, and disintegration occurred.

Other detailed thermogravimetric and X-ray studies were made with whole pellets of coprecipitated, mechanically blended, and sol-gel-derived (U,Pu)O₂ having Pu/U+Pu ratios of 0.15 to 0.28.

These results confirmed those obtained with pellet fragments, except that the ceramic quality and size of the specimen also affected the rate and degree of oxidation at Pu/U+Pu ratios of ≥ 0.15 . High-pressure (500-psi) oxygen at 600°C was used to force the oxidation of a homogeneous $(U_{0.75}Pu_{0.25})O_2$ pellet beyond the M_4O_9 stage to the $M_3O_8 + MO_2$ phase, where pulverization occurred.

Hot-cell tests indicated that, in nearly every case, more than 99% of the tritium was released from irradiated UO_2 or $(U,Pu)O_2$ when the fuels were oxidized at temperatures of 350°C and higher. About 98% of the iodine and about 98% of the krypton were volatilized from highly irradiated fuel specimens; however, more typical releases were on the order of up to about 45% of the krypton and 75% of the iodine.

I. INTRODUCTION

This document describes investigations of a new head-end step that has potential for removing volatile fission products as gases prior to the aqueous processing of spent LMFBR fuel. The objective of this step, which has been termed "voloxidation," is to remove tritium, iodine, xenon, and krypton from the sheared fuel and blanket materials for trapping and ultimate storage as wastes. Conceivably, this may be realized by heating the sheared fuel to about 650°C or less in air or oxygen to release the volatile fission products via thermal evolution or oxidation; the released gases are then carried out of the voloxidizer unit for subsequent trapping and retention within the processing plant. The ultimate aim of the studies on voloxidation is to limit the releases of fission products such that they conform to existing and anticipated regulations.

The major emphasis is centered on the removal of tritium from UO_2 and UO_2 - PuO_2 fuels since the tritium would otherwise be irretrievably diluted into aqueous streams during dissolution of the fuel. The voloxidation process also should effectively deactivate "tramp" sodium¹ (from the reactor coolant) that may have leaked into the fuel elements, thus eliminating a potential explosion hazard when

nitric acid is contacted in the subsequent dissolution step. The removal of radio-iodine (^{129}I and ^{131}I) is not considered essential since effective techniques are being developed to remove iodine from the dissolver solution²⁻⁴ and off-gases. However, efficient removal (>99%) of iodine in the voloxidation step would be an advantage in the overall control of this fission product. The same comment applies to the noble gases, xenon and krypton, which are evolved during dissolution. The removal of volatile fission products is a new technology that will require development of extensive chemical and engineering data. Tests have been made in the hot cell and laboratory over a wide range of variables: with temperatures of up to 850°C; with helium, air, or oxygen; with short- and long-cooled fuel; and with fuel burnups up to 100,000 MWd/ton. Oxide fuels containing up to 28% plutonium were used in most of the tests; however, the fuel types have been varied: sol-gel, mechanically blended, and coprecipitated oxides in the form of microspheres, shards, and pellets.

1.1 Background Information

The head-end processing step, voloxidation, for the volatilization of gaseous fission products – tritium, iodine, xenon, and krypton – from irradiated LMFBR oxide fuels was a logical development stemming from hot-cell studies that were made to determine the quantity and identification of fission products which might be released during the interim storage of baskets of sheared, short-cooled LMFBR fuel in air. Preliminary tests at ORNL indicated that ^{85}Kr and ^{131}I were released when irradiated $(\text{U,Pu})\text{O}_2$ was heated in a stream of air.²⁻⁵ Measurements made of fuel solutions indicated that the tritium had also been volatilized during oxidation.³⁻⁵ In some cases, we also found that the mixed oxide powdered and fell out of the cladding;² this comminution of the fuel appeared desirable as a means for providing shorter diffusion paths for the volatile fission products as well as possibly increasing the rate of dissolution by increasing the available surface area.

A survey of the literature on the subjects of disintegration of $(\text{U,Pu})\text{O}_2$ and fission product volatility during high-temperature oxidation was made in 1969, and

the references from that survey are tabulated here.⁶⁻²⁹ In general, the literature, which covers work at Harwell, Eurochemic, Atomics International, NUMEC, ANL, and others, indicated that fuel disintegration and release of noble gases occurred when pure UO_2 was oxidized to U_3O_8 . Variable results were obtained with $(\text{U,Pu})\text{O}_2$, depending primarily on the plutonium concentration of the fuel and/or the type of fabrication. Favorable results in the literature and in ORNL scouting experiments^{2-4,6} indicated that the development of such a process should be pursued.

This document consists of six sections, each of which describes different phases of the investigation into the chemical and engineering aspects of the volatilization of fission products from irradiated UO_2 and $(\text{U,Pu})\text{O}_2$ fuels. The hot-cell studies and engineering aspects of the investigation are being continued.

1.2 Fabrication Parameters Affecting Voloxidation

The fabrication parameters that are most likely to influence the voloxidation behavior are: (1) the chemical form of the fuel, (2) the plutonium concentration, (3) the homogeneity and degree of solid solution of the uranium-plutonium mixture, (4) the anion-to-metal ratio (for oxide fuels, O/M), (5) the fuel density, (6) the method and procedures of fuel fabrication, and (7) the fuel shape.

Chemical Form of the Fuel. — The Fast Test Reactor (FTR) "reference" fuel is composed of mixed oxides of uranium and plutonium. Other potential LMFBR fuels are carbides, nitrides, oxysulfides, etc. Each form will require a specific series of head-end tests.

Plutonium Concentration. — Proposed LMFBR oxide fuels contain varying concentrations of plutonium and normal uranium. The FTR reference fuel is 25% PuO_2 —75% UO_2 ;³⁰ the PuO_2 contents of oxide fuels for other reactors range from 16 to 21%.³¹ The plutonium concentration influences the irradiation conditions. Results of experiments described here have shown that the plutonium concentration influences the effectiveness of the voloxidation treatment, the rate of dissolution, and the completeness of dissolution in nitric acid as well. Solid solutions containing more than

approximately 40% PuO_2 have been shown to behave differently during oxidation at elevated temperatures than those of lower PuO_2 concentration, and also to require fluoride for dissolution.³²⁻³⁵

The LMFBR blankets consist of depleted UO_2 . Since the processing of the core alone or of a combination of the core and blankets is a viable option, studies of the behavior of UO_2 during voloxidation are needed.

Homogeneity of the Uranium-Plutonium Mixture. — The homogeneity and the degree of solid solution are important in the case of oxide fuels. The formation of solid solutions is promoted by the selection of appropriate manufacturing parameters, typically sintering time and temperature.^{36,37} The degree of powdering (and the resulting release of fission gases during oxidation) is strongly affected by the homogeneity. Solubility and dissolution rates in nitric acid have been found to be sensitive tests for oxide fuel homogeneity and the degree of solid solution. Generally, reasonable dissolution rates and total solubility of the unirradiated LMFBR fuel in pure nitric acid can be expected when the fuel is in solid solution and the PuO_2 content is less than 40%.³² Irradiation generally improves the dissolution characteristics; however, irradiation under certain conditions (flux, O/M, temperature gradient, power, etc.) may lead to localized changes in plutonium concentration and thereby influence the head-end behavior.

Anion-to-Metal Ratio. — For oxide fuels, this parameter is the oxygen-to-metal (O/M) ratio. Ratios of O/M in the range slightly below 2.0 are now considered desirable for LMFBR fuel. This ratio increases with irradiation due to the fission of plutonium, and will influence many of the transport and migration properties of uranium, plutonium, and the fission products during irradiation.³⁸⁻⁴³ Consequently, this factor will influence the release of fission gases to the plenum, migration of volatile fission products along the thermal gradient, separation of uranium and plutonium during irradiation, alloying with noble metal fission products, and volatilization of fission products in head-end reprocessing systems.

Method of Fuel Preparation. — The FTR reference fuel consists of sintered pellets of mechanically blended oxides of uranium and plutonium. Sol-gel and coprecipitated oxides are also being considered for use in commercial LMFBRs. Each type of fuel has characteristic advantages and disadvantages. Data on the behavior of all three materials are needed to assist in optimization studies for the complete fuel cycle.

Lerch, at WADCO, is engaged in a program⁴⁴⁻⁴⁸ to determine which mechanical-blending fabrication parameters exert the greatest influence on the dissolubility of the fuels (i.e., the completeness with which unirradiated candidate fuels dissolve in 12 M nitric acid). As mentioned above, this is a sensitive measure of the homogeneity and degree of solid solution of the fuel mixture. Results of Lerch's dissolubility studies showed that the sintering temperature, the source of PuO_2 , and the percent of PuO_2 in the mixture used for preparing mechanically blended fuels have the greatest effect on the final fuel homogeneity, as determined by the dissolubility of the fuel. Therefore, these fabrication parameters will influence the fuel behavior during voloxidation.

Fuel Form. — It is unlikely that the physical form of the fuel (i.e., pellets, Vipac shards, Sphere-Pac microspheres, U-fine microspheres, or others) will strongly affect the volatility of fission products after irradiation and shearing if each particle has an adequate degree of homogeneity of UO_2 and PuO_2 . This will be confirmed as part of the overall LMFBR fuel cycle optimization studies.

1.3 Irradiation Parameters Affecting Voloxidation

The irradiation parameters that are most likely to influence voloxidation behavior are: (1) burnup, (2) type of flux, (3) ^{235}U enrichment, (4) degree of fuel restructuring, and (5) radial temperature gradient. Almost every document prepared by DRDT contractors describes studies relative to the irradiation effects of fuel specimens. However, since the reference reactor (FTR) has not been completed, candidate fuels from various development programs are being fabricated and tested in substitute reactors (e.g., EBR-II, ETR, etc.). To obtain specific performance data, certain deviations from reference fuel composition and irradiation conditions must be made. An analysis of

the validity of thermal and fast flux irradiation tests in existing reactors has been described by Olsen et al.⁴⁹

Burnup. — Burnup is a major correlating factor for fuel performance studies and serves as a convenient summation of many irradiation processes for head-end studies as well. As mentioned above, burnup influences the O/M ratio; in addition, it may affect the release of fission gases and it can influence the Pu/U ratios in localized areas.^{38-43,50-55} Burnup is usually quoted as a rod average or a peak value; in head-end reprocessing studies, however, a "local" burnup value is advantageous. Fuel samples irradiated in thermal fluxes have been found to have two to ten times higher burnups near the cladding than near the center of the fuel; samples irradiated in fast fluxes have flatter radial burnup profiles. Burnup differences also exist along the length of a rod because of variations in the axial flux profile. Each may affect the burnup of a particular sample.

Type of Flux and Uranium Enrichment. — Because of compromises made to simulate reference conditions in existing reactors,⁴⁹ the final state of an irradiated fuel sample will depend on the type of flux (thermal or fast) to which the sample was exposed and the amount of ^{235}U present in the fuel. The magnitude or seriousness of differences in fission product content due to the yields from ^{235}U and ^{239}Pu and the distribution of the fission products throughout the fuel must be determined experimentally.

Temperature of Irradiation. — At least three components are associated with the temperature of irradiation: centerline temperature, radial temperature gradient, and linear heat rating. Another significant factor may be the temperature at the inner cladding wall. The effects of the fuel temperature of interest to fuel reprocessing studies are primarily concerned with fission gas release during irradiation and shearing, fuel restructuring, and migration and transport of fuel and fission product material along temperature gradients. Temperatures are dependent on neutron flux, as well as plutonium (and ^{235}U) concentration, overall fuel thermal conductivity, outer cladding temperature, and smear density of the fuel.

Degree of Fuel Restructuring. — The degree of fuel restructuring is a physical property measured in postirradiation examinations (metallography). Fuel behavior models are being developed to predict the radius of the central void, the radius of the columnar grain region (a measure of the centerline temperature and gradient, $\sim 1700\text{--}1800^\circ\text{C}$), the radius of the equiaxed grain growth region ($\sim 1600\text{--}1800^\circ\text{C}$), and the unrestructured zone (original fuel grain size $< 1600^\circ\text{C}$).⁵⁶ The degree of restructuring, expressed as weight percent of the fuel, may be one of the major correlating factors affecting voloxidation, possibly interacting strongly with burnup. The amount, physical distribution, and bubble size of fission gases in irradiated fuels have been studied by ANL, the General Electric Company, and PNL.^{39,42,43,51,52,55} The unrestructured region may behave much the same as the unirradiated (or lightly irradiated) fuel with regard to release of gases and dissolubility. The release of fission gases (Xe + Kr) from this region by voloxidation is restricted by the dispersal of these gases at trapping sites within the many small crystallites as tiny, separated gas bubbles.⁵⁷

The situation within the equiaxed grain growth region is similar. It is possible that a greater fraction of the fission gas in this region may have been trapped at the grain boundaries or dislocations rather than in the crystallites and, therefore, could be released on voloxidation. In fuels that have been irradiated at high thermal powers for reasonably long times (years), this region may be uranium rich as the result of vapor phase movement of the UO_2 out of the melted zone. For this to occur, the O/U ratio must be approximately 2. Mobile fission products, such as cesium, iodine, ruthenium, and rhodium, will also have migrated along the thermal gradient toward the cladding.

The columnar grain region is fully restructured by a vaporization process. The gaseous fission products (Xe and Kr) coalesce into large lenticular bubbles ($\sim 1\text{ mm}$) that sweep up the thermal gradient (by a fuel vaporization-condensation mechanism) and release the gases to the central void. This action creates the columnar grains. The release of Xe-Kr from the columnar grain region by voloxidation is expected to be virtually complete. The plutonium concentration in this region near the void is

higher than in the as-fabricated fuel (subject to the effects of extremely high burnups) since the UO_2 is preferentially transported to cooler regions by vapor phase condensation.

Recent ORNL Results with Unirradiated Fuels. — Summaries of ORNL experiments on the voloxidation process have been included in the LMFBR Fuel Cycle Studies Progress Reports,⁵⁸⁻⁷⁹ which are issued monthly. Studies relative to the basic chemistry of the process have been reported by Tennery and by Fitzgerald in the same progress report series, beginning with the November 1970 issue.⁷²⁻⁷⁹ Other studies (previously unreported) were performed by Farrar and Haire⁸⁰ and by Baybarz;⁸¹ these are summarized in Sect. 4. Tennery's reports included pertinent references to U-Pu-O phase studies.⁸²⁻⁸⁹ All of this work is reported by the investigators in Sects. 2-6.

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2. PRELIMINARY THERMOGRAVIMETRIC STUDIES ON THE OXIDATION OF UNIRRADIATED (U,Pu)O₂ PELLETS IN AIR

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2.1 Summary

The oxidation behavior of two kinds of unirradiated (U,Pu)O₂ pellets was studied using a thermobalance. Significant oxidation occurred only at temperatures higher than 350°C and appeared to be a first-order process that is diffusion controlled. Weight gains, however, indicated incomplete (~ 85%) conversion of the UO₂ to U₃O₈. Analysis of the oxidized material showed that no gross segregation of the PuO₂ occurred as a result of the treatment.

2.2 Oxidation of Unirradiated (U,Pu)O₂ Pellets

The oxidation behavior of unirradiated NUMEC and WADCO sintered UO₂-PuO₂ pellets was studied using a thermobalance. The NUMEC pellets were of two types: coprecipitated (U_{0.8}Pu_{0.2})O₂, designated as Batch 5 and Batch 6; and mechanically blended (U_{0.75}Pu_{0.25})O₂, called Task 7 pellets. The WADCO pellets were mechanically blended (U_{0.75}Pu_{0.25})O₂ and are termed FTR "Reference" pellets. ("Reference" refers to a special batch of pellets fabricated for a dissolution study, not prototypical reactor fuel.)

A differential thermogram showing the rate of weight gain of an unirradiated FTR "Reference" pellet that was heated in air while the temperature was increased from 50 to 700°C is presented in Fig. 2.1. The rate of weight gain (oxidation) was significant only at temperatures higher than 350°C. The calculated percent conversion of UO₂ to U₃O₈, based on the weight gain, was 84.2% at the time the temperature reached 700°C. Increasing the temperature to 800°C and heating to constant weight increased the percent conversion only to 84.4%.

Other "Reference" pellets were oxidized in air at 750°C for 7 hr, a treatment which reduced them to a fine powder. The powder was sieved, and the Pu/U atom

Fig. 2.1. Thermogravimetric Analysis of 75% UO_2 --25% PuO_2 FTR "Reference" Pellet (Rate of Weight Gain During Air Oxidation of a Pellet Initially Weighing 1.03 g). Rate of temperature rise was 5°C/min . Numbers in parentheses show the calculated percent conversion to U_3O_8 .

ratio was determined for each fraction. About 96% of the material was finer than 200 mesh. Within experimental error, the plutonium concentration was uniform in all size fractions (Table 2.1); hence the voloxidation treatment does not cause plutonium segregation. This conclusion is in agreement with those inferred from our dissolution tests.

Table 2.1. Particle Size Distribution of FTR "Reference" Pellets
After Oxidation in Air at 750°C for 7 hr

Screen Size	Weight Retained (g)	% Retained	Pu/U Atom Ratio
+80	0.0392	0.70	0.31
+100	0.0211	0.37	0.31
+200	0.1551	2.75	0.32
+325	1.3386	23.74	0.36
+400	0.7653	13.57	0.35
-400	3.3204	58.88	0.33
Total	5.6397	100	0.33 (original)

The FTR "Reference" pellets were characterized by the nitric acid dissolubility test. We found that about 85% of the PuO_2 dissolved in 8 M HNO_3 , and was thus apparently in solid solution with the UO_2 at a concentration of less than about 40 wt % PuO_2 . The remaining 15% of the PuO_2 was in the nitric acid--insoluble residue at a concentration of about 80 wt % PuO_2 --20 wt % UO_2 . Electron microprobe analysis of this batch of pellets showed discrete 20- μm PuO_2 areas in a UO_2 matrix, which may explain the dissolution behavior.

The oxidation behavior of single, whole FTR "Reference" and NUMEC Task 7 pellets was also studied using two modes of operation: programmed heating, and isothermal. The steps in the procedures were: (1) heat in air while increasing the

temperature at 5°C/min until constant weight is attained (programmed mode), (2) heat in inert gas to 450°C, then switch to air and maintain temperature until constant weight is attained (isothermal mode), and (3) heat in inert gas to 650°C, then switch to air and maintain temperature until constant weight is attained (isothermal mode). Table 2.2 indicates that the oxidation behavior was dependent on the manner in which the experiment was conducted and the previous history of the sample. The FTR pellet (procedure 3) and NUMEC Task 7 (procedure 1) oxidized as a first-order reaction to weight gains of 2.54 and 2.14%, respectively. Oxidation of the NUMEC pellets did not follow first-order reaction behavior when procedures 2 and 3 were used, but a larger weight gain was observed in each case than when procedure 1 was used. The NUMEC Task 7 pellets did not disintegrate to a fine powder after oxidation as did the "Reference" pellets.

Table 2.2. Results of Thermobalance Studies with Mechanically Blended FTR and NUMEC ($U_{0.75}Pu_{0.25}$)O₂ Pellets

Pellet Type	Procedure	Weight Gain (%)	Uranium Unoxidized (% of total)	Rate Constant (min ⁻¹)
FTR "Reference"	3	2.54	14.0	0.13864
NUMEC Task 7	1	2.14	28.1	0.02386
NUMEC Task 7	2	2.39	19.6	-
NUMEC Task 7	3	2.31	22.2	-

The oxidation behavior of NUMEC ($U_{0.8}Pu_{0.2}$)O₂ coprecipitated pellets was also studied using the above procedures. The results are presented in Table 2.3, and typical weight gain curves at 450°C are shown in Fig. 2.2. The rate constants with both Batch 5 and Batch 6 pellets increased in the order of procedures 1, 2, and 3, but total weight gains were unpredictable. These pellets disintegrated upon oxidation.

Fig. 2.2. Differential and Integral Weight Gain Curves for NUMEC Batch 6
($U_{0.8}Pu_{0.2}$) O_2 Pellets at 450°C.

Activation energies, estimated for Batches 5 and 6 from a rate constant-vs- $1/T$ plot, were 4.5 and 4.6 kcal/mole, respectively. These values indicate a diffusion-controlled oxidation process.

Table 2.3. Results of Thermobalance Studies with NUMEC
Coprecipitated $(U_{0.8}Pu_{0.2})O_2$ Pellets

Pellet Source	Procedure	Weight Gain (%)	Uranium Oxidized (%)	Rate Constant (min^{-1})
Batch 5	1	2.78	88.6	0.04348
Batch 5	2	2.39	76.0	0.04530
Batch 5	3	2.65	84.3	0.08943
Batch 6	1	2.33	74.0	0.02607
Batch 6	2	2.24	71.2	0.04845
Batch 6	3	2.51	79.7	0.09753

3. THE OXIDATION OF UO_2 AND $(\text{U,Pu})\text{O}_2$ - A THERMOGRAVIMETRIC AND X-RAY DIFFRACTION STUDY

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3.1 Summary

The solid solution $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_2$ oxidized, via a two-stage process, to a final O/M ratio ≈ 2.55 at reasonable rates only within a narrow temperature range of about 500 to 600°C. Rapid oxidation to an O/M ratio ≈ 2.35 occurred over a wider range of temperatures, and the product of this first stage of the oxidation was tetragonal M_3O_7 , or, in this case, $\text{U}_{2.4}\text{Pu}_{0.6}\text{O}_7$. The kinetics of the first-stage process in a coprecipitated $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2$ fuel were analyzed using a simple nucleation model; the activation energy for the process in this fuel was approximately 10 kcal/mole. The second stage of the oxidation, which results in disintegration of the fuel, occurred when the M_3O_7 phase converted to $\text{M}_3\text{O}_8 + \text{MO}_2$. The kinetics of this process were also analyzed using the nucleation model; the activation energy was about 40 kcal/mole. The kinetics of this process were strongly dependent on temperature, as noted previously, and also on the procedure used to homogenize the uranium and plutonium, the process by which the fuel was fabricated, or possibly some other factor. The observations from this work indicate that the fuels having a Pu/U+Pu ratio of 0.2 can be ranked according to the ease with which the second oxidation stage was achieved. With the first being easiest, the order of fuel types at 550°C was: coprecipitated, sol-gel, and mechanically mixed. This may be an indication that the second stage of the oxidation is very sensitive to either the microhomogeneity of the plutonium or other unknown factors.

The solid solution $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_2$ oxidized readily to an O/M ratio ≈ 2.35 but went to higher O/M ratios only with great difficulty. This was true for both mechanically mixed and sol-gel fuel. The partially oxidized material consisted of a cubic phase corresponding to the M_4O_9 phase reported by Markin and Street, but was apparently M_4O_{9+x} since the O/M was obviously higher than allowed by

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stoichiometric M_4O_9 . This M_4O_9 -type phase apparently has the formula $M_{4.4}O_9$, at least at the phase boundary with the $M_{3.8}O_8$ phase. Small traces of $M_{3.8}O_8$ were detected in some of the oxidized samples; however, conversion of $M_{4.4}O_9$ to $M_{3.8}O_8 + MO_2$ was strongly inhibited in the materials examined in this investigation.

The oxidation behavior of mechanically mixed and coprecipitated (U,Pu) O_2 fuels was studied by means of TGA and X-ray diffraction techniques. The oxidation kinetics, as well as the final O/M ratio of the oxidized fuel, were determined at Pu/U+Pu ratios of 0.20 and 0.25. The partial phase diagram for the U-Pu-O system (Fig. 3.1) provides useful information concerning what occurs during the oxidation of these materials to O/M ratios higher than 2.0. In this isothermal ternary diagram, the left-hand side represents the binary system uranium-oxygen and the right-hand side represents the plutonium-oxygen system; the upper apex of the triangle is the oxygen end member. This diagram is essentially that of Markin and Street.¹ The more recent work of Sari *et al.*² did not represent a major modification of the low-temperature part of the diagram. Figure 3.1 (a) is a representation of the system at 25°C, while Fig. 3.1 (b) shows how the diagram changes as the temperature is increased to 400-800°C.

As a given fuel oxidizes, the composition moves toward the oxygen corner of the diagram along the line representing its respective Pu/U+Pu ratio. Thus, starting with single-phase face-centered cubic (fcc) MO_2 , the first phase boundary which would be crossed during oxidation would be that between the phase fields for MO_{2+x} and the field represented by $M_4O_9 + fcc MO_{2+x}$ at an O/M of about 2.2 for a Pu/U+Pu ratio of 0.20. Since the M_4O_9 crystal structure is not drastically different from that of the fcc MO_{2+x} phase, we did not expect to observe major mechanical damage in MO_2 fuels oxidized to O/M ratios near 2.2 or 2.3. In fact, the X-ray density of U_4O_9 at 25°C is given by Gronvold³ as 11.16 g/cc, whereas the data of Markin and Street¹ were used to calculate the density of $U_{0.85}Pu_{0.15}O_{2.18}$ (MO_{2+x} phase at the edge of the MO_{2+x} phase field) as 11.27 g/cc. The X-ray density of $U_{4-y}Pu_yO_9$ is probably not greatly different from that of U_4O_9 . The small difference in these

Fig. 3.1. Partial Phase Diagram of the U-Pu-O System According to Markin and Street (See Ref. 1).

densities was not expected to lead to appreciable mechanical disintegration of the fuel during oxidation.

In order to disintegrate the fuel and convert it to powder form, the $M_3O_{8-y} + M_4O_9$ phase field must be entered; and, in order to produce the maximum amount of the M_3O_8 phase, the tie line between U_3O_8 and PuO_2 should be reached during oxidation. The X-ray density of U_3O_8 is given by Gronvold³ as 8.34 g/cc, and the decrease in density resulting from the formation of this phase ($\sim 25\%$ reduction in density for conversion of $U_4O_9 \rightarrow U_3O_8$) should be more than sufficient to powder the fuel.

3.2 Initial Experimental Studies with UO_2

Two types of thermogravimetric measurements were made. One (i.e., the programmed mode) consisted of heating a bulk sample in air at a specified programmed rate and observing the weight gain due to oxidation until the specimen weight remained constant at some elevated temperature. The other (i.e., the isothermal mode) consisted of rapidly inserting a sample into the furnace at a fixed temperature and measuring the weight gain due to oxidation as a function of time until the sample weight remained constant.

The initial work consisted of several thermogravimetric runs using dense pieces of high-purity UO_2 pellets ($\sim 95\%$ theoretical density). All of the runs were made in "breathing air" atmospheres at a flow rate of 0.8 cfh. The sample mass and the temperature programming rate were varied as parameters to establish base-line information on the behavior of unirradiated UO_2 so that later comparisons could be made with unirradiated (U,Pu) O_2 . The data obtained by Fitzgerald and Farrar on an "FTR" reference pellet [mechanically blended, sintered $(U_{0.75}Pu_{0.25})O_2$, $\approx 90\%$ theoretical density, see Sect. 2] have also been analyzed and compared with the UO_2 data.

Figure 3.2 shows the oxidation behavior of two UO_2 specimens weighing approximately 108 mg each at two heating rates, along with the data for the (U,Pu) O_2 "FTR"

Fig. 3.2. Oxidation of UO_2 Fragments and an FTR "Reference" Pellet.

pellet. Curve A shows that the UO_2 oxidized very rapidly at temperatures above about 430°C when a heating rate of $5^\circ\text{C}/\text{min}$ was used. Increasing the heating rate to $15^\circ\text{C}/\text{min}$ for a 108-mg sample of UO_2 (curve B) resulted in an increase in the temperature at which gross oxidation started. The oxidation for curve B was incomplete at 800°C , whereas that for curve A was essentially complete at 500°C . The data for the "FTR" pellet (curve C) appear to be somewhat similar to that for curve B except that the weight gain stabilized at 2.5%, about 87% of that expected if the reaction can be represented by:

The theoretical weight gain for this reaction is 2.96%.

The role of the programmed heating rate was also examined in the oxidation of UO_2 of fixed mass. These results are shown in Fig. 3.3 for rates of 5, 10, and $15^\circ\text{C}/\text{min}$ on a mass of about 108 mg. In general, the lower the heating rate, the lower the temperature at which complete oxidation was attained.

3.2.1 Programmed-Rate Runs with UO_2

The UO_2 specimens used for this work consisted of dense chunks fractured from ceramic UO_2 pellets having a density about 95% of theoretical and an initial O/U ratio of about 2.01. The programmed-rate UO_2 runs were made at various rates. Oxidation curves for this type of experiment are presented in Fig. 3.3. The UO_2 began to oxidize rapidly at about 430°C when the heating rate was $5^\circ\text{C}/\text{min}$; at a heating rate of $10^\circ\text{C}/\text{min}$, rapid oxidation began at about 500°C . In both the $5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$ runs, the weight gain of the sample was about 4.0%. This is very close to the theoretical value of 3.96% for the reaction

Total oxidation was complete at 525°C . When the sample was heated at $15^\circ\text{C}/\text{min}$, complete oxidation was not observed even at 800°C , indicating that UO_2 exhibited an optimum "temperature range" for rapid and complete conversion to U_3O_8 . In all

Fig. 3.3. Oxidation of UO₂ Fragments.

of the programmed-heating-mode experiments, the samples completely fragmented and were reduced to a fine powder by the oxidation procedure.

3.2.2 Isothermal Runs with UO_2

The isothermal UO_2 runs provided insight into the kinetics of the oxidation of the specimens; runs were conducted at 300, 400, 450, 475, 480, 600, and 700°C. The data for the lower five temperatures are shown in Fig. 3.4. Essentially no oxidation occurred at 300°C, although the literature indicates that UO_2 powders will oxidize at this temperature.⁴ This illustrates the importance of considering the morphology of the specimen as well as its composition when evaluating the oxidizability of ceramic specimens. At 400°C there was an "incubation" period of about 12 min before significant oxidation commenced. Total oxidation to U_3O_8 required about 72 min. Increasing the temperature progressively to 480°C progressively decreased the time required to attain the theoretical weight gain. At 480°C, only about 12 min was required to achieve a weight gain of 4.07% (0.09% above the theoretical value).

The isothermal oxidation of UO_2 at temperatures higher than 480°C resulted in a decrease in the kinetics of oxidation, as shown in Fig. 3.5. The inflection observed at 600°C corresponds approximately to an O/U ratio of 2.35, which is the composition U_3O_7 as well as the composition of the γ_1 tetragonal phase in the uranium-oxygen system. This lower-temperature phase then converted to more oxygen-rich phases, although the observed weight gain never did attain the expected value for complete transformation to U_3O_8 . Oxidation at 700°C led to even lower reaction rates. An inflection at about a 0.5% weight gain corresponded to an O/U ratio of about 2.1, which was essentially where one would expect to cross the phase boundary between $\text{UO}_{2+x} + \text{U}_4\text{O}_{9-y}$ and UO_{2+x} in this system at this temperature.

Further oxidation led to a gradual approach to an O/U ratio of 2.67 (U_3O_8), but the sample was not completely oxidized in 40 min at 700°C. All of the UO_2 samples shown in Figs. 3.4 and 3.5, except for the sample heated at 300°C, transformed to a fine powder during oxidation.

Fig. 3.4. Isothermal Oxidation of UO_2 Pellet Fragments.

Fig. 3.5. Isothermal Oxidation of UO_2 Pellet Fragments.

3.3 Studies With UO_2 - PuO_2 "Reference" Pellets

3.3.1 Programmed-Rate Runs

The first mixed oxide samples that were examined consisted of chunk fragments of FTR "Reference" fuel having a U/Pu atom ratio of 3 and a density about 90% of theoretical. The molar composition of the fuel was approximately $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{1.98}$.

Single chunks having masses of about 100 mg were fractured from pellets and were oxidized in the thermogravimetric (TGA) apparatus in both the programmed heating and isothermal modes. The atmosphere and flow rate were identical to those used for the UO_2 runs discussed previously (i.e., 0.8 scfh of air that had been passed through molecular-sieve columns).

The programmed-heating mode data are shown in Fig. 3.6, where the specimen heating rate was the parameter that was varied. Oxidation of the $(\text{U,Pu})\text{O}_2$ was similar to oxidation of UO_2 in that the sample attained a given O/M ratio at progressively higher temperatures as the heating rate was increased from 5 to 20°C/min. However, even at the highest heating rate employed, the $(\text{U,Pu})\text{O}_2$ oxidized to the same O/M ratio as when heated at only 5°C/min. Specimen D in Fig. 3.6 was obtained from a different pellet than were specimens A, B, and C; thus, the obvious displacement of the D curve to higher temperatures may have been due to some variability in the oxidizing characteristic between pellets. In any case, the maximum observed weight gain was 2.76%, which was below the theoretical value of 3.08% for the reaction

A comparison of the results obtained by oxidizing the $(\text{U,Pu})\text{O}_2$ and UO_2 in the programmed-heating mode is shown in Fig. 3.7. Under the conditions used, the mixed oxide started to oxidize at a much lower temperature than did the UO_2 ; however, the rate was always lower than that observed in the UO_2 . Estimates were made of the O/M ratio of the higher oxide phase which corresponded to the weight gain indicated by

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Fig. 3.6. Programmed-Rate Oxidation of $U_{0.75}Pu_{0.25}O_{1.98}$ FTR "Reference" Pellets.

Fig. 3.7. Programmed-Rate Oxidation of UO_2 and UO_2 - PuO_2 FTR "Reference" Pellet Fragments.

the various inflections apparent in the plots of Fig. 3.6. In the case of curve A, a noticeable inflection occurred at a weight gain of about 1.5%. Assuming that the oxidation reaction can be represented by

where some plutonium and uranium are mixed in both products in the disproportionation process, and assuming that the stoichiometry of the $\text{Pu}_{y-z}\text{U}_z\text{O}_2$ phase is essentially ideal, the O/M ratio of the $\text{U}_{x-z}\text{Pu}_z\text{O}_{2+w}$ product can be estimated as a function of the observed weight gain. A weight gain of about 1.5% corresponds to an O/M ratio in the $\text{U}_{x-z}\text{Pu}_z\text{O}_{2+w}$ product of about 2.35, if the assumption that this phase becomes $\text{U}_{x-z}\text{Pu}_z\text{O}_{2.67}$ (i.e., $\text{U}_{3-z}\text{Pu}_z\text{O}_8$) upon complete oxidation is correct (i.e., that it is not strongly oxygen deficient). The value of z is relatively unimportant at this point due to the similarities of the atomic weights of uranium and plutonium. The O/M ratio of 2.35 is essentially the same value noted in the isothermal runs for UO_2 discussed earlier. Apparently, the inflection is indicative that a phase boundary had been crossed at this point during the run and that the oxidation rate had subsequently increased. All of these samples were converted to powder by the oxidation.

3.3.2 Isothermal Runs

Isothermal experiments on specimens from three FTR "Reference" fuel pellets yielded the results plotted in Fig. 3.8. Except for minor differences to be discussed later, all of the pellets appeared to oxidize in essentially the same manner. At low temperatures ($< 350^\circ\text{C}$), the oxide reacted with oxygen very slowly; at 300°C , a sample gained 1% by weight but did not crack or fragment. Using the assumptions discussed previously, the O/M ratio of the $\text{U}_{x-z}\text{Pu}_z\text{O}_{2+w}$ product was about 2.2. The 350°C sample did disintegrate, although the oxidation rate was relatively slow. A temperature of 400°C led to relatively rapid oxidation, but the weight gain essentially leveled off at about 2%. Oxidizing at 450°C caused a more rapid reaction; however, the weight gain became constant at about 1.96% as before.

Fig. 3.8. Isothermal Oxidation of UO₂-PuO₂ FTR "Reference" Pellet Fragments.

Oxidation temperatures higher than 450°C led to higher weight gains up to about 480°C, where the maximum oxygen uptake occurred (~2.5%). It then decreased with increasing oxidation temperature, as shown in Fig. 3.8. At 600°C, the total oxygen peaking (~2%) was essentially complete in about 2 min. All of these samples were fragmented by the oxidation process; however, the morphology of the oxidation product changed as the oxidation temperature was increased from 450 to 600°C. The oxidation product was a fine powder at the lower temperatures; at temperatures above about 500°C, the particles of the oxidation product were larger, though friable, and many were needle-like.

The maximum observed weight gain (plotted as a function of the isothermal temperature) for specimens from three of the FTR pellets are shown in Fig. 3.9. A gentle peak in the weight gain occurs in the vicinity of 450 to 480°C, indicating that a maximum uptake of oxygen occurs over a rather narrow temperature range. It is possible that maximum fragmentation of the (U,Pu)O₂ fuel correlates with the maximum observed weight gain, but this remains to be verified. This temperature range corresponds to the temperature of maximized oxidation kinetics observed for pure UO₂ discussed previously.

In summary, the (U,Pu)O₂ FTR "Reference" pellets reacted with oxygen approximately as expected, except that the maximum predictable weight gain was not achieved. For the FTR material, a temperature range of about 470 to 500°C led to the largest weight gains upon oxidation. The rate of oxidation was very rapid at temperatures above about 450°C. The temperature range where the (U,Pu)O₂ exhibited maximum oxygen uptake (~2.5%) corresponded very closely with the temperatures where the most rapid oxidation of pure UO₂ to U₃O₈ was observed. The TGA data for the (U,Pu)O₂ however, did not appear to correlate with expected results as estimated from the phase diagram in Fig. 3.1. In fact, this material exhibited some of the oxidation characteristics of UO₂ reported previously; that is, the oxidation kinetics actually decreased in the temperature range 450 to 700°C. The oxidation data for the "FTR" fuel are shown in Fig. 3.10, which is essentially the same as Fig. 3.8 except that an appropriate O/M scale is shown on the right-hand side.

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Fig. 3.9. Maximum Observed Weight Gain During Isothermal Oxidation of $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{1.98}$ FTR "Reference" Specimens.

Fig. 3.10. Isothermal Oxidation Properties of FTR "Reference" Fuel in Air.

Two things should be noted: (1) the fuel tended to oxidize to an O/M ratio of about 2.33 except in a relatively narrow temperature range of 450 to 600°C, and (2) the fuel pulverized during oxidation at 350°C, where the O/M was less than 2.3. Detailed electron microprobe and metallographic examination⁵ of this fuel revealed that it was heterogeneous and that regions approximately 20 μm in diameter contained high concentrations of plutonium. The effect of this inhomogeneity was to provide a microstructure consisting of a UO_2 matrix surrounding PuO_2 -rich regions. About 15% of the total PuO_2 in the fuel was insoluble in nitric acid (Sect. 2), indicating that much was isolated in the PuO_2 -rich regions. The general behavior of this fuel during oxidation was, therefore, somewhat similar to that of UO_2 (due to the matrix), except that the final maximum O/M attained could not be correlated with the phase diagram because of the inhomogeneous nature of the material.

3.4 Studies with Other (U,Pu) O_2 Specimens

3.4.1 Isothermal TGA Runs

Because of the apparent anomalous behavior of the FTR "Reference" fuel, several mixed oxide fuel pellets produced by NUMEC were examined. These pellets, which had densities about 90% of theoretical, consisted of coprecipitated and mechanically mixed (U,Pu) O_2 with a Pu/U+Pu ratio ≈ 0.2 and mechanically mixed (U,Pu) O_2 with a Pu/U+Pu ratio ≈ 0.25 . The latter is designated by NUMEC as Task 7 fuel. Fragments having masses in the range of 80 to 100 mg were fractured from these pellets for use in oxidation runs. All of the oxidation runs were made in an atmosphere of 0.8 scfh of breathing air that had been dried by passage through columns of a molecular sieve prior to entry into the glove box.

The isothermal thermogravimetric results for the coprecipitated fuel containing 20 mole % PuO_2 are shown in Fig. 3.11. Two observations should be made. The fuel oxidized rapidly to an O/M ratio ≈ 2.3 , irrespective of the isothermal temperature. This O/M value apparently corresponds to a phase boundary in the system, and examination of Fig. 3.1 indicates that it must be the boundary between the M_4O_9 + fcc $\text{MO}_{2\pm}$

Fig. 3.11. Isothermal Oxidation Properties of $U_{0.8}Pu_{0.2}O_2$ (Coprecipitated Type) in Air.

phase field and that of $M_3O_{8-y} + M_4O_9$. According to published diagrams, this boundary should occur at $O/M = 2.25$, as in the case for U_4O_9 ; our results, on the other hand, indicate that the boundary may actually be located nearer to $O/M \approx 2.32$ in the ternary system. The kinetics of the oxidation producing the M_3O_8 phase were very temperature dependent at this composition. At 480° , 190 min was required for the specimen to attain equilibrium, which was at an $O/M = 2.57$, essentially the ratio predicted from the location of the U_3O_8 - PuO_2 tie line in the ternary diagram. At $600^\circ C$, total oxidation occurred within 17 min. Only those samples that were oxidized to O/M ratios ≈ 2.57 were pulverized. Samples oxidized to only $O/M \approx 2.3$ were apparently as strong as they were initially.

The thermogravimetric results for the mechanically mixed fuel are shown in Fig. 3.12. Curves 1 and 2 represent two isothermal oxidations of fuel having a $Pu/U+Pu$ ratio of 0.20. This material oxidized essentially like that shown in Fig. 3.11, except that the kinetics of the oxidation during the traverse of the $M_3O_{8-y} + M_4O_9$ phase field were somewhat slower than in the case for the coprecipitated fuel. However, the fuel having a $Pu/U+Pu$ ratio of 0.25 (Task 7) behaved differently in that oxidation proceeded rapidly to the edge of the phase field where M_3O_8 should appear and then stopped. As shown in curve 3 of Fig. 3.12, holding the fuel isothermally at $525^\circ C$ for 200 min did not lead to further oxidation and the O/M remained constant at approximately 2.36.

3.4.2 Programmed-Rate Oxidations of UO_2 - PuO_2

Several experiments were performed in which $(U, Pu)O_2$ samples were oxidized in thermogravimetric runs in which the temperature was increased linearly with time. Previous work had shown that a heating rate of $5^\circ C/min$ was sufficiently slow to allow these samples to essentially equilibrate with the oxygen in the furnace during the run. Figure 3.13 shows the results obtained for the three kinds of mixed oxide fuels studied. Curves A and B for the 20 mole % PuO_2 fuel exhibit behavior which would be predicted from the phase diagram. However, the 25 mole % (Task 7) PuO_2 fuel presented an anomaly, as was the case (see Fig. 3.12) for isothermal oxidation of

Fig. 3.12. Isothermal Oxidation Properties of Mechanically Mixed $(U,Pu)O_2$ in Air.

Fig. 3.13. Programmed-Rate Oxidation Properties of $(\text{U,Pu})\text{O}_2$ in Air.

this material. This particular material could not be oxidized to the M_3O_8 phase; consequently, it did not pulverize during oxidation. Only the specimens that oxidize to O/M ratios greater than 2.3 were pulverized during the experiment. X-ray diffraction measurements of the "pretest" fuel were made to confirm its phase homogeneity.

3.5 Studies of the Effect of Fuel Fabrication Route

The oxidation properties of $(U,Pu)O_2$ having Pu/U+Pu ratios of 0.2 and 0.25 in air were studied using thermogravimetric balance and X-ray diffraction techniques. Fuels of coprecipitated, sol-gel, and mechanically mixed origin were used to determine whether the process used in producing the mixed oxide led to the significant changes in the oxidation properties.

Descriptions of the fuel samples used in these studies are given in Tables 3.1 and 3.2.

3.5.1 Isothermal TGA Experiments with UO_2 - PuO_2

We have shown that in order to disintegrate homogeneous $(U_{0.8}Pu_{0.2})O_2$ by oxidation it is necessary to approach the tie line between U_3O_8 and PuO_2 in the U-Pu-O system (Fig. 3.1). The tie line for $U_{0.8}Pu_{0.2}O_2$ occurs at an O/M ratio of approximately 2.55. Mechanical disintegration results from the presence of an orthorhombic M_3O_8 phase in the oxidation product, where M consists of some combination of uranium and plutonium atoms, the exact ratio depending on several parameters. Using coprecipitated fuel, we found that two distinct oxidation processes were involved in the oxidation. One occurred relatively rapidly to an O/M ratio ≈ 2.33 ; the other, for $O/M = 2.33 \rightarrow 2.55$, occurred relatively slowly and was very temperature dependent up to 600°C . Higher temperatures led to a more rapid attainment of an O/M ratio ≈ 2.55 (Fig. 3.11). We examined the oxidation properties of this fuel in the range 600 to 750°C . The results are shown in Fig. 3.14. Surprisingly, the oxidation across the phase field indicated as $M_3O_{8-y} + M_4O_9$ in Markin and

Table 3.1. Crystal Lattice Parameters and Comparison of O/M Ratios for NUMEC Coprecipitated and Mechanically Mixed Fuels

Fuel Designation	Fuel Type	NUMEC Designation	Pu/U+Pu Ratio	Lattice Parameter at 25°C (Å)	O/M Ratio	
					X-Ray Analysis	TGA Analysis
A	Coprec.	Batch 5	0.20	5.4671 ± 0.0002	1.955	1.96
B	Coprec.	Batch 6	0.20	5.4616 ± 0.0002	1.974	1.99
C	Mech. Mix	Batch 16	0.20	5.4628 ± 0.0003	1.969	1.99
D	Mech. Mix	Task 7	0.25	5.4617 ± 0.0002	1.957	1.98

Table 3.2. Crystal Lattice Parameters and Comparison of O/M Ratios for ORNL Sol-Gel-Derived Fuels

Fuel Designation	ORNL Designation	Pu/U+Pu Ratio	Lattice Parameter (Å)	O/M Ratio	
				X-Ray Analysis	TGA Analysis
E	WD-2	0.20	5.4643 ± 0.0002	1.970	1.96
F	WD-3	0.25	5.4586 ± 0.0003	1.975	1.97

Fig. 3.14. Isothermal Oxidation of $U_{0.8}Pu_{0.2}O_2$ (Fuel B, Coprecipitated). Breathing air, 0.8 CFH.

Street's diagram (see Fig. 3.1) became more difficult at temperatures above 600°C. For example, an O/M ratio of only 2.34 could be attained at 750°C, whereas an O/M of 2.58 was achieved at 525°C. The oxidized fuel having an O/M ratio $\approx$ 2.34 was apparently as strong as it was prior to oxidation. In order to determine whether this behavior was due to some undetermined characteristic of the coprecipitated fuel, we made a series of thermogravimetric runs using sol-gel fuel having an initial composition $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{1.96}$. The results (Fig. 3.15) are basically the same as those given in Fig. 3.14, except that the time between the attainment of an O/M ratio $\approx$ 2.33 and the entry into the $\text{M}_3\text{O}_8 + \text{M}_4\text{O}_9$ phase field was much longer than was the case for the coprecipitated fuel. However, the same behavior at temperatures higher than 525°C was observed; that is, the final observed O/M decreased as the isothermal oxidation temperature was increased.

We investigated the oxidation properties of coprecipitated fuel having a Pu/U+Pu ratio of 0.20 in order to determine whether the physical state of the starting sample had a significant effect on the oxidation kinetics (Fig. 3.16). Two chunks weighing approximately 87 mg each were removed from the same region of a sintered fuel pellet. One chunk was oxidized directly in the thermal balance, while the other was crushed to pass a 100-mesh screen and was then oxidized in the thermal balance. It is obvious from Fig. 3.16 that, at 650°C, there is no appreciable difference in the oxidation characteristics of the two specimens. On the other hand, the initial oxidation of the crushed sample was faster than that for a chunk; also, the data for the powdered sample showed a distinct inflection at an O/M ratio $\approx$ 2.35, whereas that for the solid sample did not. The solid sample did not fragment as a result of the oxidation.

The oxidation of NUMEC Task 7 mechanically mixed fuel having a Pu/U+Pu ratio of 0.25 was examined in some detail since previous work had indicated that this composition did not oxidize to an O/M ratio >2.35 in air. Heat-treated samples of 25% PuO_2 of sol-gel origin were run at temperatures up to 650°C (in air). The data obtained, along with some previous results, are shown in Fig. 3.17. None of the fuel specimens fragmented. The two materials essentially behaved in the same way;

Fig. 3.15. Isothermal Oxidation of $U_{0.8}Pu_{0.2}O_{1.96}$ (Fuel E, Sol-Gel Origin).
Breathing air, 0.8 CFH.

Fig. 3.16. Isothermal Oxidation of $U_{0.8}Pu_{0.2}O_2$ (Fuel B, Coprecipitated) at 650°C. Breathing air, 0.8 CFH.

Fig. 3.17. Isothermal Oxidation of $U_{0.75}Pu_{0.25}O_{2-x}$ in Air.

that is, oxidation proceeded to an O/M ratio ≈ 2.35 and stopped. Many oxidation runs were made using samples of the Task 7 mechanically mixed fuel (D). Some effort was made to establish the reproducibility of the data on a given material when TGA specimens from different sintered pellets were used. Typical results are shown in Fig. 3.18; samples A and B represent fragments from two different pellets of the Task 7 fuel. Higher oxidation temperatures resulted in slightly higher final O/M ratios in the oxidation product, but the differences were small. None of these oxidized samples fragmented. These results and the X-ray diffraction results (presented subsequently) indicate that the observed behavior is strongly dependent on the plutonium content of the mixed oxide.

The lattice parameters of the mechanically mixed and the sol-gel fuel having a Pu/U+Pu ratio of 0.25 had values that would be expected from the literature. These results indicated that the way in which the plutonium and uranium were combined to form the solid solution or the microstructural morphology did not appear to be controlling the oxidation process in this composition, since the Task 7 fuel was a dense sintered ceramic and the sol-gel fuel was in the form of a calcined shard.

3.5.2 Programmed-Rate Oxidations of Sol-Gel $\text{UO}_2\text{-PuO}_2$

The oxidation properties of sol-gel-derived mixed oxide in air were measured for fuels having Pu/U+Pu ratios of 0.20 and 0.25, using a constant heating rate (Fig. 3.19). Note that curve B closely resembles curve C for mechanically mixed Task 7 fuel (see Fig. 3.13 above), thus indicating again that, for the composition represented, two samples having markedly different origins exhibit essentially the same oxidation characteristics. The results shown by curve A were unexpected. Results for additional samples of this material were identical. It was expected that the oxidation of these samples would yield data similar to those plotted as curves A and B in Fig. 3.13. These previous data, plus those shown in Fig. 3.15 indicate that, under some conditions as yet undetermined, even fuel with a Pu/U+Pu ratio of 0.2 will not readily oxidize to O/M ratios in excess of 2.4.

Fig. 3.18. Isothermal Oxidation of Mechanically Blended $U_{0.75}Pu_{0.25}O_{1.98}$ (Fuel D--NUMEC Task 7) as a Function of Temperature. Breathing air, 0.8 CFH.

Fig. 3.19. Programmed-Rate Oxidation of $U_{1-x}Pu_xO_{2-y}$ (Sol-Gel Origin).
 $\Delta T/\Delta t = 5^\circ\text{C}/\text{min}$; breathing air, 0.8 CFH.

3.6 X-Ray Diffraction Measurements

3.6.1 As-Received Fuels

We determined the crystal lattice parameters for the four mixed oxide fuel types that had been produced by NUMEC (Table 3.1). Knowing the Pu/U+Pu ratio and the lattice parameters, we estimated the O/M ratios from the data of Markin and Street.¹ (These results are given in Table 3.1.) The agreement between the initial O/M ratios determined by X-ray and by chemical methods appears reasonable. The tendency for the O/M ratio determined by X-ray methods to be lower than that measured by chemical methods is probably due to the fact that the self-fission damage imparted to the oxide crystal structure by the plutonium increases the lattice parameter as does a decrease in the O/M ratio. Since these fuel samples had been stored for some time since they were last thermally annealed, the self-damage was partly responsible for some of the lack of agreement between O/M ratios determined by the two methods.

The lattice parameters of the two sol-gel-derived fuels were also measured (Table 3.2). These two fuels had been thermally annealed about 45 days prior to the determination of the lattice parameters. The good agreement of the O/M ratios determined by the two methods gave us confidence that our experimental samples had the heavy metal contents and initial O/M ratios assumed for interpreting the TGA results.

3.6.2 Oxidized Fuels

On conclusion of the TGA oxidation experiments, Debye-Scherrer X-ray patterns were produced for several of the samples in order to identify the phases corresponding to the observed O/M ratios. The data for the sample represented by curve 3 of Fig. 3.12 [Fuel D, NUMEC mechanically blended Task 7 $(U_{0.75}Pu_{0.25})O_{1.98}$] and the 600°C sample in Fig. 3.11 [NUMEC Fuel B, coprecipitated $(U_{0.8}Pu_{0.2})O_2$] are shown in Tables 3.3 and 3.4. The patterns indicated that the oxidized fuel having a Pu/U+Pu ratio of 0.25 consisted of a cubic phase whose diffraction pattern could be

Table 3.3. X-Ray Diffraction Data for $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2.35}$ ^a
 (NUMEC Task 7 Mechanically Blended Pellets)

Oxidized in air at 525°C for 200 min
 Tentatively identified as M_4O_9 phase with $\text{O}/\text{M} \approx 2.35$

d-Spacing (Å)	Relative Intensity	(h,k,l)
3.097	Strong	111
2.673	Medium	200
1.904	Strong	220
1.624	Strong	311
1.556	Medium	222
1.349	Weak	400
1.239	Medium	331
1.208	Medium	420
1.104	Medium	422
1.038	Medium	511 333
0.9571	Weak	440
0.9154	Strong	531
0.9030	Medium	600 442
0.85688	Medium	620
0.82664	Medium	533
0.81743	Medium	622
0.78271	Weak	444

^aAfter oxidation.

Table 3.4. X-Ray Diffraction Data for U_3O_8 and $U_{0.8}Pu_{0.2}O_{2.54}$ ^a
(Cu K α Radiation)

d-Spacing ($\text{\AA}$)		
U_3O_8	$U_{0.8}Pu_{0.2}O_{2.54}$	Cubic Phase with $a_o = 5.428 \text{ \AA}$
4.090	4.099	
3.397	3.366	
3.329	3.107	3.097 (111)
	2.688	2.673 (200)
3.612	2.616	
2.056	2.066	
1.984		
1.944	1.954	
	1.911	1.904 (220)
1.786	1.766	
1.758		
1.706	1.693	
1.673	1.627	1.624 (311)
1.575		
1.552	1.565	
1.431	1.422	
1.414		
1.382	1.378	
1.315	1.313	
1.299		
1.277	1.278	
1.240	0.247	
1.223	1.228	
1.214	1.210	
1.1386		
1.1348	1.1279	
	1.1074	1.104 ? (442)
1.099	1.094	
1.074		
1.035	1.040	
0.9992		
0.9903	0.9924	
0.9473	0.9426	
0.9196	0.9172	
0.80592	0.80836	

^aAfter oxidation.

indexed with h, k, l , either all odd or all even, as shown in Table 3.3. The lattice parameter of this phase was determined by extrapolation to be $5.4276 \pm 0.0003 \text{ \AA}$. The diffraction lines were reasonably sharp. Markin and Street report this value to be the lattice parameter of the M_4O_9 phase in equilibrium with M_3O_{8-y} at plutonia contents of 11, 15, and 30 mole %. The M_4O_9 phase reportedly has no homogeneity width at 25°C at 11 mole % PuO_2 but had a detectable width at 15 mole % PuO_2 . As noted in Table 3.3, the pattern contains no superstructure lines which would be indicative of the larger unit cell that has been reported for the U_4O_9 compound by Belle.⁶ The same results were observed by Markin and Street. We conclude, therefore, that oxidation of this particular sample proceeded until the edge of the $M_4O_9 + M_3O_{8-y}$ phase field was reached and then stopped. Both the TGA and X-ray data support this conclusion. No M_3O_{8-y} phase was detected on the X-ray pattern; therefore, if this phase was present in this sample, its concentration could not have been more than 3 to 4%. The exact O/M ratio of the M_4O_9 phase in this system has not been determined as a function of temperature, PuO_2 content, or oxygen potential. Markin and Street assumed that it was near 2.25 (as for U_4O_9) but stated that their measurements could only place it between 2.22 and 2.34. Our results indicated that the value may be near the latter figure.

The coprecipitated sample (Fuel B) having a Pu/U+Pu ratio of 0.20 consisted of orthorhombic M_3O_8 and a cubic phase (Table 3.4). The M_3O_8 phase was the major one, as would be expected from the phase diagram. It was not possible to make a lattice parameter extrapolation of either phase due to the diffuseness of the high angle diffraction lines. The measured d-spacings were compared with those of U_3O_8 produced in the TGA apparatus during oxidation of UO_2 (see Table 3.4). The diffraction lines of the cubic phase are also identified.

The d-spacings observed for the cubic phase in the sample $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{2.54}$ (Table 3.4) were slightly larger than those measured for the M_4O_9 phase (given in Table 3.3). This means that the parameter of this phase is greater than $5.428 \text{ \AA}$. Brett and Fox⁷ reported a measured O/M of 2.54 during the oxidation of $\text{U}_{0.802}\text{Pu}_{0.198}\text{O}_2$ with the minor cubic phase having a parameter $a = 5.400 \text{ \AA}$. From this

observation and the assumption that the uranium valency in this phase was near 5, they deduced that the PuO_2 content of the cubic phase was of the order of 90 mole %. We could not measure the low angle diffraction lines with sufficient accuracy to deduce the plutonium content of the cubic phase represented by the PuO_2 end of the tie-line between U_3O_8 and PuO_2 . Because of the large X-ray absorption errors and the nature of our X-ray camera, we could not obtain accurate a_0 values from measurements of low angle lines. The capillary of $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{2.54}$ was run in the same X-ray camera as was that of $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2.35}$. Using the low angle lines of $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2.35}$ and knowing the true parameter from the extrapolation procedure, we can estimate the error to be expected in calculating the parameter from a given low angle diffraction line at a given Bragg angle. This procedure was used to estimate the lattice parameter of the MO_{2+x} phase (also referred to as the M_4O_9 phase by Markin and Street) in the oxidized sample $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{2.54}$. The estimated value, approximately 5.44 Å, is slightly larger than the parameter of the M_4O_9 phase observed in the $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2.35}$ sample, as discussed previously. The value of 5.44 Å is somewhat higher than the value measured by Brett and Fox for this phase (i.e., ~ 5.41 Å), but this discrepancy may be due to the unavoidable inaccuracy of our determination.

Farrar and Haire⁸ oxidized an entire NUMEC Task 7 (Fuel D) pellet, with an initial composition $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{1.98}$, by heating isothermally at 650°C in air. The sample oxidized to an O/M ratio ≈ 2.36 ; however, the X-ray pattern indicated a small concentration of M_3O_8 phase in addition to the predominant cubic phase. The cubic phase was not well crystallized, although a parameter extrapolation indicated $a = 5.409 \pm 0.001$ Å rather than 5.428 Å as measured for the sample in our thermo-balance oxidation experiments. The pellet also failed to disintegrate upon oxidation (see Sect. 4).

Several other X-ray diffraction patterns of oxidized fuels A through C were prepared (Table 3.1); these samples had a Pu/U+Pu ratio of 0.2. The results were consistent and depended in an orderly manner on the isothermal oxidation temperature. Those fuel samples which exhibited a two-stage oxidation process and which attained

a final O/M ratio of approximately 2.5, or greater, always consisted of two phases. One was orthorhombic and very similar to U_3O_8 , while the other was cubic and resembled PuO_2 with $a \approx 5.428 \text{ \AA}$. The data in Fig. 3.14 are interesting since they indicate that, as far as the final O/M ratio is concerned, fuel B appeared to attain the same final oxidation state at 480°C as at 750°C . X-ray patterns of both fuel B and fuel E revealed that this was actually the case and that the phase existing in fuel having a Pu/U+Pu ratio of 0.2 at an O/M ≈ 2.35 was a tetragonal phase identified as M_3O_7 in the literature.⁹ The X-ray patterns were distinct, and it appeared that these oxidized samples essentially consisted of 100% of this phase under the conditions stated in Table 3.5. Table 3.5 compares the observed diffraction lines in oxidized samples of fuels B and E when they both had a final O/M ratio ≈ 2.35 . It is obvious from an examination of these data that the fuels consisted of essentially pure $U_{2.4}Pu_{0.6}O_7$ (i.e., M_3O_7) at an O/M ratio very close to the theoretically expected value of 2.33. The M_3O_7 phase was an intermediary in the oxidation of this fuel from the MO_2 phase to a mixture of $M_3O_8 + MO_2$; and the reaction

which leads to physical powdering of the fuel, proceeded at reasonable rates only when the oxidation temperature was in the approximate range of 500 to 600°C .

The TGA results indicated that fuel having a Pu/U+Pu ratio of 0.25 could be oxidized relatively easily to an O/M ratio ≈ 2.35 but would not oxidize further in air at temperatures up to 750°C . The X-ray patterns indicated that these oxidized samples consisted of a cubic phase. The X-ray data for typical samples are given in Table 3.6. The two very weak lines observed in the fuel D (mechanically blended) sample oxidized at 750°C apparently belong to the M_3O_8 phase, indicating that a small amount of the orthorhombic phase can be formed from the parent cubic phase. The lines of the cubic phase were indexed, and the lattice parameters of the samples in Table 3.6 were determined. The 600°C sample of fuel D had $a = 5.4276 \pm 0.0003 \text{ \AA}$, and the 750°C sample of fuel D had $a = 5.4271 \pm 0.0006 \text{ \AA}$. We conclude, therefore, that the cubic phases in these samples were identical and that the lattice

Table 3.5. X-Ray Diffraction Data for Oxidized (U,Pu)O₂ with a
Pu/U+Pu Ratio = 0.20 and an O/M Ratio $\approx$ 2.35^c

Fuel B ^a Isothermal Mode: 750°C, Air, 60 min		Fuel E ^b Isothermal Mode: 525°C, Air, 20 min		M ₃ O ₇ ^c		
d(Å)	Relative Intensity	d(Å)	Relative Intensity	d(Å)	(hkl)	Relative Intensity (I/I _o)
3.10	Str	3.099	V Str	3.15	111	100
2.74	Wk	2.73	Wk	2.77	002	22
2.66	Med	2.66	Med	2.70	020	40
1.92	Str	1.91	Str	1.934	022	58
1.886	Med	1.884	Med	1.908	220	35
1.650	Med	1.647	Med	1.665	112	39
1.616	Str	1.613	Str	1.630	131	65
1.560	Wk	1.558	Med	1.569	222	VVW
1.378	Wk	1.375	Wk	1.385	004	18
1.342	Wk	1.337	Wk	1.347	040	9
1.245	Med	1.244	Med	1.252	133	37
1.228	Med	1.227	Med	1.235	024	34
1.206	Med	1.204	Med	1.209	240	22
1.199	Med	1.198	Med			
1.116	Wk	1.114	Wk	1.120	224	15
1.100	Med	1.099	Med	1.103	242	32
1.063	Wk	1.060	Wk	1.063	115	24
1.043	Wk	1.042	Wk			
1.034	Med	1.033	Med	1.037	151	28
		0.9608	Wk			
0.9484	VV Wk	0.9488	VV Wk			
0.9280	Med	0.9261	Med	0.9284	006	31
0.9156	Med	0.9170	Med	0.9170	153	34
0.9075	Med	0.9070	Med			
0.8968	V Wk	0.8956	Wk	0.8974	060	15
0.8725	Wk	0.8716	V Diffuse	0.8737	026	18
0.8590	VV Wk		V Diffuse			
0.8525	Med	0.8509	V Diffuse	0.8517	062	29
0.8344	V Wk	0.834	V Diffuse			
0.8251	V Wk	0.824	V Diffuse			
0.8186	VV Wk					
0.8130	Diffuse	0.812	V Diffuse			
0.7836	VV Wk					
0.7768	Wk					

^aCoprecipitated fuel.

^bSol-gel fuel.

^cIndexing of ref. 9 was used.

Table 3.6. X-Ray Diffraction Data for Isothermally Oxidized (U,Pu)O₂
with a Pu/U+Pu Ratio of 0.25

Fuel D ^a 600°C, 200 min; O/M = 2.32		Fuel D ^a 750°C, 40 min; O/M ≈ 2.39		Fuel F ^b 650°C, 24 min; O/M ≈ 2.33		(hkl) (M ₄ O ₉)	(hkl) ^c (M ₃ O ₈)
d(Å)	Relative Intensity	d(Å)	Relative Intensity	d(Å)	Relative Intensity		
		4.02	VV Wk				001
		3.44	VV Wk				130
3.10	Str	3.11	Str	3.10	Str	111	
2.67	Med	2.70	Med	2.69	Med	200	
1.90	Str	1.91	Str	1.90	Str	220	
1.62	Str	1.63	Str	1.63	Str	311	
1.56	Med	1.56	Med	1.56	Med	222	
1.35	Wk	1.35	Wk	1.35	Wk	440	
1.24	Med	1.24	Med	1.24	Med	331	
1.21	Med	1.21	Med	1.21	Med	420	
1.104	Med	1.105	Med	1.105	Med	422	
1.038	Med	1.042	Med	1.041	Med	511	
						333	
0.9571	Wk	0.9585	Wk	0.9580	Wk	440	
0.9154	Str	0.9159	Str	0.9157	Str	531	
0.9030	Med	0.9035	Med	0.9031	Med	600	
						442	
0.8569	Med	0.8570	Med	0.8572	Med	620	
0.8266	Med	0.8274	Med	0.8268	Med	533	
0.8174	Med	0.8178	Med	0.8176	Med	622	
0.7827	Wk	0.7829	Wk	0.7831	Wk	444	

^aMechanically blended fuel.

^bSol-gel fuel.

^cThe orthohexagonal indices of ref. 10 were used.

parameter of this phase in equilibrium with M_3O_{8-y} is $5.4271 \pm 0.0006 \text{ \AA}$. Markin and Street¹ reported a value of $5.4277 \pm 0.0003 \text{ \AA}$ for the parameter of M_4O_9 in equilibrium with M_3O_{8-y} . The parameter of the fuel F (sol-gel) sample, which was oxidized at 650°C , was $a = 5.4256 \pm 0.0002 \text{ \AA}$. The reason for the difference between the parameters for the M_4O_9 phase in the D and F fuels is not presently understood.

For mixed oxide fuel having a Pu/U+Pu ratio of 0.25, the data indicate that the oxidation to $M_3O_8 + MO_2$ occurs according to the reaction

This reaction is extremely difficult to accomplish in the materials studied in our investigation.

3.6.3 Interpretation of Oxidation Kinetics for Fuel B

An attempt was made to interpret the TGA oxidation data for fuel B [coprecipitated $(U_{0.8}Pu_{0.2})O_2$] in terms of several plausible kinetic models. The models were applied to both the first- and second-stage oxidation processes in this material. The oxidation data for fuel B were analyzed extensively since they covered a broader temperature range than was available from the data for the other fuels. Three models were examined. One was the random nucleation model, which, with some simplifying assumptions, leads to the Erofeev¹¹ equation:

$$-\ln(1 - \alpha) = (Kt)^n , \quad (7)$$

where

α = fraction of reactant which has reacted,

K = rate constant,

t = time,

n = numerical exponent.

The other two were spherical diffusion and spherical interface-controlled models. The data available for both stages of oxidation appeared to fit the nucleation model best, and the data analyses were done on this basis. The data for the first oxidation

stage, which represented the transformation of MO_2 to M_3O_7 , are shown in Fig. 3.20 for temperatures from 435 to 650°C. The straight lines are indicative that the kinetic model works reasonably well with $n = 1$ at the beginning of the first stage of the oxidation but not after the reaction is beyond about 96% completion. The slopes of these lines, which were analyzed in the conventional manner, are shown plotted vs $1/T$ in Fig. 3.21. The activation energy for the line shown is approximately 10 kcal/mole. The 650°C data point did not agree with the others, indicating perhaps that the activation energy increases for this process at the higher oxidation temperatures. A similar analysis was done for the available data for the second stage reaction. These data, which covered the temperature range 480 to 600°C, fit the nucleation model reasonably well to 15% remaining reactant. The activation energy for the process was approximately 41 kcal/mole, with an error band as large as $\pm 40\%$.

The activation energy of approximately 10 kcal/mole for the first stage of the oxidation is less than would be expected for oxygen bulk diffusion in the MO_2 phase. No interpretation of this result is yet available. The ΔH value of about 41 kcal/mole is of a magnitude approximating the activation energy for cation self-diffusion in many fcc oxides, although it is considerably less than the 80 to 100 kcal/mole reported for the diffusion of uranium in UO_2 . The activation energy for oxygen self-diffusion in UO_2 is about 28 kcal/mole. No data could be found for uranium diffusion in U_3O_7 .

3.6.4 Spectrographic Analyses of (U,Pu) O_2 Fuel Samples

In order to preclude the possibility that the differences in oxidation behavior reported for the mixed oxides were due to an unknown trace impurity, several of the materials were analyzed using a spark-source spectrograph. Since the results showed that all of the fuel samples were of approximately the same purity, the differences in their oxidation characteristics must be attributed to some other cause.

Fig. 3.20. First-Stage Oxidation Process for $U_{0.8}Pu_{0.2}O_2$ (Fuel B).

ORNL-DWG-71-8583R1

Fig. 3.21. First-Stage Oxidation Process for $U_{0.8}Pu_{0.2}O_2$ (Fuel B).

3.7 Development of a Stand-In Fuel for (U,Pu)O₂

The necessity for developing mechanical and chemical equipment for processing spent LMFBR fuels makes it desirable to obtain a nonplutonium-bearing stand-in fuel having oxidation characteristics like the particular (U,Pu)O₂ of interest. This would eliminate the disadvantages of working with plutonium. Because of the similarity of the relevant parts of the phase diagrams of U-Th-O and U-Ce-O to the phase diagram of U-Pu-O, it is possible that certain solid solutions of either UO₂-CeO₂ or UO₂-ThO₂ may have oxidation characteristics closely approximating those of (U,Pu)O₂. The oxidation properties of one sample each of UO₂-CeO₂ and UO₂-ThO₂ were examined. These specimens, which were sintered ceramics from another program, had the molar compositions U_{0.8}Th_{0.2}O₂ and U_{0.8}Ce_{0.2}O₂. In both cases, X-ray and metallographic examination of the starting samples had shown that the processing and sintering treatment used did not result in the formation of complete homogeneous solid solutions. Nevertheless, the samples were analyzed by thermogravimetric methods. The results for the case of programmed-rate oxidations are shown in Fig. 3.22. The UO₂-CeO₂ specimen did not disintegrate during oxidation, but could be broken by squeezing it with tweezers. The UO₂-ThO₂ specimen was a soft chunk after oxidation instead of a fine powder as had been the case for many of the U_{0.8}Pu_{0.2}O₂ samples when oxidized to an O/M ratio $\approx$ 2.55. No isothermal oxidations of these samples were conducted. The U_{0.8}Ce_{0.2}O₂ sample oxidized in a manner similar to that which is characteristic of U_{0.75}Pu_{0.25}O₂. Either of these systems may contain compositions that oxidize similar to (U,Pu)O₂ having a Pu/U+Pu ratio of 0.2; however, further work would be required to demonstrate this fact. The onset of gross oxidation in these two potential stand-in materials in programmed heating was approximately the same as that observed in the (U,Pu)O₂ examined.

3.8 References for Section 3

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Fig. 3.22. Programmed-Rate Oxidation of Sintered $U_{0.8}M_{0.2}O_2$.
 $\Delta T/\Delta t = 5^\circ\text{C}/\text{min}$; breathing air, 0.8 CFH.

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4. A STUDY OF THE OXIDATION BEHAVIOR OF (U,Pu)O₂ FUELS WHICH RELATES TO THE VOLOXIDATION PROCESS

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4.1 Summary

Based on data obtained from experiments with unirradiated (U,Pu)O₂ fuel specimens, several conclusions about the voloxidation process have been reached. Apparently, the oxidation and pulverization of homogeneous (U,Pu)O₂ ceramic fuel are mainly dependent on three variables: (1) the Pu/M ratio, (2) the ceramic quality of the specimen, and (3) the physical size of the sample.

The most important variable in the oxidation process was found to be the Pu/M ratio of the material because it controlled the level of oxidation that could be attained by the sample. Since pulverization of the ceramic results from the formation of an orthorhombic M₃O_{8-y} phase (due to the increase in the unit cell volume of the crystal matrix), samples that did not oxidize beyond M₄O₉ were not powdered on oxidation.

Samples with a Pu/M ratio of 0.20 or less were oxidized in two steps to give a total weight gain up to 3.4%. The weight gains corresponded to an intermediate product with an O/M ratio of 2.3 (M₃O₇) and a final product with an O/M ratio of 2.6. X-ray diffraction analyses of the oxidized samples indicated only a cubic phase or a mixture of cubic and orthorhombic phases (M₄O₉ and M₃O_{8-y} phases). A tetragonal M₃O₇ phase was not observed. Samples with Pu/M ratios ≥ 0.25 were resistant to oxidation above the cubic M₄O₉ phase and did not pulverize, except when the oxidation was forced beyond M₄O₉ by high-pressure oxygen at elevated temperatures.

The ceramic quality of the specimen was found to be relatively unimportant when the Pu/M ratio was 0.15; however, it did affect the rate and the degree of oxidizability for samples with higher plutonium contents. The ceramic quality of the material was used to explain the difference in behavior of samples having the same Pu/M ratio.

For example, the relative ease of pulverizing coprecipitated pellets, as compared with mechanically blended pellets (each with a Pu/M ratio of 0.20), was explained by the inferior quality of the coprecipitated pellets used in this study. These coprecipitated pellets consisted of a "network" of ceramic material held together in a "loose" structure, rather than a single ceramic body with voids.

The physical size of the specimen appeared to be a factor only when the Pu/M ratio of the ceramics was greater than 0.2. In these cases, the oxidation behavior of powdered-pellet material and of microspheres (200 to 600 μ in diameter) was essentially the same, whereas whole pellets (6 mm in diameter) were far more resistant to oxidation. In one instance, a pellet was found to have gained only about 10% of the weight gained by a powdered sample which had been obtained from an identical pellet, after both had been treated for 2 hr at 650°C in oxygen (Pu/M = 0.25). The only difference observed between whole pellets and UO_2 or $(\text{U,Pu})\text{O}_2$ powder samples with a Pu/M ratio of less than 0.2 was that the whole pellets had a slightly lower rate of oxidation.

From the results of this study, it was concluded that the $(\text{U,Pu})\text{O}_2$ samples prepared by coprecipitation were most easily pulverized on oxidation, that specimens prepared by mechanical mixing were somewhat more resistant to oxidation and pulverization, and that sol-gel pellets and microspheres were the most difficult to pulverize. However, these conclusions are justified only if the samples examined here are representative of their fabrication method.

The conclusion reached from data obtained in studies on the surface areas and X-ray diffraction line-broadening measurements was that the oxidation process probably caused pulverization of the ceramics by fracturing along the grain boundaries. The particles comprising these powders, then, would not be individual crystallites but aggregates of them. Thus the maximum amount of pulverization would be expected to occur when the ceramic structure was completely reduced to the individual grains that made up the original material. Further reduction to the ultimate crystallite size did not occur.

Based on the information derived in this study and the fact that all of the volatile fission products are not removed from voloxidized, irradiated fuel specimens,¹⁻³ a speculation can be made about the release of the fission gases. If it is assumed that the gases collect at void spaces, both at the grain boundaries and in voids internal to the individual grains, then during oxidative pulverization the volatile fission products at the grain boundaries would be readily removed while those inside the resulting particles would be "trapped." These voids in the smaller particles may originate during fission or restructuring, or they may have existed in the original ceramic. Tritium would be expected to diffuse more easily through the oxide than the other volatile fission products, and should be removed. Krypton and iodine would be expected to show a more variable behavior, their release being dependent on how they were retained in the ceramic matrix and the degree of oxidation and pulverization of the sample. Oxidation of the ceramic to a M_4O_9 structure would release less of these products than oxidation to a $M_4O_9 + M_3O_{8-y}$ mixture. In either case, the internal voids of the grain fragments would likely retain some of the volatile fission products, which would be released only on dissolution. This type of behavior has been observed by others in hot-cell voloxidation studies.¹⁻³

Although several variables have been shown to affect the relative degree of oxidizability of $(U,Pu)O_2$ fuel specimens, the application of these data (obtained from unirradiated specimens) may need to be modified for irradiated fuel bodies. Restructuring, uranium migration, fission product content, and radiation damage are expected to have significant effects and hence to be potentially important variables. The ceramic nature of the irradiated material would be affected by restructuring; both extensive cracking as well as grain growth have been observed in irradiated samples.⁴ Extensive uranium migration during irradiation also produces phases of various Pu/M ratios, each of which would behave differently.⁵ These factors would affect the behavior of irradiated $(U,Pu)O_2$, and additional studies are required before a complete evaluation of the voloxidation process can be made.

4.2 Introduction

The behavior of volatile fission products during the processing of spent LMFBR fuels is a subject of considerable interest. Several studies of both irradiated and unirradiated (U,Pu) oxide fuel materials have been made, and most of the information has been reported in monthly LMFBR Fuel Cycle Studies Progress Reports. The volatilization process was initially conceived as a method for volatilizing gaseous fission products and possibly pulverizing the solids to facilitate their removal from the cladding. Pulverization occurs as the result of an increase in lattice volume as the MO_{2+x} cubic phase is converted to the orthorhombic M_3O_{8-y} phase.

Markin and Street⁶ have reported that UO_2 or $(\text{U}_{0.95}\text{Pu}_{0.05})\text{O}_2$ can be completely oxidized to M_3O_8 , which would result in powdering of the sample. However, oxidation of (U,Pu) O_2 samples with Pu/M ratios greater than 0.3 resulted in a M_3O_7 or M_4O_9 structure that did not powder.⁷ The projected LMFBR fuels have a Pu/M ratio of approximately 0.2, and the behavior of these intermediate compositions is of interest to the fuel reprocessing community.

In order to understand more clearly what occurs during the oxidation of these materials to O/M ratios greater than 2.0, the partial phase diagram for this system is shown in Fig. 4.1. The ternary phase diagram for U-Pu-O has been determined by Markin and Street.⁶ In this isothermal ternary diagram, the left-hand side represents the binary system uranium-oxygen, and the right-hand side represents the plutonium-oxygen system. Figure 4.1(a) is a representation of the system at 25°C, while Fig. 4.1(b) shows how the diagram changes over the temperature range 400 to 800°C.

As a given fuel oxidizes, the composition moves toward the oxygen corner of the diagram, along the line representing its respective Pu/(U+Pu) ratio. Thus, starting with single-phase fcc MO_2 , the first phase boundary which would be crossed during oxidation would be that between the phase fields for MO_{2+x} and the field represented by $\text{M}_4\text{O}_9 + \text{fcc } \text{MO}_{2+x}$. This would occur at an O/M of approximately 2.2 for a material with a Pu/M ratio of 0.2. The M_4O_9 crystal structure is also fcc, and its density differs from the density of MO_2 by only about 2%. Thus, we would not

Fig. 4.1. Ternary U-Pu-O Phase Diagram.

expect to observe major mechanical damage in MO_2 fuels oxidized to O/M ratios near 2.2 or 2.3.

In order to disintegrate the fuel and convert it to powder form, the $\text{M}_3\text{O}_{8-y} + \text{M}_4\text{O}_9$ phase field must be entered. To achieve maximum disintegration of the fuel, the tie line between U_3O_8 and PuO_2 should be reached during the oxidation. The density calculated from X-ray data is 8.34 g/cm^3 for U_3O_8 , compared with 11.16 g/cm^3 for U_4O_9 ; and this decrease in density which results from the formation of the U_3O_8 phase ($\sim 33\%$ increase in unit cell volume for the conversion of M_4O_9 to M_3O_8) should be more than sufficient to powder the fuel.

It was initially found by other workers that complete removal of the volatile fission products was not achieved by the voloxidation process and that the different fuel specimens varied as to the degree in which they pulverized.¹⁻³ The information presented here summarizes studies, on unirradiated UO_2 and $(\text{U,Pu})\text{O}_2$ specimens, that were designed to better define some of the variables in the voloxidation process.

4.3 NUMEC $(\text{U,Pu})\text{O}_2$ Fuels

The studies reported here were performed initially with NUMEC $(\text{U,Pu})\text{O}_2$ fuel pellets (unirradiated) and later with sol-gel microspheres and pellets prepared at ORNL. The NUMEC pellets, with Pu/M ratios of 0.20 and 0.25, were prepared from both coprecipitated and mechanically blended materials and were heat treated to give O/M ratios of 1.96 to 1.99. The ORNL sol-gel material was sintered to the same O/M ratios as the NUMEC fuels but had Pu/M ratios from 0.15 to 0.28. In addition, comparative studies were also made on high-density $\text{UO}_{2.0}$ pellets.

A summary of the results obtained with the NUMEC $(\text{U,Pu})\text{O}_2$ pellets and the UO_2 pellets is given in Table 4.1. A thermobalance was used to continuously follow the changes, some of which took several days to complete. Whole pellets were used, whenever possible, in the experiments, but the limited number of pellets required fragments to be used in some cases. The three types of fuels examined are designated as A, B, and C. Type A is coprecipitated fuel with a Pu/M of 0.20 (Batch 5); type B is

Table 4.1. Data for Voloxidation of (U,Pu)O₂ and UO₂ Fuel Pellets

Specimen	Type	Pu/M (%)	Initial Lattice Parameter (Å)	Treatment	Weight Gain (%)	O/M Ratio	Product ^a	
							Surface Area (m ² /g)	Results (lattice parameters given in Å)
1. C-5	Coprec.	20.34	5.464	a. 450°C, air ^b	2.68	2.45	0.42	Cubic + trace of orthorhombic phases; pellet powdered; a _o = 5.434 ^c
				b. 650°C, air ^b	2.67	2.45	0.51	Similar to "a"; a _o = 5.423 ^c
				c. 850°C, air ^b	2.78	2.47	0.14	Similar to "a"; a _o = 5.457 ^c
				d. 650°C, O ₂ ^b	3.25	2.55	-	M ₃ O _{8-y} , M ₄ O ₉ , powdered; a _o = 5.425 ^c
				e. H ₂ -O ₂ cycle ^d	3.30	2.56	0.42	Similar to "d"; a _o = 5.424 ^c
2. C-6	Coprec.	20.34	5.462	a. 450°C, air ^b	2.38	2.40	< 0.1	Cubic + trace of orthorhombic phases; pellet did not powder; a _o = 5.430 ^c
				b. 650°C, air ^b	2.62	2.52	0.26	Similar to "a", but pellet powdered; a _o = 5.429 ^c
				c. 850°C, air ^b	2.45	2.41	< 0.1	Similar to "b", a _o = 5.454 ^c
				d. H ₂ -O ₂ cycle ^d	3.30	2.56	0.72	M ₃ O _{8-y} , M ₄ O ₉ , powdered; a _o = 5.425 ^c
3. M-16	Mech. Blend	19.41	5.463	a. 450°C, O ₂ ^b	2.61	2.44	< 0.2	Cubic + orthorhombic phases; formed chunks; a _o = 5.435 ^c
				b. 2-H ₂ -O ₂ cycles ^d	3.21	2.54	0.45	M ₃ O _{8-y} , M ₄ O ₉ ; pellet powdered; a _o = 5.424 ^c
				c. 650°C, O ₂ ^b	3.2	2.5(4)	-	Similar to "b"
				d. 300°C, 500-psi O ₂ , ^e 200-psi H ₂ O	-	2.0	-	No change in fragment
				e. 300°C, 500-psi O ₂ ^e	0.6	2.1	< 0.02	No change in fragment; a _o = 5.440 ^c
				f. 450°C, 500-psi O ₂ ^e	2.0	2.3(4)	< 0.1	M ₄ O ₉ ; fragment formed "sand"; a _o = 5.425 ^c
				g. 600°C, 500-psi O ₂ ^e	3.2	2.5(4)	0.4	Similar to "b"; fragment powdered
4. T-7	Mech. Blend	24.88	5.488	a. 450°C, O ₂ ^b	2.39	2.40	-	M ₄ O ₉ ; pellet did not powder; a _o = 5.425 ^c
				b. 850°C, O ₂ ^b	2.39	2.40	< 0.1	Similar to "a"
				c. 850°C, O ₂ ^b	2.14	2.36	-	Similar to "a"
				d. 3 H ₂ -O ₂ cycles ^d	2.52	2.42	< 0.1	M ₃ O _{8-y} , trace, M ₄ O ₉ ; pellet did not powder; a _o = 5.425 ^c
				e. 600°C, 500-psi O ₂ ^e	2.2	2.3(7)	< 0.1	M ₄ O ₉ ; fragment formed chunks
				f. 600°C, 250-psi O ₂ ^e	2.4	2.4(0)	0.2	M ₄ O ₉ ; similar to "e"; plus some powder
				g. 600°C, 500-psi O ₂ ^e	3.0	2.5(1)	0.4	M ₄ O ₉ , M ₃ O _{8-y} ; fragment powdered
5. UO ₂ -1	Mech. Blend		5.470	a. 550°C, air	3.95	2.67	1.0	U ₃ O ₈ , pellet completely powdered; a _o = 6.716, b _o = 3.980, c _o = 4.147
				b. 850°C, air	3.95	2.67	0.25	Similar to "a"; a _o = 6.723, b _o = 3.990, c _o = 4.151
				c. 650°C, O ₂	-	-	1.30	-
				d. 450°C, O ₂	-	-	0.70	-
				e. Mech. ground	-	-	0.30	-

^aWhole pellets of ~1.3 g used except where noted. (U,Pu)O₂ pellets supplied by NUMEC.^bSamples heated to constant weight (1/2 to 2 hr) at isothermal conditions.^cCubic lattice parameter. M₃O_{8-y} phase gave parameters very close to those for α-U₃O₈.^dOxidized in O₂ at 450°C; reduced in 4% H₂-Ar at 800°C; and reoxidized in O₂ at 450°C. Reactions proceeded until at constant weight for 1 to 2 hr.^eHeld at temperature for 1 hr.

mechanically mixed fuel with a Pu/M ratio of 0.20 (Batch 16); and type C is mechanically mixed fuel with a Pu/M ratio of 0.25 (Task 7). It was quite evident from the experiments that, based on their pulverization behavior on oxidation, the $(U,Pu)O_2$ pellets could be classified into three groups: those that readily powdered (Type A); those that were difficult to powder (Type B); and those that did not powder without treatment under extreme conditions (Type C). The UO_2 pellets pulverized readily under milder conditions and at lower temperatures than any of the $(U,Pu)O_2$ pellets.

In going from UO_2 to $(U_{0.75}Pu_{0.25})O_2$ pellets, it was evident that the possibility of pulverization greatly diminished and that the higher plutonium content was probably responsible for this. The apparent difference in behavior for coprecipitated and mechanically blended pellets, both having Pu/M ratios of 0.2, was of special interest. The observed differences involved pulverization behavior and rate of oxidation rather than final weight gain or O/M ratio. These differences were more evident for whole pellets than for small pellet fragments. It appears, then, that $(U_{0.8}Pu_{0.2})O_2$ materials can be oxidized in O_2 up to an O/M ratio of approximately 2.5 to 2.6, which is sufficient to pulverize the fuel. Fragments may attain this O/M ratio in air,² whereas some of the whole pellets that did not attain this O/M level probably had not reached equilibrium. Although the $(U_{0.8}Pu_{0.2})O_2$ may be oxidized up to an O/M ratio of 2.6, the rate and ease of reaching this value may be a function of other factors. When the Pu/M ratio reaches a value of 0.25, the results indicate that the highest O/M ratio attainable by oxidizing in air or oxygen is 2.3 to 2.4. Higher O/M ratios can be achieved only by using extreme conditions, for example, 500-psi O_2 at 600°C. It appears that an O/M ratio of 2.4 to 2.6 is required before a sufficient quantity of the orthorhombic phase is generated to pulverize material with a Pu/M ratio of 0.2 to 0.25. Thus, in air or 1 atm of oxygen, it was possible to pulverize the $(U,Pu)O_2$ fuels with a Pu/M ratio of 0.2 or less, while fuels with a Pu/M ratio of 0.25 did not powder.

During the course of this work, it was noted that oxidation in an oxygen atmosphere often gave products with higher O/M ratios than did oxidation in air. The effect of oxygen at higher pressures was evaluated on the more difficult-to-oxidize fuels (Types

B and C). Although the Type B (Batch 16) sample could be oxidized to the expected O/M limit (2.5 to 2.6) with oxygen at 650°C, it was noted that oxygen at a pressure of 500 psi had little effect below 450°C, and 600°C was required to form a fine powder. With the Type C (Task 7) material, 500-psi oxygen at 600°C resulted in more extensive oxidation than was obtained in any run in 1 atm of air or oxygen, and provided complete pulverization. Lower pressures of oxygen produced chunks. With three cycles of reduction (500-psi 4% H₂--Ar at 800°C) and oxidation (500-psi oxygen at 600°C), the surface area was increased to 0.9 m²/g (vs 0.4 m²/g for a single high-pressure oxidation). Thus, a significant reduction in particle size was obtained with the extensive treatment.

Examination of the starting materials by metallography provided a possible explanation for the differences in behavior between Type A and Type B samples. Metallographs of Types A and C pellets are given in Figs. 4.2 and 4.3. It was found that the Type C sample was definitely a better-quality ceramic material than the Type A sample, although it had considerable porosity. The Type A pellet appeared to consist of islands of ceramic material, rather than being a single ceramic body with voids. The etched metallographs of Types A and C [HNO₃, HF, Ce(III) nitrate] showed that the grain size was similar, although the average size was slightly larger and the grain structure more dense for Type C. The Type B pellets were classified as intermediate between Types A and C in ceramic quality; the general appearance was similar to that of Type C, but the grain structure resembled that of Type A. Since the Type C pellets did not powder on oxidation, it was possible to examine an oxidized pellet. Figure 4.4 shows the extensive cracking that took place during the oxidation. The grain structure of the oxidized pellet appeared similar to that observed for the original A and B pellets. A second phase (M₃O₈) was not observed in the metallographs. The oxidized Type C pellets did not visually appear to be changed after oxidation, and a considerable amount of force was required to grind one of these pellets for X-ray diffraction analysis.

Alpha autoradiograms of the three types of pellets were also made to ensure that the plutonium was homogeneously distributed throughout the oxide matrix. Examination

Fig. 4.2. Metallograph of Type A Pellet. (a) and (b) Section of 4.5-mm pellet as polished; (c) etched pellet.

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Fig. 4.3. Metallograph of Type C Pellet. (a) and (b) Section of 4.5-mm pellet as polished; (c) etched pellet.

Fig. 4.4. Metallograph of Type C Pellet After Oxidation. (a) and (b) Section of 4.5-mm pellet as polished; (c) etched pellet.

of these autoradiograms indicated that all samples were comparable in plutonium distribution and homogeneity.

The ceramic nature of the fuel pellet is not the only important variable with respect to pulverization behavior. For example, the UO_2 pellets, which were similar to Type C in ceramic quality, were readily oxidized and powdered. However, a difference in ceramic nature can be used to explain the ease of powdering and oxidation of Type A pellets as compared with Type B pellets. Although both types of pellets had about the same Pu/M ratio, the Type B pellets oxidized more slowly and were more difficult to pulverize. The final O/M ratios obtained for a given set of conditions were similar for both pellets.

4.4 Sol-Gel (U,Pu) O_2 Fuels

Since the plutonium content appears to have a definite effect on the pulverization behavior of the (U,Pu) O_2 specimens, additional work was performed to help define this variable. Six types of sol-gel material were examined as follows: (1) three samples of (U,Pu) O_2 microspheres (300 to 400 μ in diameter) with Pu/M ratios of 0.17, 0.25, and 0.28; and (2) three samples of (U,Pu) O_2 pellets (6 mm x 4.5 mm) with Pu/M ratios of 0.15, 0.20, and 0.25. The microspheres were prepared by the ORNL sol-gel process and calcined in 4% H_2 --Ar to give O/M ratios of 1.96 to 1.99. The pellets were pressed from sol-gel powder and were calcined in a similar manner, but at slightly higher temperatures, to attain the desired densities.

Metallographic examination of the microspheres and pellets showed that all of the microspheres were of similar quality, with differences noted as follows: (1) the microspheres with a Pu/M ratio of 0.28 had the least microporosity but showed an unusually small grain size (0.05 to 0.2 μ); (2) the microporosity and grain size of the microspheres with a Pu/M ratio of 0.25 showed some variation (grain size was 0.5 to 1.5 μ); (3) the microspheres with a Pu/M ratio of 0.17 were intermediate in microporosity and grain size (0.2 to 0.6 μ). The porosity of the pellets was greater than that of the microspheres, but the three different pellets showed very similar microstructure and grain size. The grain size of the pellet matrix measured 0.3 to

2 μ . All six samples could be classified as being a good-quality ceramic oxide. Figure 4.5 shows etched micrographs for the microspheres having Pu/M ratios of 0.17 and 0.28 and pellets having Pu/M ratios of 0.15 and 0.25. The average grain size of the pellets appeared to be larger than that of the microspheres.

The oxidation of these sol-gel $(U,Pu)O_2$ microspheres, pellets, and mechanically powdered pellets was followed by thermogravimetric analysis (Fig. 4.6). No significant difference in oxidation behavior was observed for whole or mechanically powdered microspheres. A comparison of oxidation behavior for whole pellets and powders (mechanically ground) showed a striking difference for pellets with a Pu/M ratio ≥ 0.2 . The results were as follows: (1) a pellet having a Pu/M ratio of 0.25 exhibited little weight gain after 2 hr at 650°C, whereas the powder readily oxidized to an O/M ratio of 2.33; (2) the pellet with a Pu/M ratio of 0.2 gained about one-third of the weight gained by the powder; and (3) the pellet with a Pu/M ratio of 0.15 behaved identically to its powdered form with regard to weight gained on oxidation.

The TGA and differential thermal analysis (DTA) curves for the sol-gel microspheres and powdered-pellet samples are shown in Figs. 4.7-4.10. The thermal analysis curves for the microspheres with a Pu/M ratio of 0.17 and for the pellet material with Pu/M ratios of 0.15 and 0.20 show a two-step oxidation process. The samples with a Pu/M ratio of 0.25 or 0.28 show only a single oxidation step, and their final O/M ratio indicated a M_4O_9 product. Only the microspheres with a Pu/M ratio of 0.17 powdered on oxidation. These results are in accord with those obtained with the NUMEC samples. From the curves in the above figures, it can also be seen that a temperature of 550 to 600°C is required for oxidizing $(U,Pu)O_2$ material (Pu/M = 0.20) to a $M_4O_9 + M_3O_{8-y}$ product.

X-ray diffraction analysis of the oxidized products in Figs. 4.7-4.10 showed a mixture of orthorhombic M_3O_{8-y} and cubic M_4O_9 phases for materials with a two-step oxidation, and essentially only a M_4O_9 cubic phase for samples that oxidized in a single step. Some of the latter samples did give a few weak diffraction lines that indicated the presence of a small amount of a M_3O_{8-y} phase.

Fig. 4.5. Etched Metallographs of (U,Pu)O₂ Microspheres and Pellets. (a) Microspheres, Pu/M = 0.17; (b) microspheres, Pu/M = 0.28; (c) pellet, Pu/M = 0.15; (d) pellet, Pu/M = 0.25.

Fig. 4.6. Weight Gain of Sol-Gel $(U,Pu)O_2$ Powdered and Whole Micro-spheres and Pellets in Oxygen.

Fig. 4.7. TGA Curves for $(U,Pu)O_2$ Microspheres in Oxygen.

Fig. 4.8. DTA Curves for (U, Pu)O₂ Microspheres in Oxygen.

Fig. 4.9. TGA Curves for $(U,Pu)O_2$ Powdered Pellets in Oxygen.

Fig. 4.10. DTA Curves for $(U,Pu)O_2$ Powdered Pellets in Oxygen.

As discussed in an earlier section, it was found that some of the whole pellet samples were resistant to complete oxidation, and that a lower O/M ratio was obtained than was expected on the basis of their plutonium content. Thus, a few of the X-ray diffraction results for the whole pellets (NUMEC, type A) should be interpreted on the basis that the equilibrium O/M ratio was not reached during oxidation.

It is also of interest to note that when the microspheres with Pu/M ratios of 0.25 and 0.28 were subjected to 500-psi oxygen at 600°C, they did not powder and oxidized only to M_4O_9 . This was in contrast to the results for NUMEC Type C pellets, which oxidized to M_3O_{8-y} . At present, we have no explanation for the difference in the behavior of these samples with the same plutonium content.

4.5 Comparative Analyses of Voloxidation Materials

4.5.1 UO₂ Oxidation

The oxidation of UO₂ pellets in oxygen was analyzed by TGA and DTA, using programmed heating rates of 6°C/min and 10°C/min, respectively. Figure 4.11 shows TGA and DTA curves for a UO₂ pellet and for powder obtained by grinding the pellet. The DTA analysis of the UO₂ showed two major changes. The first occurred at about 320°C, and the second at about 500°C. X-ray diffraction analysis was then done on two UO₂ samples that had been heated in the same equipment under identical conditions; one was quenched at 340°C, while the second was quenched at 520°C. The first sample was found to be a mixture of two fcc structures. One set of diffraction lines gave a lattice parameter value of 5.470 Å, which is identical to that for UO_{2.00}. The other pattern was too weak to permit a calculation of the unit cell, but the position of the lines indicated the parameter to be smaller than 5.470 Å. These data can be interpreted as evidence of the disproportionation of UO_{2.0+x} to UO_{2.0} and UO_{2.25} (U₄O₉, $a_o = 5.430$ Å). Quenching the sample probably produced a poorly crystallized U₄O₉ structure which failed to give a good diffraction pattern. The second sample gave a diffraction pattern that corresponded to the orthorhombic U₃O₈ structure. No inflection was present in the TGA curve to indicate the formation of

Fig. 4.11. TGA and DTA Curves for UO_2 in Oxygen.

an intermediate oxidation product. Oxidation of the pellet was identical to oxidation of the powdered sample, except that the pellet required more time to reach constant weight.

Uranium dioxide pellets, before and after oxidation, were analyzed by X-ray diffraction and scanning electron microscopy; in addition, surface area measurements were made on the materials. Hydrogen-oxygen-cycled mixed oxide samples (500°C oxygen, 800°C hydrogen) were also examined. The results are summarized in Table 4.1. The surface area measurements for the UO_2 samples showed that the highest area was obtained after oxidizing at 650°C in oxygen with values ranging from 0.3 to 1.3 m^2/g . Heating the oxidized samples to 850°C in air or oxygen decreased the surface area to 0.1 to 0.3 m^2/g . Powders obtained by mechanically grinding unoxidized pellets had surface areas of about 0.3 m^2/g . The size of the particles making up the powders can be estimated from these measured surface areas, if we assume that the particles are uniform, geometric cubes. The particles comprising the 550°C oxidized powders were estimated to be approximately 0.7 μ in size. For a mechanically ground UO_2 powder or UO_2 that had powdered on being heated to 600–800°C, the particle size was approximately 4 μ . From metallographs of etched UO_2 pellets, the grain size was estimated at 3 to 15 μ (average, $\sim 10 \mu$).

Examination of the starting UO_2 material and the oxidized products by X-ray line broadening analysis indicated that the cubic phases had an X-ray crystallite size of 1500 to 2000 Å. The crystallite size in the orthorhombic phase appeared, in some cases, to be smaller (500 to 1200 Å), but the line broadening may also be indicative of poor crystallinity or a variation in the M_3O_{8-y} stoichiometry. Whether a size reduction occurs on oxidation was not conclusively shown. However, all of the X-ray diffraction patterns indicated crystallite sizes of less than 2000 Å (0.2 μ).

Electron micrographs of samples obtained from the UO_2 pellets are shown in Fig. 4.12. The first photograph (a) was taken from a fractured section of the untreated pellet and shows the dense ceramic matrix with its internal voids. The second view (b) is of UO_2 powder obtained by mechanically grinding a UO_2 pellet. This material consisted of a mixture of large chunks and small particles. The powder obtained by

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Fig. 4.12. Electron Micrographs of a UO_2 Pellet. (a) Section of original pellet; (b) powder from mechanically ground pellets; (c) powder from oxidized (550°C in air) pellet; (d) powder after heating to 850°C in air.

heating a UO_2 pellet in air to 550°C is shown in (c). This powder is made up of rather uniform particles of 2 to 4 μ , which agrees with values previously obtained from surface area measurements. Heating to 850°C caused some agglomeration or densification of the particles [Fig. 4.12 (c)] to form the powder shown in Fig. 4.12 (d). (This change was also indicated by a decrease in the surface area of the powder.) The change did not involve crystallite growth, but appeared to involve the surfaces between the particles. The decrease in surface area and "densification" of the material may be used to explain the slower oxidation rate and lower O/M ratios obtained for oxidations above 700°C .

Values for the crystallite size and surface area were also obtained for most of the oxidized (U,Pu) products. The surface area values are listed in Tables 4.1 and 4.2. The starting and final crystallite sizes for the (U,Pu) O_2 materials were slightly smaller than for the UO_2 samples (cubic phases, 1100 to 1600 $\text{\AA}$ vs 2000 $\text{\AA}$). Surface area measurements of the oxidized (U,Pu) O_2 products gave values which ranged from 0.1 to 1.5 m^2/g but generally fell within the 0.2 to 0.7 m^2/g range. Examination of the surface area data indicated a trend in the surface areas of the starting material and oxidized products as a function of the plutonium content. Lower surface areas were obtained for materials with a higher Pu/M ratio.

Calculation of the particle size from the surface areas of the (U,Pu) materials was complicated in some of the samples by the existence of two crystal phases. Approximations of the particle size from the surface areas indicated that the samples contained particles 1 to 10 μ in size, which is in agreement with the particle size observed and calculated for the U_3O_8 powders.

From the above X-ray crystallite and surface area measurements, it appears that, if sufficient oxidation occurs to powder the samples, pulverization is effected by fracturing along the grain boundaries of the ceramic matrix. Thus, the particles making up the final powders would not be the individual crystallites (1000 to 2000 $\text{\AA}$) but particles the size of the grains in the starting material (0.3 to 3 μ).

Table 4.2. Data for Voloxidation of (U,Pu)O₂ Pellets and Microspheres

Specimen	Type ^a	Pu/M (%)	Maximum Temperature ^b	Weight Gain (%)	O/M Ratio	Surface Area (m ² /g)		Product (lattice parameters given in Å)
						Initial ^c	Product	
1. SpH-17	Sol-gel	17.39	a. 800°, O ₂	3.38 ^d	2.57	-	-	M ₄ O ₉ , M ₃ O _{8-y} ; spheres powdered
			b. 800°, O ₂	3.35 ^c	2.56	0.36	1.35	M ₄ O ₉ , M ₃ O _{8-y} ; only two to four poor cubic diffraction lines; good orthorhombic pattern
2. SpH-25	Sol-gel microspheres	24.91	a. 800°, O ₂	2.20 ^d	2.37	-	-	M ₄ O ₉ ; spheres intact
			b. 800°, O ₂	2.20 ^c	2.37	0.22	0.41	M ₄ O ₉ ; a ₀ = 5.423 ^e
			c. 600°, ^f 500-psi O ₂	-	-	-	-	M ₄ O ₉ ; spheres intact
3. SpH-28	Sol-gel microspheres	28.26	a. 800°, O ₂	2.15 ^d	2.36	-	-	M ₄ O ₉ ; spheres intact
			b. 800°, O ₂	2.28 ^c	2.39	0.26	0.51	M ₄ O ₉ ; a ₀ = 5.426 ^e
			c. 600°, ^f 500-psi O ₂	-	-	-	-	M ₄ O ₉ ; spheres intact
4. Pel-15	Pellets from sol-gel powder	15.23	a. 800°, O ₂	3.35 ^c	2.57	0.48	1.50	M ₄ O ₉ , M ₃ O _{8-y} , a ₀ = 5.425 ^e ; poor cubic diffraction lines; M ₃ O _{8-y} gave good pattern
			b. 650°, O ₂ ^g	3.17 ^d	2.54	-	-	Pellet powdered completely
5. Pel-20	Pellets from sol-gel powder	19.62	a. 800°, O ₂	2.93 ^c	2.50	0.27	0.64	Cubic and orthorhombic phases; a ₀ = 5.442 ^e
			b. 650°, O ₂	0.85 ^d	2.1(4)	-	-	Pellet was only slightly cracked
6. Pel-25	Pellets from sol-gel powder	25.25	a. 800°, O ₂	1.96 ^c	2.33	0.20	0.27	M ₄ O ₉ ; a ₀ = 5.424 ^e
			b. 650°, O ₂	0.25	2.0(4)	-	-	Pellet appeared unchanged

^aAll (U,Pu)O₂ starting ceramics had been prepared to produce MO₂-MO_{2-x} products (O/M = 1.96-2.00).

^bLinear heating rate of 6°C/min to maximum temperature.

^cMicrospheres or pellets mechanically ground prior to use.

^dWhole microspheres (200 to 400 μ in diameter) or whole pellet (1.3 g) used (ORNL manufactured).

^eM₄O₉ cubic lattice parameter; M₃O_{8-y} parameters were very close to α-U₃O₈ parameters.

^fHeated to temperature and held 1 hr.

^gHeld at temperature until weight was constant.

4.6 X-Ray Diffraction Analysis of Irradiated Fuel

A few experiments were also made using irradiated $(U,Pu)O_2$ fuels that had an original Pu/M ratio of 0.25. The history and results of the X-ray diffraction analyses of the samples are given in Table 4.3.

Both samples had an apparent reduction in the O/M ratio compared to the initial fuel composition. The more highly irradiated sample (FR-88) gave an X-ray O/M ratio of 1.93, assuming that Vegard's Law is obeyed in the irradiated fuel⁶ and that the larger lattice parameter is due solely to the O/M ratio. Radiation damage to the crystal would also give an expanded lattice parameter, but the magnitude should be smaller than was observed. Thus, the larger parameter may reflect both radiation damage and a decrease in the O/M ratio.

Metallographic examination showed that the FR-87 (4000-MWd/metric ton) sample had not restructured during irradiation. Oxidation of this sample in air at 650°C gave predominantly a M_3O_8 product. Examination of the FR-88 (14,500-MWd/metric ton) sample showed that it had restructured; and, on oxidation under similar conditions, an M_4O_9 product was obtained.

4.7 References for Section 4

1. LMFBR Fuel Cycle Studies Progress Report for May 1970, No. 15, ORNL-TM-3018 (June 1970), p. 11.
2. LMFBR Fuel Cycle Studies Progress Report for March 1971, No. 25, ORNL-TM-3375 (April 1971), pp. 9-22.
3. LMFBR Fuel Cycle Studies Progress Report for July 1971, No. 29, ORNL-TM-3534 (August 1971), pp. 11-29.
4. W. J. Lackey, Fuels and Materials Development Program for Period Ending March 31, 1971, ORNL-TM-3416, pp. 33-37.
5. J. L. Miller and W. J. Lackey, Ibid., pp. 39-43.

Table 4.3. Data Obtained from X-Ray Analysis of Irradiated Fuel

	Sample FR-87	Sample FR-88
Fabrication Conditions		
WADCO fabrication batch	ME-20	ME-22
Fuel composition	25 wt % PuO_2	25 wt % PuO_2
O/M ratio	1.98	1.99-2.00
Sintering temp., $^{\circ}\text{C}$	1600	1650
Sintering time, hr	8	8
Sintering atmosphere	$\text{Ar--8\% H}_2$	$\text{Ar--8\% H}_2$
Sintered density, % theoretical	91.3	95.6
Reactor Conditions		
Peak burnup, MWd/metric ton	4170	14,500
Peak power, kW/ft	5.3	11.5
Centerline temperature, $^{\circ}\text{C}^a$	~ 1650	~ 2200
X-Ray Diffraction Analysis		
Mechanically pulverized	$\text{fcc } a_o = 5.462 \pm 0.001 \text{ \AA}$	$\text{fcc } a_o = 5.472 \pm 0.001 \text{ \AA}$
O/M ratio detd. by X-ray	1.96	1.93
After air oxidation (650 $^{\circ}\text{C}$, 6 hr)	orthorhombic U_3O_8	$\text{fcc } a_o = 5.420 \pm 0.001$

^aEstimated.

6. T. L. Markin and R. S. Street, J. Inorg. Nucl. Chem. 29, 2265 (1967).
7. C. Sari, U. Benedict, and H. Blank, Thermodynamics of Nuclear Materials, pp. 587-611, IAEA, Vienna, 1967.

5. VOLOXIDATION TESTS WITH IRRADIATED FUELS

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5.1 Summary

Hot-cell tests on the volatilization of fission products during the high-temperature oxidation of irradiated UO_2 and $(\text{U,Pu})\text{O}_2$ have shown that the procedure is highly effective in removing tritium but only moderately effective in removing iodine and the noble gases, xenon and krypton. More than 99% of the tritium and iodine was removed in several of the tests; in the best case, a highly restructured, high-burnup fuel released 98% of its contained krypton. In general, however, all of the tritium but only up to 75% of the iodine and up to 45% of the krypton were released by the oxidations. Purging with an inert gas, such as helium or argon, or subjecting the heated fuel to a vacuum was not as efficient as oxidation for tritium and rare gas removal; iodine on the other hand, was volatilized in an inert atmosphere. The behavior of the $(\text{U,Pu})\text{O}_2$ and the fission products appeared to be related to the composition and fabrication conditions of the fuel and to the restructuring of the fuel during irradiation. The optimum temperatures for volatilizing the fission products during oxidation appeared to correlate with the optimum temperatures for achieving efficient oxidation of unirradiated fuels.

5.2 Introduction

Results of experiments involving the voloxidation of irradiated fuels have been periodically reported in ORNL documents.¹⁻³⁴ The early tests consisted mainly of measurements of the volatility of tritium and iodine from long-cooled $(\text{U,Pu})\text{O}_2$ to which short-cooled UO_2 had been added to provide ^{131}I and ^{133}Xe tracer. In these tests, low concentrations of hydrogen gas were usually added to the air stream to act as a "carrier" for tritium. Since quantitative analytical procedures for Xe-Kr had not been developed in the early tests, Xe-Kr analyses were not made. Techniques were refined in later experiments, and gave quantitative recoveries.

5.3 Volatility of Iodine and Xenon-Krypton

5.3.1 Tracer Tests

The addition of short-decayed (<30 days) UO_2 to highly irradiated but long-decayed PuO_2 - UO_2 permitted us to follow the behavior of iodine during the heating-oxidation treatment. In an early experiment, NUMEC 20% PuO_2 --80% UO_2 that had been irradiated to a burnup of 20,000 MWd/metric ton in Capsule NU-17 was heated at 450°C for 3 hr in a mixture of oxygen plus argon--4% hydrogen; 98.3% of the iodine was volatilized from the fuel during this treatment. A film of "tarlike" material deposited on the walls of the quartz furnace tube just outside the heated zone. At the end of the test, the equipment was leached with CCl_4 and HNO_3 . Only a portion of the brown deposit was soluble in CCl_4 ; the remainder dissolved completely in warm 8 M HNO_3 . The radioactivity of the material was due mostly to ^{131}I ; however, ruthenium and some other fission products were also detected. Of the total iodine found in the experiment, about 48% was located on the walls of the quartz tube just above the furnace, 32% was in the head of the burner packed with glass wool (roughing filter), and 18% was adsorbed on the activated charcoal and molecular sieve traps.

In another test, NUMEC 20% PuO_2 --80% UO_2 fuel that had been irradiated to a burnup of 49,000 MWd/metric ton in Capsule NU-18 (plus short-decayed UO_2) was heated at 750°C, first in a stream of nitrogen for 3 hr and then in a stream of oxygen for 3 hr. This treatment removed about 90% of the ^{131}I from the fuel. About 71% of the total ^{131}I was found in the tubing located just beyond the heated zone. Another 18% of the total ^{131}I collected was found in traps outside the furnace; 94% of this ^{131}I volatilized during the 3-hr heatup in nitrogen, and the remaining 6% volatilized during the 3-hr oxidation, indicating that volatilization of iodine did not require oxygen.

We also determined the relative amounts of iodine that volatilized from the fuel at various temperatures during heatup and during the oxidation step. A sample of mechanically blended 20% PuO_2 --80% UO_2 that had been irradiated to a burnup

of 50,000 MWd/metric ton in NUMEC Capsule NU-18 (plus short-decayed UO_2) was heated to 750°C stepwise (1 hr at each of these temperatures: 450, 550, 650, and 750°C) in a stream of argon--4% hydrogen. The gas stream was then changed to pure oxygen, and heating at 750°C was continued for 3 hr. A charcoal trap located just beyond the burner was replaced after each step. About 56% of the total ^{131}I was found on the walls of the burner just outside the heated zone, while about 18% was left in the oxidized fuel and the burner. Additional fractions (14, 0.9, 0.6, and 1%) of the ^{131}I were found in charcoal traps removed after heating at 450, 550, 650, and 750°C, respectively; 9% was collected in the charcoal trap during the oxidation step.

5.3.2 Tests with Short-Cooled Fuel

The behavior of the volatile radionuclides in processing was studied in 1969, using four irradiated stainless-steel-clad fuel rods containing sol-gel 15% PuO_2 --85% UO_2 microspheres.⁹⁻¹² The rods had been irradiated in the ETR as Capsule 43-116 to about 20,000 MWd/metric ton and cooled 32 to 65 days. About 50% of the ^{85}Kr and 50% of the ^{133}Xe but essentially no other radionuclides were released when the rods were sheared [60% total ^{131}I fixed in plenum; 40% in $(\text{U,Pu})\text{O}_2$].

In the voloxidation tests, the fuel rod segments were heated in a stream of helium and then oxidized at 450, 650, or 750°C for 4 or 8 hr in pure oxygen ($0.1 \text{ ft}^3/\text{hr}$). From 32 to 74% of the ^{131}I in the fuel rods was removed; the best result, 74%, was obtained at 650°C (Table 5.1). About 50% of the ^{85}Kr and ^{133}Xe in the sheared fuel rod segments was removed by the voloxidation treatment. Based on the total amounts found in shearing, voloxidation, and dissolution of the fuel following voloxidation, it was estimated that about 75% of the ^{85}Kr and ^{133}Xe and from 63 to 81% of the ^{131}I had been separated from the sheared fuel rods prior to dissolution.

More recent (1971) experiments with short-cooled fuel, irradiated to a peak burnup of 2.5% FIMA, were made to study the release of the volatile fission products from mechanically blended $(\text{U}_{0.75}\text{Pu}_{0.25})\text{O}_{1.98}$ pellets of the FTR "Reference" type.^{1,26,27}

Table 5.1. Removal of ^{131}I from Short-Cooled Irradiated Fuel by Voloxidation Treatment

Length of Sheared Section (in.)	Voloxidation Conditions		^{131}I Removed (%) ^a
	Time (hr)	Temperature (°C)	
1/4	8	450	41
1/4	8	650	74
1/4	4	750	32
3/4	8	750	50

^aPercent of total ^{131}I fed to the voloxidizer.

The oxidations were performed at 480°C, the optimum temperature for the rapid disintegration of these pellets.²⁴ About 30% of the residual ^{85}Kr in the fuel and 30 to 70% of the ^{131}I were released by the oxidation, generally confirming the 1969 results.

5.3.3 Effect of Temperature

Tests with NUMEC mechanically blended or coprecipitated $(\text{U,Pu})\text{O}_2$, irradiated to a burnup of about 100,000 MWd/metric ton, showed that more ^{85}Kr was released at 750°C than at 800 or 850°C.^{2,3,6,7} Short sections of NUMEC 316L stainless-steel-clad, mechanically blended 20% PuO_2 --80% UO_2 , irradiated to 100,000 MWd/metric ton and decayed about 16 months, were heated in a slow (50 cc/min) flow of oxygen for 3 hr at 450°C and then 7.4 hr at 750°C. (NUMEC reported that 43% of the noble gases had previously been released from this fuel upon puncturing of the fuel rod.) The oxidation treatments volatilized a total of about 98% of the remaining ^{85}Kr , even though none of the restructured fuel was dislodged from the cladding:

<u>Oxidation Treatment</u>	<u>^{85}Kr Removed (% of total)</u>
3 hr at 450°C	58.6
4 hr at 750°C	34.6
3.4 hr at 750°C	<u>4.6</u>
Total	97.8

Significant fractions of fission product Ru, Cs, Sb, and Nb were also volatilized. Most of this material, as well as about 2% each of the uranium and plutonium, was found on the walls of the quartz "burner" and in the burner head, which contained a glass wool filter (Table 5.2). About 3% of the ^{106}Ru and 8% of the ^{137}Cs penetrated to a trap containing type 5A molecular sieve, which was attached to the gas exit on the head of the burner. The ^{85}Kr was adsorbed at -78°C on activated charcoal traps located downstream of the molecular sieve.

We oxidized the segmented remnants of another NUMEC fuel rod (316L stainless-steel-clad, coprecipitated 20% PuO_2 --80% UO_2 , irradiated to 100,000 MWd/metric ton) at 850°C. In this experiment millicurie quantities of a submicron cesium "smoke" were volatilized and passed successively through a NaOH scrubber and a disposable, 2-in.-diam Gelman Type A Fiberglass "absolute" filter, finally reaching the charcoal traps used to retain ^{85}Kr . Cesium contamination of the traps prevented an absolute determination of the quantity of ^{85}Kr released by the oxidation procedure. However, based on the amount of ^{85}Kr in the initial fuel and the amount found in the oxidized fuel, only about 80% of the ^{85}Kr was released by the 5-hr oxidation treatment. About 32% of the gamma-emitting radionuclides in the fuel sample were also volatilized in this experiment.

In a third experiment, sections of NUMEC stainless-steel-clad, mechanically blended 20% PuO_2 --80% UO_2 (irradiated to 100,000 MWd/metric ton) were oxidized for 6 hr at 800°C. Again, the fuel pellets did not disintegrate; one pellet split lengthwise but was otherwise intact. About 87% of the ^{85}Kr was removed by this treatment.

Table 5.2. Distribution^a of Uranium, Plutonium, and Fission Products
After Oxidation at 750°C

Procedure: Fuel rod segments heated in oxygen for 3 hr
at 450°C and then 7.4 hr at 750°C

Constituent	Oxidized Fuel + Cladding	Burner Walls	Burner Head	Molecular Sieve	Activated Charcoal
Uranium	97.9	1.3	0.9	Trace	
Plutonium	96.6	1.9	1.5	Trace	
⁸⁵ Kr	2.2	Not detected			97.8
⁹⁵ Nb	90.6	9.4			
¹⁰⁶ Ru	56.7	6.3	34.2	2.7	
¹²⁵ Sb	73.1	19.1	~6.7		
¹³⁷ Cs	71.0	18.8	2.4	7.9	
¹⁴⁴ Ce	96.5	2.5	0.8		

^aPercent of total found.

Decreasing the oxidation temperature from 850°C to 800°C in the third experiment decreased the amounts of some fission products volatilized from the fuel but increased the release of ⁸⁵Kr. At 800°C only about 10% of the gamma-emitting nuclides were found on the cooler upper burner walls and in the aqueous scrubber following the burner; this compares with over 30% found at 850°C. The release of ⁸⁵Kr as a function of temperature was as follows:

Temperature (°C)	⁸⁵ Kr Released (%)
750	98
800	87
850	79

The smaller release of ^{85}Kr at the higher temperatures may have been due to sintering of the fuel during oxidation, which would have prevented the escape of the fission gas, or to changes in the crystal structure such as those observed by Tennery (Sect. 3). Results of these tests indicate that the voloxidation temperature should be limited to 750°C , and preferably lower. In the experiments at 800 and 850°C , the stainless steel cladding disintegrated into a magnetic powder and flakes;³ this did not occur at 750°C . Weight-gain measurements indicated that 85 to 95% of the stainless steel was probably converted to oxides. The oxygen attack on the cladding is apparently due to the irradiation as well as the temperature of oxidation. Unirradiated type 316 and 304L stainless steel tubing segments, when heated in air for 6 hr at 850°C , turned black on the surface but showed essentially no weight gain.

5.3.4 Comminution of Fuel

In a series of tests with 1-in. sections of stainless-steel-clad, low-burnup (1800 MWd/metric ton), coprecipitated 20% PuO_2 --80% UO_2 , heating the fuel in oxygen at temperatures in the range of 450 to 750°C for 4 to 11 hr dislodged only about 10% of the fuel from the cladding and removed only about 10% of the krypton. Removing the fuel from the cladding and crushing it to a powder prior to the heating-oxidation treatment did not increase the amount of krypton released. In all of these tests, however, more than 95% of the tritium was removed.

A cyclic oxidation-reduction treatment was used in an attempt to powder the fuel pellets. A charge of 0.5- to 1.0-in.-long sections of a stainless-steel-clad, coprecipitated 20% PuO_2 --80% UO_2 fuel rod was heated alternately in argon--4% hydrogen and in oxygen. Four cycles of treatment at 650 to 750°C over a period of 21 hr removed only about 10% of the krypton from the fuel. The fuel was not dislodged from the cladding by this treatment.

A similar experiment was made with 20% PuO_2 --80% UO_2 fuel that had been irradiated by NUMEC to a burnup of 20,000 MWd/metric ton and decayed 30 months. Heating a 2.1-g sample of the fuel to 450°C in argon--4% hydrogen and then in a

1:1 mixture of oxygen and argon--4% hydrogen for 3 hr at 450°C removed 94% of the tritium but did not powder the pellets.

5.3.5 Effects of Process Variables

In order to test the effects of temperature, the oxygen concentration of the purge gas, and the flow rate of the purge gas on the volatility of ^{131}I and ^{85}Kr - ^{133}Xe , we irradiated microspheres of sol-gel UO_2 and conducted a simple 2^3 factorial oxidation experiment. The experimental conditions were:

	<u>Low</u>	<u>High</u>
Temperature, °C	450	750
Oxygen content, %	25	75
Flow rate, cfh	0.2	1.0

Statistical analysis of the test results (Table 5.3) showed that more ^{131}I and ^{85}Kr were released at the higher than at the lower temperature but that the oxygen content of the purge gas or the gas flow rate had little effect.³ These results suggested that a peak in the release of fission products may occur at temperatures between 450 and 750°C. Another test with coprecipitated $(\text{U,Pu})\text{O}_2$ that had been irradiated to a burnup of 1800 MWd/metric ton showed essentially no release of ^{85}Kr at temperatures less than 300 to 350°C.¹⁵ This might be expected since thermogravimetric analyses of samples of unirradiated $(\text{U,Pu})\text{O}_2$ showed that no significant oxidation occurred at temperatures less than 350°C.²⁰ These results are consistent with the phase and oxidation rate studies on the U-Pu-O system by Tennery (Sect. 3) and by Haire et al. (Sect. 4).

A 2^3 factorial experiment was performed to determine the effects of time and temperature of voloxidation (in air) and the fuel particle size on the release of ^{85}Kr from irradiated $(\text{U,Pu})\text{O}_2$.¹⁶⁻¹⁸ Parameters of the tests were:

Particle size: large, $>250\ \mu$ (60 mesh); small, $<74\ \mu$ (200 mesh)

Time: 16 hr and 4 hr

Temperature: 550°C and 350°C

Table 5.3. Effects of Temperature, Atmosphere, and Gas Flow Rate on the Volatilization of ^{85}Kr and ^{131}I from UO_2

Temp. (°C)	O_2 Conc. (%)	Gas Flow (cfh)	Volatilized (%)	
			^{85}Kr - ^{133}Xe	^{131}I
450	75	0.2	19	~ 8
750	75	1.0	69	~ 99
450	25	0.2	23	~ 85
750	25	1.0	42	~ 90
450	75	1.0	36	~ 33
750	75	0.2	76	~ 95
450	25	1.0	11	~ 38
750	25	0.2	~ 99	~ 92

The fuel, which was unclad coprecipitated 20% PuO_2 --80% UO_2 Vipak powder (from GE experiment F1F) that had been irradiated to approximately 1800 MWd/metric ton in EBR-II, was crushed by shearing and sieved.

Analysis of the results, based on the percent of the total ^{85}Kr in the fuel that was released during voloxidation, indicated that the major effect (95% confidence level) was that of particle size. The temperature and time-temperature interactions had a lesser effect (90% confidence level), while the time after 4 hr had little effect. Contrary to expectations, the largest lumps of fuel (>30 mesh) released ^{85}Kr more readily and completely (up to about 70% at 550°C) than <100-mesh particles, which released up to 32% (Fig. 5.1). We examined differences in the particles other than particle size that might explain the results. One finding was that the $^{137}\text{Cs}/\text{U}$ ratio in the small particles was about 60% higher than in the large particles. This may have been related to fuel restructuring and cesium migration during irradiation. Figure 5.2 illustrates that the plutonium and ^{144}Ce compositions were essentially the

Fig. 5.1. Release of ^{85}Kr from 1800-MWd/metric ton $(\text{U,Pu})\text{O}_2$ During Oxidation with Air at 550°C .

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Fig. 5.2. Variations in the Composition of Fuel and in the Amount of ^{85}Kr Released on Voloxidation as a Function of Fuel Particle Size.

same for each size fraction but that the ^{137}Cs concentration was about 70% higher in the -200-mesh fraction than the +30 mesh fraction. (Data for uranium are not shown; however, uranium was at about the same concentration in each fraction.) The +30-mesh lumps released from 55 to 70% of the contained ^{85}Kr , while the -200 mesh fraction released about 32% upon voloxidation. Based on the quantities of ^{85}Kr released and the proportion of large to small particles in the fuel, we calculated that about 39% of the ^{85}Kr would be released from a mixture of the two sizes; we actually measured 41% release when 1/2-in.-long segments of fuel rod were oxidized in the hot cell. Later experiments showed that the ^{85}Kr was released – and the oxidation apparently completed – within 30 min after the air was turned on at 650°C.²⁵ Tenner's rate data (Sect. 3) complement these hot-cell results.

We conducted a set of eight experiments to determine the effects of voloxidation and flux spectrum (fast or thermal) on the release of fission products and other behavioral characteristics during the voloxidation and dissolution of mechanically blended 25% PuO_2 --75% UO_2 pellets. The pellets in the experiments were prepared from UO_2 of natural enrichment; later tests may include 45% and 93% enriched uranium to provide a comparison of the effect of ^{235}U enrichment and/or fission product concentration. Fuel scraps from the postirradiation examination of WADCO specimens PNL X-1 and PNL 59-5 were used (Table 5.4). The fuel rod segments were cut into 1/8-in.-long pieces in a single-pin hydraulic shear to dislodge the fuel from the cladding and permit studies that were free of possible cladding effects. The crushed fuel was sieved to determine the size ranges before and after oxidation (Table 5.4); each size was sampled for metallography and then recombined into four replicate test batches. The higher-burnup, highly restructured rod (PNL 59-5) contained more fine fragments than rod PNL X-1, which had little or no restructuring. This had been noted previously with irradiated sol-gel fuel.²⁰

In a typical experiment with a sample of PNL X-1 (irradiated in EBR-II to about 4170 MWd/metric ton), about 22% of the crushed (+60-mesh) fuel powdered during oxidation at 650°C:

Table 5.4. Characteristics of WADCO Mechanically Blended
25% PuO₂--75% UO₂ Fuels Used in Voloxidation Tests

Irradiated specimen No.	PNL X-1	PNL 59-5
Segment of specimen	BT-93	6, 12
Irradiated in reactor	EBR-II	GETR
Flux spectrum	Fast	Thermal
Peak burnup of specimen, MWd/metric ton	4170	18,000
Average burnup of segment, MWd/metric ton	3680	~17,300
Peak linear heat rating, kW/ft	5.3	13.5
Peak centerline temperature, °C	1650	~2200
Pellet fabrication batch	ME-20	ME-22
O/M ratio as fabricated	1.98	1.99-2.0
Sintered density, % theoretical	91.3	95.6
<u>As crushed:</u> +60 mesh, %	58.5	48.4
+100 mesh, %	12.4	10.7
-100 mesh, %	29.1	41.0
<u>After oxidation:</u> +60 mesh, %	48.6	50.9
+100 mesh, %	10.5	8.0
-100 mesh, %	41.0	41.1

<u>Mesh Size</u>	<u>Sample Before Voloxidation (%)</u>	<u>Sample After Voloxidation (%)</u>
+60	63.1	48.6
+100	12.6	10.5
-100	24.3	41.0

The weight of the $(\text{U,Pu})\text{O}_2$ sample increased by 90 mg, which is equivalent to 2.9% of the original weight. The theoretical weight gain is about 3.1% for the conversion of the UO_2 to U_3O_8 from an original O/M ratio of 1.98.

Essentially no powdering of the fuel occurred during the oxidation of the $(\text{U,Pu})\text{O}_2$ from PNL 59-5. (Lerch at WADCO reported that unirradiated pellets from the same batches did not powder but did gain an average of about 71% of the theoretical gain in weight for UO_2 to U_3O_8 when oxidized under the same conditions.) X-ray diffraction analysis of the oxidized, irradiated powder by Haire *et al.* (Sect. 4) showed that most of the UO_2 in the PNL X-1 sample (FR-87) had been converted to U_3O_8 , while the UO_2 in the intact PNL 59-5 lumps (FR-88) had only reached the U_4O_9 phase. Tennerly (Sect. 3) and Haire *et al.* (Sect. 4) have shown that the U_3O_8 - PuO_2 tie-line in the U-Pu-O phase diagram must be approached before the fuel will disintegrate.^{24,26}

The rod with the low heat rating, PNL X-1, released 26% of the contained ^{85}Kr during voloxidation. The more highly restructured rod, PNL 59-5, released 63% of the contained ^{85}Kr under the same conditions. These results indicate that the irradiation conditions probably have a significant effect on the efficiency of release of noble gases during subsequent oxidation of the fuel. However, the degree of fuel powdering appears to be influenced by the fabrication as well as the irradiation conditions.

Operation of an in-line multichannel gamma analyzer and an off-gas flowmeter permitted closer observation of the behavior of the fuels during oxidation (Fig. 5.3). The oxidation (and release of ^{85}Kr) took place in less than 30 min after the flow of

Fig. 5.3. Release of ^{85}Kr During Oxidation of PNL X-1 (U,Pu) O_2 in Air at 650°C (Run FR-92).

air was started (bottom curve, Fig. 5.3). Note the decreased flow of off-gas due to the consumption of oxygen during oxidation. Essentially all of the ^{85}Kr was swept through the multichannel analyzer within 1 hr (top curve). The long residence times in the oxidizer used in other experiments (4 to 6 hr) were thus apparently not necessary, except to carry the ^{85}Kr to the collection-analysis system. About 26% of the total ^{85}Kr in the PNL X-1 fuel was released in this test, about 11% during the inert (helium) heatup and about 15% during the actual oxidation. The 26% release agrees with other data obtained for low-heat-rated fuel.

5.3.6 Tritium Release

An experiment was made to determine the temperature at which tritium was released during voloxidation. Segments of stainless-steel-clad, coprecipitated 20% PuO_2 --80% UO_2 that had been irradiated to a burnup of 1800 MWd/metric ton were heated for a total of about 48 hr in a stream of moist air (25 cc/min) while the temperature was increased stepwise. The off-gases were passed through hot copper oxide and a number of Type 5A molecular sieve traps prior to measuring the gas volume and sampling for ^{85}Kr . (The fuel was cooled to cell ambient temperature without purge each night.) The molecular sieve traps, which were changed for the various temperature intervals, were desorbed at about 500°C and a pressure of 10 μ . The desorbed water was collected in a cold trap at liquid nitrogen temperature, diluted, and counted for tritium. Although tritium release began at 100 to 150°C, the peak concentrations in the voloxidation off-gases occurred at about 450°C and higher. These temperatures also correspond to the temperatures at which the oxidation rate (Fig. 5.3) and the ^{85}Kr release were at a maximum. In this experiment, we recovered about 0.17 μCi of $^3\text{H}_2$ per gram of $(\text{U,Pu})\text{O}_2$, or about 4.5% of the calculated yield for this fuel. This quantity agreed with other measurements on the same fuel and confirmed that most of the tritium had escaped from the fuel rod during irradiation.

As in other tests with LMFBR fuel specimens, effective separation of tritium from the PNL X-1 and PNL 59-5 fuel was accomplished by a voloxidation treatment (Table 5.5). Only a small fraction of the calculated amount of tritium was found in the fuel,

Table 5.5. Removal of Tritium from Mechanically Blended
(U,Pu)O₂ by Oxidation in Air at 650°C

	Tritium in Fuel (%) ^a	
	PNL X-1	PNL 59-5
Unoxidized	3.33	1.21
After voloxidation	0.03	0.02

^aBased on the calculated amount formed during irradiation.

the balance apparently having been lost during irradiation. The voloxidation treatment removed about 99% of the residual tritium in the fuel.

5.3.7 Effect of Vacuum or Inert Atmospheres

We also conducted experiments (PNL 59-5 and 59-7) with segments of 25% PuO₂--75% UO₂ that had been irradiated in the GETR by WADCO to burnups from about 17,000 to 69,000 MWd/metric ton. We measured the releases of krypton and tritium at 550°C under vacuum or in a helium or air atmosphere.

The release of ⁸⁵Kr from rod PNL 59-7 was determined at each stage of several treatments (Table 5.6), that is, during heating under vacuum or in helium, during oxidation in air, and finally when the (U,Pu)O₂ was dissolved in boiling nitric acid. In general (discounting the anomalous results of the second run), the data from both segments of PNL 59-7 show that 45.2 ± 4.4% of the ⁸⁵Kr was released when oxygen (air) was present and 14.5 ± 4.8% was released in the absence of air.

Table 5.7 shows the quantities of tritium remaining (based on the theoretical yield of tritium) after treatment. The data show that air or oxygen must be present for the tritium to be released effectively. The tritium content of the untreated fuel increased with burnup; however, the peak linear heat ratings of the fuel rods could

Table 5.6. Volatilization of Krypton, Using Various Head-end Treatments

Fuel No. ^a	Temperature (°C)	Head-end Treatment			⁸⁵ Kr Volatilized (% total in fuel)
		Vacuum	Helium	Oxidation	
59-7C	550			X	44.8
59-7C	550	X		X	22.4
59-7C	550		X	X	45.5
59-7C	550		X		12.5
59-7H	550	X			16.4
59-7H	550	X			14.7

^aFuel segment 59-7C (45,700 MWd/metric ton) contained 1.05×10^{10} disintegrations of ⁸⁵Kr per gram of (U,Pu)O₂. Segment 59-7H (66,300 MWd/metric ton) contained 5.97×10^9 disintegrations of ⁸⁵Kr per gram of (U,Pu)O₂. Segment 59-7H was more highly restructured than segment 59-7C.

Table 5.7. Tritium in Fuel Before and After Heat Treatments

Fuel Rod	Burnup (MWd/metric ton)	Peak Linear Heat Rating (kW/ft)	% Theoretical Yield of ³ H in Fuel		
			No Treatment	After Heat Treatment	
				O ₂ Absent	O ₂ Present
59-5	17,000	11.5	1.21		0.015
59-7C	45,700	10.0	3.57	2.06 ^{a,b}	0.074 ^a
59-7H	66,300	13.5	6.10	1.87 ^{a,c}	

^aAverage of two or three determinations.

^bHelium sweep gas.

^cVacuum.

not be correlated with the quantity of tritium present. Thus, the tritium content may be a function of the end-of-life heat rating or some other factor, rather than the peak value.

Table 5.8 summarizes typical experiments on the release of tritium by voloxidation.

Table 5.8. Release of Tritium from Irradiated (U,Pu)O₂ by Voloxidation

Run No.	PuO ₂ (wt %)	Burnup (MWd/metric ton)	Voloxidation Temperature (°C)	Residual Tritium Volatilized (%)
5	20	20,000	450	97.4
8	20	49,000	750	>99 ^a
18	20	2,000	450	>93.7 ^a
19	20	2,000	650	99.8
21	20	2,000	750	>99
66	20	2,000	650	95
87	25	3,630	650	95.2
88	25	17,000	650	>99.9
91	25	17,000	650	>99.9
104	25	17,000	750	99.6
105	25	17,000	750	98.5
106	25	45,700	525	96.1
108	25	45,700	550	98.1
109	25	45,700	550	99.6

^aDetermination limited by radiochemical counting statistics.

5.4 Voloxidation of LWR Fuels

Only trace amounts of tritium are released when irradiated UO_2 is dissolved in nitric acid. However, essentially all of the tritium is volatilized when UO_2 is oxidized in air (Table 5.9). Voloxidation of LWR UO_2 appears to be a satisfactory method for removing tritium but does not necessarily volatilize the ^{85}Kr .

In experiments with Zircaloy-2-clad UO_2 segments from the blanket of the first core of the Shippingport PWR, more than 99% of the tritium, but only about 13% of the ^{85}Kr , was volatilized. This fuel had been irradiated at a time-averaged linear heat rating of less than 5 kW/ft to about 32,000 MWd/metric ton and had been fully characterized as to fission product content. Replicate runs were made in which a 0.5-in.-long fuel segment was heated at 450°C in a flow of moist oxygen at about 1 atm for 4 hr; the predicted time for complete oxidation was less than 2 hr. Analyses showed that less than 0.1% of the initial tritium was left in the fuel.

Apparently the relatively low removal of ^{85}Kr in these experiments with UO_2 was due to two main factors: (1) lack of restructuring during irradiation, and (2) possible sintering during oxidation. Lynam at Bettis reported in WAPD-TM-433 that no microstructural changes had occurred in the UO_2 from a blanket rod that had experienced the peak heat rating (10.3 kW/ft) for the first core of the PWR. Thus, we would expect the ^{85}Kr to be dispersed throughout the fuel matrix as individual atoms instead of being collected as larger bubbles at the grain boundaries. Hence, its release would be difficult. A puncture release of ^{85}Kr of less than 0.5% from the PWR blanket rods tended to confirm this. Apparently, oxidation of the UO_2 did not release all of the dispersed ^{85}Kr from the matrix, even though it converted the pellets to a fine powder (92% < 200 mesh). Restructured fuel, however, would be more amenable to releasing the fission gases since a large fraction of the krypton collects in the form of bubbles at the grain boundaries.

The low release may also have been the result of sintering during the oxidation step; sintering limits the conversion of UO_2 to U_3O_8 . Sintering can occur even at 450°C because the highly exothermic reaction in oxygen can produce excessive local

Table 5.9. Release of Tritium from Irradiated LWR UO_2

Run No.	Burnup (MWd/metric ton)	Voloxidation Temperature ($^{\circ}\text{C}$)	Tritium Volatilized ^a (%)
UO_2^{-6}	35,000	450	99.4
UO_2^{-7}	35,000	450	99.7
UO_2^{-8}	35,000	450	>99.9
FR-20	63,000	650	>99.9
LWR-1	32,000	450	98.7
LWR-2	32,000	450	99.4
LWR-3A	32,000	450	99.7
LWR-3B ^b	32,000	450	<1

^a Dissolutions of UO_2 in nitric acid volatilized ≤ 0.1 to 0.4% of the tritium in the fuel; the remaining 99.6+% was found in the $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solutions.

^b UO_2 pellet adjacent to end plug of fuel rod not reached by air because of bridging of U_3O_8 within cladding tube in static bed. Remaining U_3O_8 (LWR-3A) fell out of cladding upon oxidation of UO_2 .

temperatures. In these runs, the reaction proceeded so rapidly that the oxygen supply rate limited the rate of reaction, and the reactor pressure dropped markedly during conversion. It may be necessary to limit surface temperatures by using diluted oxygen.

The inefficient release of krypton (10 to 15%) achieved in these experiments is consistent with data on LWR fuel pellets from other sources. Although data reported in Atomics International documents on the AIROX process gave the impression that essentially all of the noble gases were released by alternate air oxidation and hydrogen reduction of UO_2 , we were not able to confirm these results. Discussions with Atomics

International personnel indicated that their experiments were on a relative, rather than an absolute, basis and did not include a determination of ^{85}Kr remaining in the U_3O_8 after oxidation.³⁵ It is possible, therefore, that all of the ^{85}Kr was not released in their cyclic oxidation-reduction experiments.

5.5 Solubility of Plutonium

The effect of voloxidation on the solubility of $(\text{U,Pu})\text{O}_2$ in boiling nitric acid was also studied. Statistical analysis of data on the amount of undissolved plutonium remaining after coprecipitated 20% PuO_2 --80% UO_2 , irradiated to about 2000 MWd/ton, had been refluxed for 10 to 12 hr in boiling 8 M HNO_3 indicated that voloxidation had essentially no effect on the extent of plutonium dissolution. The results were as follows:

Oxidized: $0.19 \pm 0.08\%$ plutonium undissolved

Not oxidized: $0.21 \pm 0.12\%$ plutonium undissolved

Data from the 2³ experiment on the effects of time and temperature of voloxidation of coprecipitated 20% PuO_2 --80% UO_2 and fuel particle size (see above) indicated that, although the time of oxidation (>4 hr) had no effect, slightly more insoluble plutonium remained after the 550°C oxidations than after the 350°C oxidations. The larger particles (>60 mesh) dissolved more slowly than the small particles (<100 mesh), as expected, thereby reflecting a simple rate effect.

Studies of unirradiated FTR-type mechanically blended 25% PuO_2 --75% UO_2 "reference" pellets showed there was no significant difference in the dissolution of plutonium from untreated pellets as compared with pellets that were oxidized (650°C) or resintered in argon--4% hydrogen at 1450°C (Fig. 5.4). Dissolution data on irradiated mechanically blended fuel from other fabrication batches, however, suggested that voloxidation may decrease the rate of dissolution, but not the recovery, of the plutonium. Lerch, at HEDL, concluded voloxidation of mechanically blended oxide fuel had no adverse effect on the dissolubility of the fuel.³⁶ These same fuels were used in our tests.

Fig. 5.4. Dissolubility of FTR "Reference" Pellets in Boiling 8 M HNO_3 .

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6. ENGINEERING DATA

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6.1 Summary

Basic data are being collected on the oxidation of sheared UO_2 to U_3O_8 in engineering equipment; batch and continuous oxidizers are being used to determine optimum conditions. Results indicate that the rate of oxidation is enhanced by tumbling and by increasing the oxygen content of the purge gas. Close temperature control must be observed to control sintering of the U_3O_8 and to prevent adhesion to the walls of the oxidizer.

Voloxidation studies with clad and unclad urania pellets have been conducted in a Bartlett-Snow rotary calciner containing six internal lifting flights and in a steel rotary minivoloxidizer, similarly equipped. The Bartlett-Snow unit is an electrically heated, 6.5-in.-diam by 7-ft-long cylindrical retort made of stainless steel, and the minivoloxidizer is a 3-in.-diam by 2-in.-long stainless steel cylinder which operates inside an electric muffle furnace.

6.2 Bartlett-Snow Rotary Calciner

The optimum operating conditions for the rotary kiln (Bartlett-Snow rotary calciner) are being determined for sheared lengths of fuel. Variables that are receiving study include the temperature in the reaction zone, the sheared fuel length, the oxygen--inert gas content of the sweep gas, the gas flow rate, and the residence time within the reaction zone.

Depending on the materials of construction, the temperature of the rotary kiln will probably be limited to 600 to 700°C. The oxidation of UO_2 pellets has been studied in the temperature range 350 to 575°C (Sects. 3 and 4). The total reaction rate is low up to 350°C; however, at temperatures above 500°C, sintering occurs even at relatively high gas velocities. Consequently, the operating temperature may be limited to a narrow range between 450 and 500°C.

Seven runs were made in the Bartlett-Snow rotary calciner to determine the effects of residence time on the pulverization of urania. In each run, a 270-g batch of prototype stainless-steel-clad urania pellets was fed into the retort tube, which had a fixed slope of 1/16 in./ft. Each batch of clad urania consisted of about 30 pieces sheared by a multirod shear into 1-in. lengths (0.270-in.-OD x 0.55-in.-long pellets clad in 0.275-in.-ID, 15-mil-thick stainless steel).

In the first six runs, the temperature in the calciner was 475°C and the air flow rate was about 0.5 scfm. The system was maintained at a negative pressure of approximately 2 in. H₂O. The rotational speed of the retort tube for a particular run was set at 2, 4, or 12 rpm, corresponding to average residence times of about 150, 75, and 25 min. (For each revolution, the urania pellets or sheared pieces of fuel were picked up and dropped three times by the six internal lifting flights.) In these runs, 87 to 97% of the original urania pellet weight was pulverized sufficiently to be dislodged from the sheared steel cladding. The pulverization was believed to be the result of urania oxidation; however, the amount of urania dislodgement could not be correlated with the observed residence times. The U₃O₈ produced during these runs appeared to adhere to the surface of the 3-ft-long heated zone of the retort tube.

A seventh run was made with the rotary calciner at room temperature and a rotational speed of 12 rpm. After the sheared, 1-in. lengths of prototype fuel had passed through the baffled retort tube, 95% of the urania was found to be dislodged from the cladding. These results indicate that the tumbling action of the sheared fuel, rather than the urania oxidation-pulverization reaction, was primarily responsible for dislodgement of the urania from the cladding. If the pellets are mostly shattered by the shearing operation, the tumbling action easily dislodges the urania and a short oxidation time is adequate. However, if the urania pellets contained in the cladding length are intact following the shearing operation, the required oxidation time with tumbling may be much longer.

6.3 Minivoloxidizer

In order to obtain more data while conserving limited quantities of sheared, stainless-steel-clad urania, several scouting runs were made in the minivoloxidizer

at a temperature of 480°C. The rotational speed of the unit was varied from 0 to 12 rpm while the following types of fuel were processed: (1) bare urania pellets, (2) single urania pellets clad in stainless steel and cut from the parent fuel rod by a tubing cutter, and (3) stainless-steel-clad urania pellets sheared into 1-in. lengths by a multirod shear. A summary of the results of these exploratory runs follows:

- (1) The oxidation of bare urania pellets (0.27-in.-diam by 0.55-in.-long) was almost independent of the tumbling rate investigated (0-12 rpm). A single unclad urania pellet oxidized to U_3O_8 in about 1 hr under static (i.e., no tumbling) conditions.
- (2) The oxidation rate of single urania pellets clad in stainless steel and severed from the parent prototype fuel rod by a tubing cutter was enhanced by tumbling since the oxidation of the urania occurred only at the open ends of the cut pieces. Apparently, oxygen could not be supplied between the pellet and cladding at a rate fast enough to permit the pellet to oxidize to a smaller diameter and be dislodged from the cladding. A single stainless-steel-clad urania pellet oxidized to U_3O_8 in about 4 hr at static conditions, whereas the time required for oxidation decreased to approximately 2.5 hr at a rotational speed of 12 rpm (36 drops per minute).
- (3) The oxidation rate for stainless-steel-clad urania pellets sheared into 1-in. lengths by the ORNL multirod shear was also enhanced by tumbling. The lifting and dropping action within the minivoloxidizer dislodged the fuel that had been fractured during shearing from the cladding, exposing a greater surface area to the oxidation process. However, depending on the extent of fracturing during shearing, the time required for urania oxidation appeared to vary from several minutes to several hours.

Twelve additional runs were made in the 3-in.-diam baffled minivoloxidizer to determine the effects of rotational speed and oxygen concentration on the oxidation rate at 480°C of stainless-steel-clad urania pellets. Four individually clad unirradiated

urania pellets (0.27 in. in diameter by 0.55 in. long) were used for each run. The clad pellets were weighed at 30-min intervals to determine the amount of oxidation-pulverization that had occurred. (After each weighing, the interior of the minivoloxidizer required about 30 min to reheat from room temperature to 480°C. During the heatup time period, nitrogen was purged through the minivoloxidizer to prevent oxidation of the urania.)

The results of runs 11, 13, and 14 are shown in Fig. 6.1, in which the percent conversion of UO_2 to U_3O_8 is plotted against the oxidation time. Runs 11 and 13 were made with bare urania pellets, while run 14 was made with steel-clad urania pellets. The atmosphere in each run was air; a flow rate of 0.8 scfh was used in run 11, and a flow rate of 1.5 scfh was used in runs 13 and 14. The rotational speed (12 rpm) and the temperature (480°C) were kept constant. Each data point represents the average of four urania pellets, and the vertical lines for run 14 indicate the variation of individual pellets. The two dashed lines in Fig. 6.1 were determined by assuming a constant urania pulverization flux of $3 \text{ g/cm}^2\text{-hr}$. When the U_3O_8 can be removed continuously from the pellet surface, the constant flux model appears to be adequate for predicting the oxidation of a urania pellet.

The oxidation data of runs 14-19 are shown in Fig. 6.2, in which the rotational speed of the minivoloxidizer was the primary variable. Each data point is the average of either three or four stainless-steel-clad urania pellets (runs 15 and 19 were limited to three clad pellets). In all of the runs in Fig. 6.2, the air flow rate was 1.5 scfh; and, with the exception of the first 1.5 hr in run 19, the oxidation temperature was 480°C. During the first 2 hr, the oxidation rates for runs 14, 15, 16, and 17 increased logically with increasing rotational speed (0 to 12 rpm); however, at times greater than 2 hr, the oxidation-pulverization data of runs 15, 16, and 17 (0 to 6 rpm) do not seem consistent. This apparent inconsistency could be caused by experimental errors or statistical variations within the urania pellets. By increasing the rotational speed to 36 rpm, the time required for complete oxidation-pulverization appeared to be reduced significantly (1 to 1.5 hr for run 18); however, the data of run 19 (same rotational speed) did not confirm this result. In run 18, several urania chunks dislodged

Fig. 6.1. Oxidation of Bare and Stainless-Steel-Clad Urania Pellets in a 3-in.-diam Minivoloxidizer.

Fig. 6.2. Oxidation of Stainless-Steel-Clad Urania Pellets in a 3-in.-diam Minivoloxidizer with the Rotational Speed as a Parameter.

from the cladding before the oxidation reaction was complete. The partial pellet dislodgement was initially believed to be due to pellet cracks induced by the increased rotational speed. Consequently, the first 15 hr of run 19 (36 rpm) was made at room temperature to determine whether the higher tumbling rate alone could cause urania dislodgement. After 1.5 hr of tumbling at 36 rpm and a temperature of 25°C, less than 3% of the urania had been removed from the cladding. Subsequent oxidation at 480°C required between 2 and 3 hr to complete the oxidation-pulverization reaction for run 19. At this time, the results of run 18 cannot be satisfactorily explained.

The oxidation data of runs 14, 20, 21, 22, and 23 are shown in Fig. 6.3, in which the oxygen concentration in the gas stream (oxygen and nitrogen) is the primary variable. Each data point in Fig. 6.3 is the average of four stainless-steel-clad urania pellets. In all of these runs, the gas flow rate was 1.5 scfh and the oxidation temperature was 480°C. The oxidation-pulverization reaction rate definitely increased as the oxygen concentration was increased from 20 to 100%; however, a model to describe the oxidation results has not been established. After 1 hr with 100% oxygen (run 23), the oxidation reaction was essentially complete for all four clad pellets; however, about 20% of the original urania pellet weight remained in the steel hulls. After the minivoloxidizer had been operated for an additional 1.5 hr (run 23), about 10% of the initial urania (apparently sintered U_3O_8) was still tightly bound to the inner surfaces of the steel hulls. At the end of run 23, a definite bulge was apparent in the middle section of each steel hull. The average increase in diameter was approximately 7% (0.307 to 0.329 in.). If it is desired to separate the urania and steel hulls prior to dissolution, then it can be concluded that the oxidation reaction rate must be regulated to permit adequate pulverization of the U_3O_8 phase.

Oxidation studies will be continued in the 3-in.-diam minivoloxidizer to resolve the effect of increased rotational speeds and to explore the effects of different oxidation temperatures. Two larger minivoloxidizers (6.5 and 13 in. in diameter) have been fabricated and will be made operational in the near future.

Fig. 6.3. Oxidation of Stainless-Steel-Clad Urania Pellets in a 3-in.-diam Minivoloxidizer with the Partial Pressure of Oxygen as a Parameter.

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