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ORNL-4436
Supplement 1

Aqueous Processing of LMFBF Fuels
Technical Assessment and
Experimental Program Definition
Sections 4.4 and 5.4

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ORNL-4436
Supplement 1
UC-80 — Reactor Technology

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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

AQUEOUS PROCESSING OF LMFBR FUELS — TECHNICAL ASSESSMENT
AND EXPERIMENTAL PROGRAM DEFINITION.

SECTIONS 4.4 AND 5.4

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JUNE 1972

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AQUEOUS PROCESSING OF LMFBR FUELS – TECHNICAL ASSESSMENT AND EXPERIMENTAL PROGRAM DEFINITION

NOTE: This report is a revision of Sections 4.4 and 5.4 of ORNL-4436. It incorporates summaries of work completed since the issuance of the original document in June 1970 up to about October 1971.

4.4 Volatile Fission Product Removal – Task 4

4.4.1 Introduction

This section describes investigations into a new head-end processing step that has the potential of removing volatile fission products as gases prior to aqueous processing (see Task 4 in Fig. 4.1, ORNL-4436). The objective of this step, which has been termed "voloxidation", is to volatilize and remove tritium, iodine, xenon, and krypton from the sheared fuel and blanket materials for trapping and ultimate storage as wastes (see Sect. 4.10, ORNL-4436). Conceivably, this objective may be realized by heating the sheared fuel matrix to 750°C or less in air or oxygen to release the volatile fission products via thermal evolution or chemical reaction. The gases are then carried out of the voloxidizer unit for subsequent trapping and retention within the plant.

At this time, the major emphasis is centered on the removal of tritium from UO_2 and $\text{UO}_2\text{-PuO}_2$ fuels, since this fission product would otherwise be irretrievably diluted into the aqueous streams during dissolution of the fuel. In the event that dilution should occur and discharge to natural waters was prohibited because it would violate federal regulations, water recycle would become mandatory. With recycle, excess water must be discharged as vapor or shipped to an approved disposal site. The voloxidation process should also effectively deactivate tramp sodium¹ that may have leaked into fuel elements, thus eliminating a potential explosion hazard when nitric acid is contacted in the subsequent dissolution step. Efficient removal of radioiodine (^{129}I and ^{131}I) is not essential since effective techniques are being developed to

remove iodine from dissolver solutions²⁻⁴ and off-gases prior to solvent extraction. However, efficient removal (>99%) of iodine in a voloxidation step would be an advantage in the overall control of iodine. The same applies to the noble gases, xenon and krypton, which are evolved during dissolution.

This task, the removal of volatile fission products, is considered new technology. The preliminary tests at ORNL have been made over a wide range of variables: with temperatures up to 850°C; with helium, air, or oxygen atmosphere; with short- and long-cooled fuel; and with fuel burnups of 2000 to 100,000 MWd/ton. Oxide fuels containing 15 to 25% plutonium were used in most of the tests. However, the fuel types (mechanically mixed, coprecipitated, sol-gel) and physical form of the fuel (microspheres, shards, and pellets) have varied. Tests of such a wide range of fuel types were made from necessity rather than choice because of the limited amount of irradiated fuel available; however, the results obtained serve to point up process limitations and successes. For example, in the tests studying tritium behavior, little influence of input parameters was seen; for ⁸⁵Kr, however, wide variations in removal (10 to 98%) were observed, indicating the need to learn more about the release of noble gases. Two short-cooled runs have been made to study the release of iodine; other specimens are now being irradiated for additional short-cooled tests.

Problem areas associated with the development of voloxidation as a useful head-end process indicate that more information is needed in the following areas:

- (1) Basic chemistry studies with regard to the oxidation of (U, Pu)O₂.
- (2) The mechanism and kinetics of release of the volatile fission products from sheared fuel and blanket materials.
- (3) Effects of fuel fabrication variations.
- (4) Effects of plutonium concentration of the fuel.
- (5) Effects of the composition of the gas stream (i.e., inert gas, air, oxygen, other reactive gases, etc.).
- (6) Effects of temperature of the reaction.

- (7) Effects of irradiation conditions, such as burnup, thermal gradient, fuel restructuring, void formation, fission product and heavy metal migration, etc.
- (8) Effects of the presence of sodium, stainless steel cladding, and other materials of construction.
- (9) Effects of voloxidation on subsequent processing steps such as dissolution of the fuel.
- (10) Voloxidation of other LMFBF fuel forms, such as carbides and nitrides.
- (11) Oxidation of unirradiated archive samples for comparison with oxidation data for irradiated fuels.
- (12) Engineering evaluation of the voloxidation step and development of suitable voloxidation equipment.

4.4.2 Background Information

The head-end processing step, voloxidation, for the volatilization of gaseous fission products — tritium, iodine, xenon, and krypton — from irradiated LMFBF oxide fuels was a logical development stemming from hot-cell studies to determine the quantity and identification of fission products that might be released during interim storage of baskets of sheared, short-cooled LMFBF fuel in air. Preliminary tests at ORNL indicated that ⁸⁵Kr was released when irradiated (U, Pu)O₂ was heated in a stream of air.²⁻⁵ Measurements made on fuel solutions indicated that the tritium had also been volatilized during oxidation.³⁻⁵ In some cases, 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 literature⁶ on the subjects of disintegration of (U, Pu)O₂ and fission product volatility during high-temperature oxidation was made in 1969, and

the references from the survey are tabulated here.⁷⁻²⁹ In general, the literature, covering work by Eurochemic, Atomics International, NUMEC, ANL, and others, indicated that effective fuel disintegration and noble gas releases occurred when pure UO_2 was oxidized to U_3O_8 . Variable results were obtained with $(\text{U}, \text{Pu})\text{O}_2$ 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.

4.4.3 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 the 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) method and procedures of fuel fabrication, and (7) the fuel shape.

The Chemical Form of the Fuel. — The 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.

The Plutonium Concentration. — Proposed LMFBR oxide fuels have varying concentrations of plutonium in normal uranium. The FTR reference fuel is 25% PuO_2 -- 75% UO_2 ³⁰ while the PuO_2 contents of oxide fuels for other reactors range from 16 to 21%.³¹ The plutonium concentration will influence the irradiation conditions. Experiments described here have shown that the plutonium concentration also influences the effectiveness of the voloxidation treatment, the rate of dissolution, and the completeness of dissolution in nitric acid as well. For example, present specifications for FTR fuel that nominally has an average composition of 25% PuO_2 permit about 60% of the fuel to be in the form of $(\text{Pu}_{0.4}\text{U}_{0.6})\text{O}_2$. Mixtures containing more than approximately 40% PuO_2 require fluoride for dissolution.³²⁻³⁵

The LMFBR blanket is depleted UO_2 . Consequently, studies of the head-end behavior of UO_2 during voloxidation are needed.

The 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. The rate and completeness of dissolution of the fuel in nitric acid have been found to be a sensitive test for oxide fuel homogeneity and 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 when the PuO_2 content is less than 40%.³² Irradiation has generally improved the release of volatile fission products during voloxidation and 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.

The 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 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 fission gas release to the plenum, volatile fission product migration along the thermal gradient, separation of uranium and plutonium during irradiation, alloying with noble metal fission products, and volatilization of fission products in heated, inert-gas, head-end reprocessing systems (e.g., from baskets of sheared, short-cooled LMFBR fuel held in an inert-atmosphere cell).

Method of Fuel Preparation. — The FTR reference fuel consists 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 these dissolubility studies showed that the sintering temperature, the source of PuO_2 , and the percent of PuO_2 in the mixture used in the preparation of mechanically blended fuels most affect 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 fuel physical form (pellets, Vipac shards, Sphere Pac microspheres, U-Fine microspheres, or other) will affect the head-end reprocessing of LMFBR fuels 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.

4.4.4 Irradiation Parameters Affecting Voloxidation

The irradiation parameters that are most likely to influence the voloxidation behavior are: (1) burnup, (2) type of flux, (3) ^{235}U enrichment, (4) fuel restructuring, and (5) radial temperature gradient. Almost every document prepared by DRDT contractors describes studies on the irradiation effects of fuel specimens. However, since the reference reactor does not exist at this time, 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, it may be a measure

of the restructuring of the fuel, it affects 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 as a peak value. In head-end reprocessing studies, however, a "local" burnup value is required. Samples of fuels irradiated in thermal fluxes have been found to have 2 to 10 times higher burnup near the cladding than near the center of the fuel rod. Samples irradiated in fast fluxes have flatter radial burnup profiles.

Type of Flux and Uranium Enrichment. — Because of compromises made to simulate reference conditions in existing reactors,⁴⁹ the final state of the irradiated fuel samples 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. In one set of experiments, fabrication differences obscured variations due to a fast or thermal flux when normal enrichment UO_2 --25% PuO_2 was irradiated.

Temperature of Irradiation. — There are at least three components 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 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 flux dependent, and will also be dependent on 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 center temperature and gradient, ≥ 1700 – 1800°C), the radius of the equiaxed grain growth region (~ 1600 – 1800°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, is 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 ~ 2 . Mobile fission products (e.g., 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 (~ 1 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 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.

4.4.5 Recent ORNL Results with Unirradiated Fuels

Laboratory Data. — 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 on the oxidation of $\text{UO}_2\text{-PuO}_2$ have been recently reported by Tennery and by Fitzgerald in the same progress report series.⁷²⁻⁷⁹ Other oxidation studies (unreported) have been performed by Farrar and Haire⁸⁰ and by Baybarz.⁸¹ Tennery's reports included pertinent references to U-Pu-O phase studies.⁸²⁻⁸⁹

In Tennery's studies, unirradiated, sintered fuel specimens containing 20 and 25 mole % PuO_2 were oxidized isothermally and by programmed heating in a thermal-gravimetric balance, and the final O/M ratio was deduced from the observed weight gain. The phases produced by the oxidation were identified by means of X-ray diffraction.

Coprecipitated solid solutions of $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_2$ were oxidized at reasonable rates via a two-stage process to a final O/M ratio of ~ 2.55 within a narrow temperature range of $500\text{--}600^\circ\text{C}$. This is the O/M value expected for this composition, assuming that an O/M of ~ 2.55 corresponds to a composition on the tie-line between U_3O_8 and PuO_2 in the published phase diagram for the U-Pu-O system.⁸² The peak rate was at about 525°C ;⁷⁸ little or no reaction took place at less than 350°C .⁷² Rapid oxidation to an $\text{O/M} \approx 2.35$ occurred over a wide range of temperatures, and the product of this first stage of the oxidation was tetragonal M_3O_7 or $\text{U}_{2.4}\text{Pu}_{0.6}\text{O}_7$. (The M_3O_7 phase is an intermediary in the oxidation of the fuel from the UO_2 phase to a mixture of $\text{M}_3\text{O}_8 + \text{MO}_2$.)⁷⁸ The kinetics of the first-stage process were analyzed using a simple nucleation model; the activation energy for the process in this fuel was ~ 10 kcal/mole. The second stage of the oxidation is the one that results in disintegration of the fuel and occurs when the tetragonal M_3O_7 phase converts to M_3O_8 (orthorhombic phase) + MO_2 (cubic phase). 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 but were also apparently dependent on the degree of original homogeneity and the method by which the fuel was prepared, or possibly some other factor. The observations from this work indicate that the various types of fuels having a Pu/Pu+U ratio of 0.2 can be ranked according

to increasing difficulty with which the second oxidation stage is achieved, as follows: coprecipitated < sol-gel < 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. Programmed-rate heating experiments with 0.1-g samples provided similar results. X-ray diffraction patterns of the oxidation products for both coprecipitated and mechanically blended 20% PuO_2 indicated that they consisted of two phases — M_3O_8 (the major one) and a cubic phase (the minor).

The solid solution $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{1.98}$ oxidized readily in air at 525 to 750°C to an $\text{O}/\text{M} \cong 2.35$, but it is difficult to achieve higher O/M ratios. This was true for both mechanically mixed and sol-gel fuel. The oxidized material consisted of a cubic phase corresponding to the M_4O_9 phase reported by Markin and Street,⁸² but apparently had the composition M_4O_{9+x} since the O/M was obviously higher than allowed by stoichiometric M_4O_9 . This M_4O_9 -type phase appears to have the formula $\text{M}_4\text{O}_{9.4'}$ at least at the phase boundary with the M_3O_{8-y} phase. Small traces of M_3O_{8-y} were detected in some of the oxidized samples, but conversion of M_4O_{9+x} to $\text{M}_3\text{O}_8 + \text{MO}_2$ was strongly inhibited in the materials examined in this investigation. This material did not disintegrate upon oxidation, and indicated a large effect due to plutonium concentrations at some point between 20 and 25% PuO_2 ; that is, samples with higher PuO_2 contents oxidized at slower rates.

The mechanically mixed, sintered pellet fuel examined by Tennery was prepared by NUMEC under their Task 7 project, and had been characterized at ORNL, using the nitric acid dissolubility technique, as having 1.6% of the PuO_2 not in solid solution or as >40% PuO_2 in UO_2 . Farrar and Haire⁸⁰ oxidized a whole pellet from the same batch of mechanically blended oxide by heating isothermally at 650°C in air. Although the sample oxidized to an $\text{O}/\text{M} \approx 2.36$, the X-ray pattern indicated the presence of a small amount of M_3O_8 phase in addition to a cubic phase, which was predominant. This cubic phase was not well crystallized; however, a parameter extrapolation indicated that $a = 5.409 \pm 0.001 \text{ \AA}$, rather than 5.428 as measured for the sample from Tennery's thermobalance oxidation. The pellet in this

experiment also failed to disintegrate upon oxidation. However, Baybarz⁸¹ succeeded in disintegrating other pellets from the same batch by proceeding to the U_3O_8 - PuO_2 tie-line in the phase diagram via oxidation under an oxygen overpressure of 500 psig in an autoclave. He found that cyclic oxidation-reduction treatments of the mechanically blended $(\text{U}, \text{Pu})\text{O}_2$ pellets did not decrease the crystallite size of the fuel below the original 0.01 μm . This fact is probably significant in explaining the difficulty in obtaining complete release of ^{85}Kr from unrestructured irradiated $(\text{U}, \text{Pu})\text{O}_2$.

FTR-type pellets (mechanically mixed 25% PuO_2 used as reference pellets in dissolubility and irradiation studies) were characterized by the nitric acid dissolubility test.⁷² About 85% of the PuO_2 dissolved and was 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 . The pellets were oxidized in air at 750°C. This treatment converted the fuel to powder, about 96% of which was finer than 200 mesh, and 99% finer than 100 mesh. Within experimental error, the plutonium concentration was found to be uniform in all size fractions; hence, there is probably no plutonium segregation due to the voloxidation treatment. This conclusion is in agreement with the conclusions inferred from dissolution tests with voloxidized fuel. Electron microprobe analysis of this batch of pellets showed discrete 20- μm PuO_2 areas in a UO_2 matrix, which may explain why the 25% PuO_2 --75% UO_2 pellet disintegrated and the 25% PuO_2 --75% UO_2 solid solution did not.^{76,78}

Engineering Data. — Voloxidation studies with clad and unclad urania pellets were conducted in a Bartlett-Snow rotary calciner containing six internal lifting flights¹ and in a steel rotary minivoloxidizer, similarly equipped. The stainless steel Bartlett-Snow unit is a 6.5-in.-diam by 7-ft-long cylindrical retort, and the minivoloxidizer is a 3-in.-diam by 2-in.-long stainless steel cylinder.

Seven runs were made in the Bartlett-Snow rotary calciner. 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. per foot. 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 on the sheared fuel, rather than the urania oxidation-pulverization reaction, was primarily responsible for dislodgement of the urania from the cladding.

Several oxidation 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 processing the following types of fuel: (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. OD by 0.55 in. long) is almost independent of the tumbling rate investigated (0-12 rpm). A

single unclad urania pellet is 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 is enhanced by tumbling. The oxidation of the urania occurs only at the open ends of the cut piece. Apparently, oxygen cannot 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 will oxidize to U_3O_8 in about 4 hr at static conditions, whereas the time required for oxidation decreases 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 is enhanced by tumbling. The lifting and dropping action within the minivoloxidizer dislodges the fuel 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 may vary from several minutes to several hours. If the pellets are mostly shattered by the shearing operation, the tumbling action easily dislodges the urania and a short oxidation time is adequate. If the urania pellets contained in the 1-in. cladding length are intact following the shearing operation, the required oxidation time with tumbling may be as long as 3 to 5 hr.

Effect of Shearing on Voloxidation Processing. — Results of recent shearing tests with the ORNL 250-ton bundle shear using an intact prototype Atomics International fuel assembly show that the flow duct or shroud is very difficult to tear apart and that the resultant product cannot (at this time) be handled in continuous processing equipment. Sheared product (~ 1 in. long) produced by

the bundle shear contained long twisted pieces of shroud, pieces of wire wrap distorted and deformed with sharp edges, and flattened pieces of fuel rod. This type of product could probably be handled only in a batch system.

In shearing fuel tubes which have been removed from the shroud in a multirod shear, the product is easily handled and is not twisted, flattened, or deformed as is the product from the bundle shear. There are two reasons for this: (1) the shroud has been removed and the subassembly has been dismantled prior to shearing, and (2) only a relatively small number of rods (up to 50) are sheared at one time. The product from the multirod shear would be suitable for continuous processing.

4.4.6 Recent ORNL Results with Irradiated Fuels

Experiments on the voloxidation of irradiated fuels have been reported in ORNL documents.^{1-6,58-79} Results of early tests with NUMEC mechanically blended and coprecipitated (U, Pu)O₂ irradiated to about 100,000 MWd/ton, indicated that more ⁸⁵Kr (98%) was released at 750°C than at 800 or 850°C.^{2,5,58,59} Results of tests with short-cooled (U, Pu)O₂ irradiated to about 15,000 MWd/ton, showed that more ¹³¹I (74%) was released at 650°C than at 450 or 750°C.⁶³ An early 2³ factorial experiment, using irradiated (3500-MWd/ton) sol-gel UO₂ showed that more ¹³¹I and ⁸⁵Kr were released at 750°C than at 450°C and that the oxygen content of the purge gas (25 vs 75%) and the gas flow rate had little effect.² These results indicate that a peak in the release of fission products occurs at temperatures in the range of 450 to 750°C. Another test with 2000-MWd/ton low-burnup (U, Pu)O₂ showed essentially no ⁸⁵Kr release at temperatures less than 300-350°C.⁶⁷ This might be expected since thermogravimetric analyses of samples of unirradiated (U, Pu)O₂ showed that no significant oxidation occurs at temperatures less than 350°C.⁷² All of these early results are consistent with the phase and oxidation rate studies on the U-Pu-O system by Tenner.⁷⁴⁻⁷⁸

A 2³ factorial experiment on the effects of fuel particle size, temperature, and time of voloxidation showed that +30-mesh lumps of (U_{0.8}Pu_{0.2})O₂ fuel, irradiated to

2000 MWd/ton, released ^{85}Kr more readily (70%) than -100-mesh particles (32%) at 550°C.⁶⁸⁻⁷⁰ The smaller particles contained a higher concentration of ^{137}Cs than the large particles, which suggested that they may have been unrestructured (U, Pu)O₂ from the cooler, outer portions of the fuel rods.^{70,71} The larger lumps, which contained less ^{137}Cs , may have been from the restructured regions. The effect of time (greater than 4 hr) in the experiment was negligible;⁶⁹ 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.⁷⁷ Tenner's rate data complement these hot-cell results.^{75,76,78}

In a factorial experiment on the effects of flux spectrum and voloxidation on irradiated (U, Pu)O₂,⁷³⁻⁷⁵ large behavioral differences were found between two batches of mechanically blended 25% PuO₂ fuel that reportedly were prepared by the same method; one batch (PNL Batch ME-20) disintegrated upon oxidation at 650°C, while the other (ME-22) did not.^{74,75} X-ray diffraction analysis of the irradiated powder⁸¹ showed that most of the UO₂ in the ME-20 sample had been converted to U₃O₈, while the UO₂ in the intact ME-22 lumps had only reached the U₄O₉ phase.⁷⁶ Tenner has shown that the U₃O₈-PuO₂ tie-line in the U-Pu-O phase diagram must be approached before the fuel will disintegrate.^{76,78}

Recent 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^{78,79} from mechanically blended (U_{0.75}Pu_{0.25})O_{1.98} pellets of the FTR-type (Sect. 4.4.5). The oxidations were performed at 480°C, the optimum temperature for the rapid disintegration of these pellets.⁷⁶ About 30% of the contained ^{85}Kr and 30 to 70% of the ^{131}I were released by the oxidation. Correlation of these fission gas release values with the extent of restructuring of the fuel will be attempted as soon as metallographic examination of the fuel is completed.

Krypton-85. – The solubility of ^{85}Kr in the fuel has been shown to be so low that its mobility via diffusion is probably negligible during voloxidation. It can move during irradiation by diffusion, fission fragment recoil, and grain restructuring. It is

trapped in small bubbles and at grain boundaries and dislocations. A predominant means for movement during irradiation is as lenticular voids that sweep through the central fuel regions, creating the columnar grain structure. These voids move up the thermal gradient (toward the hotter portions) by vaporization of fuel materials from the hot side and condensation on the cooler side of the bubble.

Fission gas release data indicate that the quantity of ^{85}Kr in the plenum and other connected gas spaces is a function of the initial smear density of the fuel, the burnup, and the degree of restructuring of the mixed oxide, which is a measure of the fuel temperatures under reactor operating conditions. This fission gas will be released on shearing the pin. Voloxidation results have been variable. In tests with a high-burnup (100,000-MWd/ton) sample, more than 98% of the residual ^{85}Kr in the fuel was released by the voloxidation treatment; with 15,000-to 20,000-MWd/ton samples, the amount released has typically been about 25%. The interpretation of these facts must take into account the state of the krypton in the irradiated fuel, since it can exist as minute bubbles ($< 1\ \mu$) dispersed throughout the fuel, as larger bubbles in the equiaxed grain growth region and at grain boundaries, and in the lenticular voids in the columnar region. The bubbles must migrate to the surface, or the solid must be disintegrated to allow the release of the trapped bubbles to the voloxidation atmosphere. Small-scale studies of the disintegration process by voloxidation indicate that oxidation of UO_2 to U_3O_8 and even cyclic oxidation and reduction do not convert unirradiated fuel to crystallite sizes less than the original $\sim 10\ \mu$.⁸¹ Thus, the krypton trapped in the crystallites (i.e., at the trapping sites in the unrestructured zones of the fuel) will probably not be released by voloxidation even if the fuel is converted to a powder. However, presumably the krypton present in the larger voids and at grain boundaries is released by the voloxidation process if the fuel is powdered. This situation is illustrated by the results obtained with PWR fuels, where little restructuring occurred and hence a minimal release of krypton would be expected. Voloxidation treatment (4-hr oxidation at 450°C) of pellet fragments from a blanket rod from Core 1 of the Shippingport PWR, which operated at a linear heat rating of 4.85 kW/ft, released only about 12% of the ^{85}Kr during

the conversion from UO_2 (about 95% of theoretical density) to < 200 -mesh U_3O_8 powder.⁷⁵ The low release of ^{85}Kr is attributed to the microdispersion of the ^{85}Kr at the individual fission sites; restructuring of the fuel would have moved the fission gases to the grain boundaries, where it could be more easily released upon oxidation of the UO_2 to U_3O_8 powder.

Xenon-133. — Results of preliminary tests have shown that removal of ^{133}Xe from the fuel is more difficult than removal of ^{85}Kr . This may be attributable to the relatively short half-life (5.3 d) of the ^{133}Xe ; since only the ^{133}Xe formed during the last short period of the irradiation would remain, it would have had little opportunity to migrate in the fuel. In a test with short-cooled fuel,⁷⁸ the fission gases in the fuel rod plenums contained 30 dpm of ^{133}Xe per dpm of ^{85}Kr , the vol-oxidation off-gases contained 90 dpm of ^{133}Xe per dpm of ^{85}Kr , and the dissolution off-gases contained 160 to 200 dpm of ^{133}Xe per dpm of ^{85}Kr .

Iodine-131, -129, -127. — The yield of iodine is relatively large; about 317 g of ^{129}I (half-life, 1.6×10^7 years), 1.1 g of ^{131}I (half-life, 8 d), and 111 g of stable ^{127}I will be present per ton of homogenized LMFBR fuel + blanket after irradiation to 33,000 MWd/ton (average) and 30 days of cooling (see Table 4.9 of ORNL-4436). The iodine is mobile within the fuel matrix and moves up or down the temperature gradient depending on a variety of conditions. It has been reported that iodine may cause transport of the cladding materials into the fuel matrix by a volatile iodide-decomposition (van Arkel - de Boer) mechanism.⁹⁰

Since the behavior of iodine is usually determined by following ^{131}I , data can be obtained only in tests with short-cooled fuel. In tests with fuel specimens of relatively low burnup ($\sim 15,000$ MWd/ton), about 25% of the total ^{131}I was found in the fuel after voloxidation. Control of iodine valence and prevention of iodine plate-out on surfaces are difficult; consequently, iodine material balances in the voloxidation experiments have frequently been poor.

Tritium. — Tritium is formed by ternary fission. It is a mobile species and, at the high temperatures that would be typical of the LMFBR, it is lost through the stainless

steel cladding.⁹¹ Irradiated LMFBR fuel specimens obtained from other sources and studied at ORNL usually contained less than about 5% of the calculated quantity of tritium. In one experiment in which a tritium material balance was made over an entire irradiation capsule, a large fraction of the "missing" tritium had reacted with the lower-temperature NaK coolant outside the fuel rods (but inside the outer capsule).⁷⁸ In most experiments the amount of tritium escaping the fuel rods could not be determined. However, samples of other irradiated fuels and blankets that were contained in stainless steel which had low cladding temperatures ($\sim 125^{\circ}\text{C}$) contained up to the theoretical amounts of tritium when received.

More than 99% of the tritium present in the oxide fuel at the beginning of an experiment has been released by voloxidation where mass transfer conditions were favorable (i.e., no significant blockage by cladding).^{2-5,62,65,66,70,77,78} Variations in the conditions of temperature and atmosphere have not had large effects on the amounts of tritium that were released. It appears that the tritium release mechanism is relatively simple (e.g., by diffusion outgassing).⁹² This behavior would be analogous to the degassing of fabricated fuels during adjustment of the O/M ratio in the manufacturing process. In this case, the variables that would play major roles in the release of tritium would be the quantity of tritium present, the exposed surface area, and the mean diffusion path lengths.

4.4.7 Effect of Coolants or Bonding Agents

The reaction of coolants or bonding agents such as sodium or NaK with LMFBR fuels is being investigated by ANL^{52,53} and by the General Electric Company^{41-43,93,94} as part of fuel-coolant-cladding compatibility studies. Defected fuel rods release fission gases to the reactor system. It is likely that cesium would dissolve in the coolant, whereas iodine and tritium would probably react to form insoluble sodium iodide or sodium tritide.⁹⁵ Reaction between the sodium and the fuel is dependent on the stoichiometry of the $(\text{U}, \text{Pu})\text{O}_2$; hypostoichiometric fuel does not react with the coolant.⁹³ Goldberg has summarized information concerning reactions of sodium with air.

With respect to the voloxidation system, any sodium present as the result of leakage into the fuel or through its use as a bonding agent will be converted to sodium oxide (or sodium hydroxide if moisture is present). Conceivably, some of the tritium and the iodine could react to form tritiated sodium hydroxide and sodium iodide, respectively, thus preventing their release during voloxidation. The retention of a significant fraction of the tritium as NaO^3H would be a disadvantage, since the tritium would be irretrievably diluted in the dissolver.

4.4.8 Other Chemical Reactants

Some preliminary studies have been made with unirradiated UO_2 to determine if addition of certain chemicals to the voloxidation system would increase physical breakdown of the fuel and thereby enhance the release of volatile fission products. Essentially complete conversion of UO_2 to sodium uranate was obtained by heating UO_2 microspheres with sodium peroxide for 2 hr at 430°C .⁹⁶ Presumably, this change in phase would aid in release of the noble gases; however, it might also be expected to hinder the release of tritium and iodine. If this treatment were used as a routine step, it might be necessary to heat the fuel to release tritium prior to addition of the sodium. Sodium peroxide also reacts with PuO_2 under these conditions to form sodium plutonate. This would be a very important secondary advantage of such a treatment since any segregated (refractory) plutonium in the fuel might be converted to a readily soluble form. Tests with irradiated fuels have not yet been made.

When UO_2 was heated at $100\text{--}150^\circ\text{C}$ in a gas stream containing nitric acid vapors, uranyl nitrate formed readily. No uranyl nitrate was formed when moisture was excluded from the system (i.e., in an $\text{O}_2\text{--NO}_2\text{--NO}$ gas stream at $200\text{ to }350^\circ\text{C}$).⁹⁷ This treatment might be expected to increase release of ^{85}Kr from the fuel but would probably not affect refractory plutonium. Because of the need for moisture if the reaction is to proceed, prior removal of tritium from the fuel would be essential.

4.4.9 Other Fission Products

Voloxidation experiments at ORNL indicated that fission products other than the three just discussed have significant volatilities at temperatures of 750°C and higher. In one experiment made at 750°C with long-cooled fuel, 43% of the total ^{106}Ru , 29% of the ^{137}Cs , 27% of the ^{125}Sb , and 10% of the ^{95}Nb were leached from the walls of the stainless steel "burner" after the voloxidation test.² Data on the volatilization of fission products other than those desired are needed, particularly in the temperature region 475° to 650°C, the conditions presently considered most effective.

4.4.10 Reaction of Advanced LMFBR Fuels with Oxygen

The reaction of unirradiated arc-melted UC with oxygen is slow at temperatures below about 600°C but proceeds rapidly between 800 and 1000°C.⁹⁸⁻¹⁰¹ Uranium monocarbide was made reactive by extended exposure to moist air; the reactive UC ignited and burned in oxygen at about 300°C.¹⁰² Irradiated 20% PuC--80% UC has been burned at 800°C in a stream of oxygen.¹⁰³ Powdered, unirradiated UN burns rapidly in oxygen at temperatures above 450°C;¹⁰⁴ no reference to the oxidation of irradiated UN has been found.

4.4.11 Sensitization of Stainless Steel

As presently conceived, the release of volatile fission product gases from LMFBR fuel would probably take place in a voloxidizer unit at temperatures from 475 to 650°C in either oxygen or air. No significant attack of the stainless steel cladding has been noted at these temperatures. At temperatures of 800 to 850°C, however, the stainless steel cladding oxidized and disintegrated.² Extensive attack of the stainless steel will result in flaking and increased amounts of insoluble residue. It might also cause larger quantities of cladding metals to be dissolved in the dissolution step. Both of these would increase the amount of high-level waste generated.

5.4 Volatile Fission Product Removal - Task 4

The objective of Task 4 is to develop an effective head-end processing method that will volatilize fission product gases (tritium, iodine, xenon, and krypton) from sheared LMFBR fuel and blanket prior to dissolution. Such a method would also deactivate any sodium present in the sheared fuel. This is an important task, which requires the development of a new technology. Small-scale tests with unirradiated and irradiated fuel and engineering-scale tests with unirradiated samples are presented as process options in Fig. 5.10 and as a logic diagram in Fig. 5.11. A schedule of activities is presented in Fig. 5.12.

Process Development Program. — The small-scale development program consists of three major areas: studies of the basic chemistry of the process using small samples which have varied histories, hot-cell studies using larger quantities of a well-defined fuel, and, finally, collection of data for a statistical analysis of the effect of process variables. An extensive development program plan has been prepared outlining a comprehensive statistical evaluation.¹⁰⁵ The type of samples required in the near future have been designated. The experimental program includes a study of the dissolution step (see Task 5). Data derived from these studies will serve the two goals of comparing the head-end processing behavior of different irradiated fuel samples and determining which fabrication and irradiation parameters have the greatest effect on head-end processing.

Task 4.1 Laboratory Studies of Basic Chemistry

The purpose of this task is to develop data on the mechanisms controlling the oxidation of the fuel and the release of fission product gases. The program includes basic chemistry studies using thermogravimetric techniques to obtain reaction kinetics of various fuel forms in oxidative or other atmospheres. Study of the effects of vacuum degassing on the release of fission product gases is in progress. Also, the reactions of single pellets of unirradiated $\text{UO}_2\text{-ThO}_2$ and $\text{UO}_2\text{-CeO}_2$ should be studied to determine if these materials might represent a suitable stand-in fuel for

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TASK 4

Fig. 5.10. Process Options for Task 4.

Fig. 5.11. L

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Logic Diagram for Task 4.

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urania-plutonia for use in nonradioactive engineering development work without containment. Thermogravimetric studies on small samples of irradiated fuels can be used to determine irradiation effects on the rates of reaction and on relative oxygen demand (or surplus) in the irradiated fuel. The controllable parameters in such studies are temperature, residence time, sheared fuel length, particle size, atmosphere, fuel source, and plutonium content. The release of fission product gases from the irradiated $\text{UO}_2\text{-PuO}_2$ pellets as oxidation proceeds will help define possible mechanisms of release.

Studies on Unirradiated Fuel. — These studies provide the base-line evaluation for "zero" irradiation effect. In addition, fundamental studies of crystal habit and phase changes for various voloxidation conditions help to define mechanisms. Any effects of voloxidation on dissolution should be studied for various sources and types of fuel and the influence of major fabrication variables delineated. The studies should include thermogravimetric examination of the oxidation process and use of X-ray diffraction and metallography for following the phase changes that occur.

A. Fabrication Parameters

1. Plutonium content (0 to ~ 25%)
2. The homogeneity or degree of solid solution in $\text{PuO}_2\text{-UO}_2$ mixture, and its effect on process behavior
3. The anion-to-metal (O/M) ratio — initial, final
4. Fuel density
5. Method of fuel preparation — coprecipitation, mechanical blending, sol-gel
6. Fuel form — pellets, shards, microspheres, etc.

B. Processing Parameters

1. Temperature of voloxidation
2. Time of voloxidation
3. Atmosphere
4. Length of shear cut

5. Presence of other chemicals – Na_2O , reactive gases, etc.
6. Effect of the above parameters on dissolution

Studies on Irradiated Fuel. – Small-scale studies (100 to 500 mg) paralleling the nonradioactive work described above are needed to determine the effects of irradiation levels and heat ratings on the chemical and physical changes during voloxidation, the fission product release rates, and the completeness of releases and reactions. Hot-cell samples (5 to 10 g) can be used for interfuel comparisons and in factorial designs to determine which fabrication and irradiation parameters are major factors and to provide design data for the pilot plant. Large-scale studies are needed to confirm process steps in the pilot plant.

A. Irradiation Parameters of Interest

1. Type of flux – fast vs thermal
2. Burnup
3. Temperature of irradiation
4. Temperature gradient (centerline to inner clad wall) or power rating of fuel
5. Degree of restructuring of fuel
6. Enrichment of fuel

B. Fission Product Information Required

1. Tritium
 - a. Determine the amount released from UO_2 and $\text{UO}_2\text{-PuO}_2$ during irradiation at various conditions of burnup, cladding temperature, theoretical density, fuel form, etc., based on the as-received fuel.
 - b. Determine if tritium release is similar to out-gassing prepared fuel pellets, etc.
 - c. Determine the time for adequate removal at various temperatures of voloxidation.
 - d. Check tritium when sodium or sodium oxides are present.
 - e. Confirm that other fuels behave as expected.

2. Iodine-131

a. Short-cooled tests

- (1) Measure release of ^{131}I from plenum cladding during voloxidation.
- (2) Determine relationship of ^{131}I release to oxidative power of voloxidizer atmosphere.
- (3) Determine time required for adequate removal from fuel at various temperatures of voloxidation.
- (4) Determine deposition of iodine on the equipment surfaces.
- (5) Determine effect of sodium and sodium oxides on release of iodine during voloxidation.

b. Long-cooled fuels

- (1) Test neutron activation as analytical technique for following ^{129}I behavior.

3. Krypton-85 (^{133}Xe)

- a. Determine the rate of release at various temperatures of voloxidation.
- b. Determine relationship of ^{85}Kr and ^{133}Xe release to the degree of oxidation.
- c. Determine krypton release data for variety of fuels and conditions.
- d. Determine relation of ^{85}Kr release to the extent of fuel restructuring.
- e. Effect of Na and Na_2O - Na_2O_2 system on release of ^{85}Kr .

4. Other Studies

- a. Optimize the oxidative conversion of UO_2 to U_3O_8 .
- b. Explore other methods to disrupt the crystal structure and expose the phase boundaries.

Task 4.2 Engineering Development

The purpose of this task is to develop and evaluate engineering data necessary for the design and scale-up of equipment and materials useful in large-scale tests of a feasible voloxidation process. The early developmental work with unirradiated

fuel should be continued; this should include the development of equipment, components, studies on prototype and stand-in fuels, and the effects of operating parameters on the process. A number of problems are anticipated for larger-scale testing with irradiated fuels, and solutions to these problems should be investigated.

Studies on Unirradiated Fuel

A. Equipment Development

1. Minivoloxidizers (static and rotary)
 - a. Bench-top model for UO_2 and stand-in fuels
 - b. Glove-box unit for unirradiated (U, Pu) O_2
 - c. Hot-cell model for irradiated fuel tests
2. Rotary calciner
3. Batch furnaces
4. Tray dryer (rotary arm roaster)

B. Oxidative Studies of Prototype Clad and Unclad Fuels

1. UO_2
2. $\text{UO}_2\text{-CeO}_2$ (a possible stand-in fuel)
3. $\text{UO}_2\text{-ThO}_2$ (a possible stand-in fuel)
4. $\text{UO}_2\text{-PuO}_2$

Effects of Operating Parameters

1. Static operation versus tumbling operation
2. Length of sheared fuel
 - a. Multirod shear
 - b. Bundle shear
3. Temperature
4. Rate (residence time or throughput)
5. Presence of sodium
6. Separation of cladding and fuel

- a. Deposition of U_3O_8 on equipment surfaces
 - b. Deposition of U_3O_8 on the surfaces of the hulls (cladding)
 - 7. Sensitization of cladding
 - 8. Oxygen content of sweep gas
 - 9. Gas flow rate
 - 10. Vacuum
 - 11. Corrosion
- C. Some Problems with Irradiated Fuels Requiring Study
- 1. Control of reaction temperature
 - a. Requirements for heating or cooling
 - b. Fission product decay heat
 - c. Heat of reaction
 - 2. Design of gas-tight seals (equipment isolation)
 - 3. Deactivation and disposal of internal sodium (i.e., sodium inside fuel rods)
 - 4. Deposition of I_2 , Cs, Ru, etc., on equipment
 - 5. Washing and disposal of stainless steel hulls and fines
 - 6. Filtering of oxide fines from off-gas

Discussion of Engineering Problems. — The optimum operating conditions for the rotary kiln (Bartlett-Snow rotary calciner) should be determined for sheared irradiated UO_2 - PuO_2 fuel. Variables that will require investigation 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 of 350 to 575°C. The 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.

The effect of sheared fuel length has been studied using both stainless steel-clad porcelain and UO_2 pellets. The data suggest that during shearing with the multirod shear at least 10% of the heavy-metal oxide should fall out of the cladding (0.25 in. OD) when the shear cut is 1 in. In order to increase the surface area available for oxidation, it may prove necessary to shear the fuel into sections approximately 0.5 in. long, which might be expected to increase the amount of fuel dislodged to about 50 wt %. Oxidation of UO_2 to U_3O_8 can probably be achieved satisfactorily using air as the sweep gas; the oxidation rate is expected to increase as the gas velocity is increased. It will be necessary to determine the optimum velocity for achieving rapid oxidation while avoiding oxide sintering. Certainly all of the variables mentioned will have a direct influence on the residence time in the rotary kiln required to complete the oxidation.

Control of the reaction temperature will be a major problem. Within the rotary kiln for a 1-metric ton/day processing plant, the heat of reaction will contribute about 4 kW of power and the fission product decay heat will contribute an additional 4 kW (assuming a decay period of approximately 30 days after discharge from the reactor and a 45-min residence time in the kiln). Additional heat may not be needed; rather the outer walls of the rotary kiln may require a satisfactory cooling system. However, resistance heating should be available if needed along the outer kiln walls.

The design and satisfactory operation of gas-tight seals for the rotary kiln will require a considerable amount of effort. The high decontamination factor required for the ^{131}I will place a high reliability factor on any seal used throughout the system. The rotation of the kiln and the proposed operating conditions will definitely complicate the design of the seals required at each end of the reaction container.

The filtering of oxide fines from the kiln off-gas may also present a problem; however, by using dual off-gas lines and filters with an air blowback system on each, the suspended oxide fines should not seriously hamper the overall operation of the rotary kiln. The condensation of volatile fission products such as iodine, cesium,

and ruthenium at undesired locations (i.e., on the off-gas stainless steel filter) may require the use of several small resistance heaters.

The degree of conversion of any sodium present in the fuel to sodium oxide must be determined over a range of voloxidation conditions to be sure that no sodium metal will be allowed to pass to the dissolver.

The disposal of the stainless steel hulls and wires leaving the rotary kiln presents a problem of unknown magnitude until experimental data can be obtained. If the stainless steel can be mechanically separated from the U_3O_8 - PuO_2 powder efficiently, then the hulls and wires may require only moderate leaching and washing. If the U_3O_8 - PuO_2 is not dislodged from the steel cladding, either in the rotary kiln or on a vibrating screen, all of this stainless steel must be sent to the dissolver. Transporting this material into and out of the dissolver is a major problem.

Task 4.3 Effect of Coolant or Bonding Agents Such as Sodium

This task is important since the effect of the presence of sodium during fission product gas release is an unknown factor. If oxidative heat treatment is required for gas evolution, the safe destruction of sodium at these conditions could be assumed; however, tests are required over a suitable range of temperatures. Such tests would also include a determination of the competing side reactions of sodium, as with iodine or with the fuel oxides. Similarly, if an inert atmosphere is used in conjunction with heat treatment, the iodine may react almost exclusively with the sodium and be carried downstream as a solid to the dissolver. Results of such effects will have to be measured and the various reactions determined in both solid and vapor phase systems.

Task 4.4 Sensitization of the Inert Metal Components of Fuel, and Other Processing Effects

The objective of this task is twofold:

1. To confirm whether the stainless steel hulls, spacers, and grids, and nickel reflector rods are sufficiently sensitized by the oxidative (or

inert gas) heat treatment of the voloxidizer to be attacked appreciably by nitric acid dissolvent, thus incurring a significant waste penalty.

2. To define the limitations and restrictions that are imposed on the process if the operating conditions are changed such that the stainless steel components are prevented from becoming sensitized.

A study will be made of this problem, initially on a batch scale with corrosion coupons. Later, as equipment (batch, rotary, tray, etc.) is developed and evaluated, tests will be made on a larger (engineering) scale. Tests will be required for both situations in the presence and absence of sodium.

Task 4.5 Conversion of Oncoming Fuels (Nitrides and Carbides) to Oxides

The objective of this task is to determine the conditions required for converting the advanced fuels of uranium-plutonium carbides and nitrides to the corresponding oxides. There are several reasons, principally tritium removal and sodium destruction, for making the conversion. Also, the conversion would eliminate the presence of undesirable organic molecules formed by carbides during the nitric acid dissolution step. Nitrides are easily soluble in nitric acid, but conversion to the oxide would also safely deactivate sodium and prevent it from entering the dissolution step.

An experimental program to investigate the basic chemical reactions at various uranium-to-plutonium ratios and temperatures will be required. Equipment component development for the oxide conversion step may also be necessary. However, it is likely that equipment developed for the voloxidation of oxide fuels will also be useful for conversion of the nitrides and carbides.

Task 4.6 Alternative Processes

The purpose of this task is to provide suitable backup processes for the shear-leach process in the event that unforeseen obstacles in handling the LMFBR fuels should arise. Alternative processes undergoing investigation at other sites will be followed and evaluated. This includes processes such as the pyrochemical methods and melt decladding.

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