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CHEMICAL ENGINEERING DIVISION
FUEL CYCLE TECHNOLOGY QUARTERLY REPORT
January-March 1972

by

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ABSTRACT

During the period January through March 1972, work was done in the following areas: (1) conceptual design of a distillation unit for the recovery of U-Pu from Zn-Mg solutions, experimental work on the separation of U-Pu by its precipitation from Zn-Mg solutions, and laboratory work on a process to separate CaO from the reduction salt of the pyrochemical head-end process to reduce waste volume and allow recycle of the reduction salt; (2) engineering-scale work on the denitration of uranyl nitrate-plutonium nitrate solutions to $\text{UO}_3\text{-PuO}_2$ in a fluid bed, the evaluation of a jet grinder, and the dissolution of $\text{UO}_3\text{-PuO}_2$ denitration product for recycle to the denitrator; (3) investigation of the effects of original particle size and dished ends of pellets on X-ray fluorescence signals in an analytical procedure for determining Pu/U ratios in LMFBR oxide fuel; (4) study of the effect of mixing chamber configuration and entrained solids on the stability of hydraulic operation and the pumping capacity of a centrifugal contactor (for plutonium extraction steps in solvent extraction); (5) operation of a new electrolytic cell (for the reduction of plutonium for a Purex process application) to determine the effects of flow velocity on current density and to determine current efficiency from changes in electrolyte composition--i.e., Pu(IV) concentration; and (6) an estimation of the production rates and behavior of tritium and noble gases in power reactors so that procedures may be evaluated for disposing of these wastes.

SUMMARY

Liquid Metal Decladding of Reactor Fuels

The application of pyrochemical processes to the head-end treatment of irradiated reactor fuels in the reprocessing cycle is under study and development. Advantages of the pyrochemical process are that sodium adhering to the fuel is not a problem (a separate sodium-removal step is not required); the process does not require fuel shearing; xenon and krypton are collected in a small-volume dry inert atmosphere; and iodine is collected in a fused salt. In the pyrochemical head-end process, the stainless steel components of the fuel assembly are dissolved in molten zinc, which is withdrawn from the exposed fuel oxide pellets. The pellets are then reduced in a liquid zinc-magnesium-calcium alloy in the presence of molten CaCl_2 salt. The reduced uranium and plutonium dissolve in the metal phase along with some fission products. The metal phase is then separated from the salt. The uranium and plutonium are recovered from the metal solvent and are subsequently processed in an aqueous solvent extraction plant. The salt, which contains CaO (a product of the reduction) and fission products (including iodine), is a process waste.

Product Recovery. One operation of the pyrochemical head-end process is the isolation of the U-Pu product from Zn-Hg-Ca solvent, as noted above. Distillation is one of the two methods under consideration for recovering the U-Pu from the solvent.

Problems in the design and operation of a plant-scale distillation unit for evaporating 360 kg/hr of solvent metal (the rate for processing three fuel assemblies per day, as specified in the reference flowsheet) are under study along with possible solutions. Heat input rates and methods that would avoid entrainment of uranium and plutonium in the still vapors are required. To solve this problem, a continuous still concept is being considered in which the solution is fed continuously into the crucible in the heated zone at a rate of about 1/3 gpm. Another problem will be a large cooling load on the still condenser. Direct heat rejection outside the processing cell is a possible solution.

As an alternative to distillation, a procedure is being studied experimentally in which the product U-Pu is separated from its solvent by converting the U-Pu to compounds that (1) are insoluble in the solvent and (2) are suitable for acid dissolution in subsequent aqueous processing. In an initial experiment, zinc-uranium solution was contacted at 800°C with excess ZnO solid to precipitate the uranium. At equilibrium, the uranium concentration in the zinc was found to be $\leq 1.5 \times 10^{-4}$ wt %. A disadvantage of oxide precipitation would be that precipitation of uranium-plutonium is preceded by precipitation of magnesium-calcium as oxide in the process solvent; hence, the use of an oxide precipitating agent was abandoned.

Next, investigation of the use of calcium nitride as a precipitating agent was started. Uranium nitride and plutonium nitride are more stable than the nitrides of calcium and magnesium. When excess Ca_3N_2 solid in the form of -60 mesh particles was contacted with a Zn-10 wt % Mg solution containing uranium, the equilibrium concentration of uranium was found to be ≤ 0.002 wt %. In the conceptual process, the initial uranium concentration in the solvent metal solution will be about 10 wt %, and at least 99.98% of the uranium would be expected to precipitate. Since initial results are promising, kinetic studies of the reaction with larger size Ca_3N_2 particles confined in a packed bed are being undertaken, as well as equilibration experiments with plutonium in the solvent.

Recycle of Reduction Salt Waste. The volume of salt waste from the pyrochemical head-end process is about 60 ft³ per metric ton of U-Pu processed. It appears desirable to reduce this waste volume. The salt contains about 27 mol % CaO in CaCl_2 ; the CaCl_2 can be recycled if separated from the CaO.

Study of the CaO-CaCl_2 phase diagram indicated that further concentration of the CaO in the CaCl_2 might be possible so that the ultimate waste volume could be reduced and a portion of the salt used for recycle. The procedure studied applies equilibrium phase-separation methods in two steps. In the first step, the solid $\text{CaO} \cdot 2\text{CaCl}_2$ that forms in the waste is heated above 835°C, where it separates into a solid rich in CaO and a liquid containing ~20 mol % CaO. The solid is separated from the liquid and becomes the bulk of the process waste. Next, the liquid is cooled to 750°C, where it forms a new liquid phase containing 6.5 mol % CaO and a solid phase, $\text{CaO} \cdot 2\text{CaCl}_2$. The liquid is separated and blended with CaCl_2 for recycle to the head-end process.

Laboratory experiments with phase separations indicate that volume reduction by a factor of 3 to 4 should be achievable.

Melt Decladding. Work to evaluate melt decladding as a possible method of removing cladding from oxide fuel has been concluded. A topical report evaluating the method is being issued.

Continuous Conversion of U/Pu Nitrates to Oxides

Studies are continuing on a fluidized-bed process for converting uranyl nitrate-plutonium nitrate solutions to homogeneous oxide powder suitable for fuel fabrication. In successive process steps, the mixed nitrate solutions are codenitrated, yielding $\text{UO}_3\text{-PuO}_2$ powder. Then the $\text{UO}_3\text{-PuO}_2$ is reduced with hydrogen to $\text{UO}_2\text{-PuO}_2$, the required material for fuel manufacture. An integrated program of laboratory and engineering studies is in progress. Current emphasis is on the U/Pu codenitration step, using pilot-scale equipment installed in a 3- by 4-module glovebox.

A 9-hr denitration run was completed under the following modified operating conditions: bed temperature, 375°C instead of 325°C ; feed rate, 40 cc/min instead of 80 cc/min; and initial fluidizing-gas velocity of 1.4 ft/sec instead of 1.0 ft/sec. All of these changes were aimed at reducing the tendency (observed in preceding runs) of particle agglomeration in the bed. The feed solution contained 1.62M uranium and 0.05M plutonium in 2.56M nitric acid; this plutonium level is of interest for plutonium recycle fuel materials. The starting bed comprised about 8300 g of $\text{UO}_3\text{-PuO}_2$ powder from the preceding run, sieved through a 20-mesh sieve; the bed had an average particle size of 368 μm .

The run was evaluated in an on-going manner by observations of (1) stability of the bed and reactor temperatures and pressures, and (2) trends in particle size distribution. The latter were determined by sieve analyses of hourly samples of the product and calculations of the average particle size. The first half of the run was operationally uneventful except that significant particle growth was evident. Apparently, the rate of production and utilization of seed particles was not adequate to maintain a steady-state particle size distribution in the bed. The growth rate was such that after about five hours, the fluidization velocity had to be increased to maintain "good quality" fluidization. Particle growth continued for the remaining four hours of the run, and a compensating increase in fluidization velocity was made during that period. The fluidizing-gas velocity at the end of the run was 2.2 ft/sec. The run was terminated because it was impractical to further increase the fluidizing-gas velocity. The average particle size of the final bed was 549 μm , about 1 1/2 times that of the starting material. The product and bed were free flowing.

A "jet grinder" had been built into the cone bottom of the denitration reactor in anticipation of particle growth. With this device, grinding is achieved with an air jet (90-psig air supply, 0.040-in. orifice) directed horizontally at a fixed target plate, a distance of 0.5 to 1.5 in. from the nozzle. Grinding of 2- to 6-kg batches of $\text{UO}_3\text{-PuO}_2$ powder at room temperature was studied in exploratory tests. The grinding rate achieved in these tests was considered adequate since it is in excess of the particle growth rate ($\sim 20 \mu\text{m/hr}$) experienced in runs with uranyl nitrate-plutonium nitrate-nitric

acid solution. It is planned to use the jet grinder during actual denitration in an effort to stabilize particle size in the bed.

Electron microprobe and microscopic examinations of the $\text{UO}_3\text{-PuO}_2$ product from the recent fluid-bed denitration runs clearly show an onionskin-like buildup of layers of $\text{UO}_3\text{-PuO}_2$ on the UO_3 seed material. Distribution of PuO_2 in the UO_3 matrix is considered to be homogeneous on the basis of scans and spot analyses of particles; no spots were found having uranium alone or plutonium alone.

Redissolution of the $\text{UO}_3\text{-PuO}_2$ is necessary to minimize plutonium inventory requirements in the pilot plant. This operation is conducted in a 4-in.-dia 5-ft-tall Pyrex glass vessel. The procedure is to dissolve the bulk of the UO_3 in dilute nitric acid and to dissolve the PuO_2 residue in concentrated nitric acid.

Development work on the dissolution procedure is continuing because of difficulties in dissolving the PuO_2 residue. Laboratory-scale dissolutions of PuO_2 residues have yielded significantly higher plutonium dissolutions than have pilot-plant runs. The reasons for this are being sought.

In-Line Analysis in Fuel Fabrication

The evaluation of X-ray fluorescence (XRF) as a potential in-line analytical method for determining the plutonium and uranium content of oxide fuels has continued, using $\text{ThO}_2\text{-UO}_2$ mixtures as a stand-in for $\text{UO}_2\text{-PuO}_2$.

In previous work with mixed powder, heterogeneity effects have prevented demonstration of a relative standard deviation (RSD) of 0.5% for XRF analysis. The observed variability of about 3% for powder mixtures could probably be reduced by better mixing, control of particle size distribution, and control of the density of the examined surface.

Experiments have been performed during this period on microspheres of solid solution $(\text{Th,U})\text{O}_2$ of three particle-size distributions. Results demonstrated that for solid-solution material, the signal fraction for a heavy metal, $I_U/(I_{\text{Th}} + I_U)$, is essentially independent of particle size. Although the thorium count rate and uranium count rate each decrease with increasing particle size, the ratio of the signal fraction to the chemical analysis fraction is 1.092 for microspheres having diameters of 10-20, 20-30, and 37-44 μm . In addition, the relative standard deviations (RSD) of the signal fraction (0.1 to 0.3%) are significantly lower than the root mean square of the sums of the RSDs of the count rates (1.1 to 2.3%). This indicates that the uranium and thorium count rates are associated in solid-solution particles.

For green pellets, it was desired to confirm that the effects of original particle size and surface density do not interfere with the precision of the analysis. The effect of original particle size was studied by comparing green pellets formed from urania having particle sizes of 37 to 44 μm and 10 to 20 μm . Their X-ray fluorescence intensities relative to that of uranium metal were 1.040 and 1.045 ± 0.005 , respectively, indicating that the particle size effect was eliminated by pelletizing.

Efforts to study the effect of density on X-ray fluorescence intensity have been frustrated by variations caused by (1) the method of pressing the pellets and (2) density gradients within a pellet. The reproducibility (RSD) of the signal fraction for polished re-pressed surfaces (0.12%) was observed to be significantly lower than the RSD of the uranium and thorium count rates (1.0%); association of the count rates for the two elements is presumed to be due to re-pressing. The preslugging operation and mill-mixing operations of a practical process would be expected to produce an effect similar to the effect of re-pressing.

Plutonium-containing samples are being fabricated by Westinghouse-Hanford in their process demonstration facility. It is planned to perform an analysis of variance of the signal fraction for green pellets and sintered pellets to determine the precision of the method for this material, as well as the reproducibility of the fabrication process.

Adaptation of Centrifugal Contactors in LMFBR Fuel Processing

The performance characteristics of a long-rotor centrifugal contactor continue to be investigated. The unit, which has a 4-in.-ID separating rotor with a 12-in.-long settling zone, is being used to evaluate centrifugal contactors having critically favorable dimensions. Contactors of this type are being considered for use in plutonium partition and isolation steps in the Purex-type solvent extraction processing of LMFBR fuel material containing high concentrations of plutonium.

A series of tests has been completed in which the aqueous and organic phases were mixed with a paddle operating in a mixing chamber just below the rotor. This mixing mode follows the basic design of the Savannah River (SR) contactors. In these tests, it was demonstrated that the combination of paddle and mixing chamber configuration was highly significant in affecting the stability of hydraulic operation. A combination that produced a pumping capacity moderately in excess of the flow throughput yielded the most stable operation.

Additional separating-capacity tests were conducted with the contactor modified to operate in the annular mixing mode. In this mixing mode, the mixing chamber and paddle are eliminated; the process streams are fed through the side of the casing and are mixed by skin friction as they flow downward through the annulus between the casing and rotor; the mixture enters the orifice in the rotor bottom. This centrifugal contactor design offers significant advantages, e.g., simplified construction, operation, and maintenance.

The most recently fabricated annular contactor has an enlarged annulus. The separating capacities (using 0.5M HNO_3 as the aqueous feed and 30% TBP in n-dodecane as the organic feed) were essentially the same as those found when the contactor was operated in the SR mixing mode. Capacities ranged from a minimum of ~ 4.5 gpm at an aqueous-to-organic (A/O) flow ratio of 2 and a rotor speed of 2000 rpm to ~ 14 gpm at an A/O flow ratio of 4 and a rotor speed of 3500 rpm.

Tests were conducted using both mixing modes to evaluate the effect of entrained solids in the aqueous feed. The solids consisted of MnO_2 suspended

in the aqueous phase at concentrations up to 2600 ppm. Operating speeds were 2000 and 3500 rpm. Solids appeared immediately in the aqueous effluent stream. Accumulations of solids in the rotor ranged from 50 to 150 g in various tests. After the equilibrium concentration of solids was reached, MnO_2 continued to be discharged with the aqueous stream. No solids were found in the organic stream effluent. Hydraulic operation was unaffected by solids accumulation in the rotor. The small amount of interface solids normally associated with solvent extraction processes is not expected to cause operational difficulties for centrifugal contactors of these two designs.

Electrolytic Reduction and Reoxidation of Plutonium in Purex Processes

Electrolytic reduction of plutonium for a Purex process application continues to be investigated. Past efforts were focussed on developing a mathematical relationship between current density and various process parameters. Work has begun now on testing the model with plutonium nitrate solutions.

The new recirculating electrolytic cell, which was designed to permit testing of the model, has been installed in a plutonium glovebox. Initial experiments were conducted with an electrolyte of 15.1 g/liter plutonium in 0.5M HNO_3 . A 45-mesh platinum screen cathode with 0.20-mm wire diameter was used. Current density versus cathode potential was measured at three flow velocities. The magnitude of the current density in the plateau region, the so-called limiting current density, increased with flow velocity as expected. The exponent for the flow velocity was 0.3, as predicted in an equation relating limiting current density to process parameters.

In further experiments, flow velocity and cathode potential were kept constant while changes in $Pu(IV)$ and $Pu(III)$ concentrations resulting from electrolysis were determined. Upon electrolysis, $Pu(IV)$ concentration decreased and $Pu(III)$ concentration increased, but the current efficiency was low. Preliminary information suggests that by addition of a very small amount of hydrazine to the electrolyte, the current efficiency can be increased.

Disposal of Tritium and Noble Gases

An evaluation is being made of the ultimate disposal of tritium and noble-gas fission products from the nuclear generation of electrical power. To support this evaluation, information is being surveyed on the behavior of tritium and noble-gas fission products in the types of reactors and fuel reprocessing plants most likely to play major roles in U. S. electric utility systems. This report summarizes information on the behavior of tritium and noble-gas fission products in a boiling-water reactor (BWR), a pressurized-water reactor (PWR), and a liquid-metal fast-breeder reactor (LMFBR), using values for 1000-MW(e) reactors wherever possible. Included are a brief description of the reactor and associated components, estimates of the rates of waste generation, estimates of the release of wastes at the reactor site (since such release rates may become indicative of processing and storage loads if release to the biosphere is prohibited in the future), and a consideration of the paths of these wastes in the reactor system.

All three types of reactors produce by fission a number of isotopes, both stable and radioactive, of xenon and krypton. The only radioactive isotope of a noble gas that requires long-term storage is 10.76-yr ^{85}Kr . The other noble-gas isotopes, many of which are formed in high relative abundance, have short half-lives.

Noble-gas fission products are contained in the plant effluent streams as a complex mixture of xenon and krypton isotopes with a composition that changes rapidly with time. Thus, although estimates of rates of generation of ^{85}Kr and stable isotopes may be readily predicted from fission yields and reactor power level, if separation of noble-gas fission products is required, the estimates of processing rates of shorter-lived isotopes are strongly dependent on arbitrary assumptions of the decay period before processing.

In all three types of reactors, tritium is generated by fission and by neutron activation of boron, lithium, and deuterium. The rates of tritium generation by neutron activation reactions differ greatly for the three types of plants.

The expected flow of tritium from a 1000-MW(e) BWR system includes:

- (1) 2.5×10^4 Ci/yr (0.8 mol/yr) in the spent fuel shipped to a reprocessing plant.
- (2) a total of 8.5 to 250 Ci/yr (3×10^{-4} to 8×10^{-3} mol/yr) present at a concentration of 6×10^{-12} to 6×10^{-13} mol THO/mol H_2O in a stream of 50,000-150,000 cfm of air. This stream is the stack exhaust; the major escape path of gaseous THO may be evaporation of plant liquids into ventilated spaces.
- (3) a total of 8.5 to 250 Ci/yr in plant liquids (the equipment drain system, the floor drain system, the fuel storage pool, and the primary coolant). At steady-state operation, the concentration of tritium in all plant liquids is assumed to be about the same, 10^{-2} to 10^{-3} $\mu\text{Ci/ml}$ or 6×10^{-12} to 6×10^{-13} mol THO/mol H_2O .

The expected flow of noble gases from a 1000-MW(e) BWR system includes:

- (1) 3.8×10^5 Ci/yr [250 liters (STP)/yr] of ^{85}Kr in spent fuel shipped to a reprocessing plant.
- (2) 260 Ci/yr [~ 0.2 liter (STP)/yr] vented to the stack. This is based on the krypton content in an estimated release* of 10^5 $\mu\text{Ci/sec}$ of total noble gases. The ^{85}Kr will originally be in the main condenser exhaust stream, which consists of 1 to 60 cfm of air.

The total concentrations of xenon and krypton in the condenser exhaust stream will be about the same as in air, 1.14 ppm for krypton and 0.08 ppm for xenon. If the air flow in the condenser exhaust stream is assumed to be 20 cfm, the total amounts produced by a process that separates xenon and krypton from other gaseous constituents are calculated to be 15 mol/yr [330 liters (STP)/yr] of krypton and 1.2 mol/yr [27 liters (STP)/yr] of xenon.

*The estimated release, which is conservative, is based on a preliminary safety analysis report for a large BWR.

For conventional waste management at a 1000-MW(e) PWR, the flow of tritium is expected to total about 3900 Ci/yr in a total of 200,000 gal of liquid waste, corresponding to a concentration of about 3 ppb THO in H_2O .

The ^{85}Kr activity in the expected flow of noble gases from the gas-decay tanks of a 1000-MW(e) PWR, using conventional waste management, is 3200 Ci/yr. This consists of 9.5×10^{-2} mol/yr or 2.1 liters (STP)/yr of ^{85}Kr in 20,000 ft^3 /yr of nitrogen, which corresponds to a concentration of 4 ppm ^{85}Kr in N_2 .

Improved PWR waste management provides for accumulation of noble-gas fission products at a reactor site and recycle of tritium in the primary coolant throughout the lifetime of the reactor. Noble-gas fission products would be continuously stripped from the primary coolant with hydrogen that would be subsequently converted to H_2O to decrease the gas volumes handled. For fuel with 1% of the fuel elements defective, the noble gases accumulated in decay tanks for a 400-MW(e) PWR during a lifetime of 40 yr would include 58,600 Ci of ^{85}Kr . That is, 1.8 moles or 40 liters (STP) of ^{85}Kr would have to be dispersed or contained.

With the improved system of PWR waste management, during recycle of primary coolant over the lifetime of a 400-MW(e) plant, unpreventable losses of tritium of <100 Ci/yr (probably as THO vapor) are expected to occur. The losses would occur in "containment purging" and "unrecoverable plant leakage." The total tritium accumulated during the lifetime of a 400-MW(e) PWR is expected to have an activity of $3.3 \mu Ci/cm^3$ in a total volume of perhaps 67,800 ft^3 (if the fuel storage pool is excluded). About 30 yr of operation is required to reach this equilibrium concentration. These figures correspond to a total of 6.3×10^3 Ci of tritium at a concentration of 2 ppb THO in H_2O .

The major streams of tritium from a 1000-MW(e) LMFBR using tantalum control rods are expected to contain up to 40,000 Ci/yr (1.4 mol/yr) as NaT in the primary cold trap, up to 2000 Ci/yr (0.07 mol/yr) as NaT in the secondary cold trap, and about 400 Ci/yr (0.01 mol/yr) as THO in liquids of the water/steam system. For a 1000-MW(e) LMFBR using B_4C control rods for burnup regulation, the numbers may be higher by a factor of three. The flow of tritium in spent fuel from a 1000-MW(e) LMFBR to a fuel reprocessing plant is expected to be about 2.2×10^3 Ci/yr (0.07 mol/yr).

The major streams of noble gases from a 1000-MW(e) LMFBR using nonvented fuel pins are expected to include:

(1) 3×10^5 Ci/yr or 200 liters (STP)/yr of ^{85}Kr in spent fuel transported to a fuel reprocessing plant.

(2) 3×10^3 Ci/yr or 2 liters (STP)/yr of ^{85}Kr in the primary cover gas, which consists of 6×10^3 to 7×10^3 ft^3 of argon. These numbers are based on the assumptions that 1% of the fuel pins are defective and that the release fraction for stable isotopes is 0.35. The quantities and total volumes of radioactive isotopes collected for storage, if cover gas is processed to remove radioactivity, will depend on the rate of processing and the efficiency of the process.

I. LIQUID METAL DECLADDING OF REACTOR FUELS (W. E. Miller)

A. Engineering Development of Zinc Decladding

A decladding procedure is being developed for short-cooled irradiated LMFBF fuel assemblies (consisting of bundles of stainless steel tubes containing mixed uranium-plutonium oxide pellets). In the procedure being studied, upon immersion of the fuel region of a discharged assembly in a pool of molten zinc at 800°C, the stainless steel components (i.e., the assembly supporting members and the cladding) dissolve, but not the fuel oxides. Next, the zinc-stainless steel solution is separated from the fuel oxide. The fuel oxide from the decladding step is then reduced to metal and dissolved in a Zn-Mg-Ca reduction alloy by contacting (stirring) the fuel with the reduction alloy in the presence of a salt containing CaCl_2 . Some fission products dissolve in the reduction alloy and others in the salt. After removal of the salt from the alloy, the uranium-plutonium is separated from the reduction alloy and subsequently processed in an aqueous solvent-extraction plant.

An alternative for cladding removal is melt decladding, that is, melting of the stainless steel components of a fuel assembly to separate them from the fuel oxide.

1. Product Recovery (J. Lenc, J. Stockbar)

One step of the pyrochemical head-end process (noted above) is the isolation of the U-Pu product from Zn-Mg-Ca solvent (Step VII, process flowsheet, ANL-7871, p. 14). The isolated product can be introduced into the aqueous-solvent extraction process in one of a number of forms. Metallic U-Pu might be obtained by evaporating the volatile Zn-Mg-Ca solvent. Alternatively, U-Pu might be obtained as insoluble U-Pu compounds that could be isolated from the liquid Zn-Mg. Both of these methods are under consideration for the product recovery step.

a. Product Recovery by Evaporation of Solvent

The problems in designing a full-scale distillation unit for evaporating 360 kg/hr of zinc-magnesium are under study. (This distillation rate would be necessary for processing three fuel assemblies in an 8-hr distillation period in a 24-hr day--see reference flowsheet, ANL-7871, p. 14.) The problems apply to distillation of a batch in a single crucible or multiple crucibles. Conceptual design of a distillation unit for the recovery of U-Pu from Zn-Mg solutions continues in order to identify potential problem areas related to equipment scale, design, and operation. Some potential problems and possible solutions are discussed below.

Heat-transfer and entrainment problems will be encountered as the liquid level in the crucible (or crucibles) drops. Distillation batch volume is 600 liters (for a daily processing rate of 380 kg $\text{UO}_2\text{-PuO}_2$), whereas the final volume of U-Pu product (the residue left after distillation of Zn-Mg) is about 20 liters. The heat-transfer problem for high rates

of surface evaporation, especially in a batch device with a constantly changing liquid level, is difficult. Also, if the still design provides for heat transfer through the wall that forms the vacuum enclosure, materials of construction suitable for vacuum service at the temperature required ($>1100^{\circ}\text{C}$) may be difficult to find. Distillation of metals must be conducted under nonturbulent conditions to avoid the problem of entrainment, which would result in nonvolatile uranium and plutonium accumulating in the vapor duct and condenser. Violent boiling must be avoided, and surface evaporation should be the mechanism of mass transfer.

To solve these problems, a continuous still concept is being considered in which the solution is fed continuously into a crucible in the heated zone at a rate of about 1/3 gpm. The crucible is heated by radiation from its tungsten secondary vessel, which is inductively coupled to an energy source. The tungsten secondary vessel is sealed to the vapor duct at its top rim. The secondary vessel is bottom-supported along with its insulation and coil and is inside a vacuum-enclosure bell jar.

This design is similar to that employed by Winsch.¹ He found that the seal at the top rim of the secondary need not be absolutely tight. Escape of vapor into the bell jar was prevented in his design by maintaining the argon pressure in the bell jar slightly higher than the zinc distillation pressure. Techniques for feeding the product solution into the heated zone and flashing off the volatiles with minimum entrainment are under study.

Other problems are related to materials for the condenser components and to a method for dumping heat from the condenser since the required heat-removal rate for the condenser is of the order of 300 kW. This quantity of heat could not be dumped to the process cell atmosphere, as was done in the Argon Cell of the EBR-II Fuel Cycle Facility (FCF). It may be possible to transfer the condenser heat to liquid sodium that circulates in tubes surrounding the condenser shell. This sodium would be circulated through the shielding wall of the processing cell, and heat would be transferred to another coolant outside the cell. A sodium-circulating system and a sodium-to-air heat exchanger would have to be designed and fabricated for this system. If small batches were distilled, multiple units would be required.

Few materials and fabrication methods are suitable for the condenser, the vapor duct connecting the crucible and condenser, and attached piping. Tantalum or tantalum-lined materials might be suitable for the condenser and accessory parts since plutonium and uranium would be absent; suitable fabrication techniques for these materials are known. The possibility of using these materials is being explored.

b. Product Recovery by Precipitation

Experiments are being conducted to determine whether product U-Pu can be separated from a zinc-magnesium or a zinc-magnesium-calcium solution by converting the U-Pu to compounds that are insoluble in the liquid metal and are suitable for acid dissolution in subsequent aqueous processing. In the present flowsheet, the U-Pu product is in solution in Zn-10 wt % Mg solution prior to the final isolation step.

An insoluble compound such as an oxide or nitride might be formed in the solution in several ways. The solution could be contacted with either oxygen or nitrogen gas to form dispersed solids in the liquid. After settling, the solvent metal would be decanted and the solid recovered from the precipitation vessel.

Alternatively, the solution could be contacted with a solid that would react with the uranium and plutonium to form insoluble compounds. Separation of the U-Pu solid could then be carried out similarly to the procedure using a gaseous precipitation agent.

If the solid-phase reactant consists of large particles, they can be placed in a confined bed; as the product solution flows through the bed and the uranium-plutonium is converted to solid uranium-plutonium compounds, these compounds could be trapped in the bed. Separation of the product from the solvent would then be possible by removing the bed from the process vessel.

In an initial experiment, zinc-uranium solution was contacted at 800°C with excess ZnO solid. The uranium concentration in zinc at equilibrium was found to be 41.5×10^{-4} wt %. However, precipitation of the U-Pu as oxides with ZnO has the disadvantage that magnesium and calcium are also precipitated as oxides. Although the presence of MgO in the oxidized U-Pu product might not cause a problem in subsequent dissolution in nitric acid, the large quantity of MgO carried along with the UO_2 - PuO_2 product would be detrimental. Study of the precipitation of U-Pu with ZnO was therefore terminated.

Next investigated was a nitride precipitation process which avoids the problem encountered in oxide precipitation since uranium nitride and plutonium nitride are more stable than calcium nitride or magnesium nitride. In one experiment, uranium nitride failed to precipitate when a zinc-uranium melt was sparged with nitrogen gas. This was attributed to poor reaction kinetics.

Thermodynamic calculations indicate that either calcium nitride or magnesium nitride should react with uranium or plutonium in Zn-10 wt % Mg. Of the two precipitating agents, calcium nitride is preferred because one of the reaction products, calcium, is needed in the process in the reduction step. Consequently, this precipitating agent has the potentiality of furnishing not only nitrogen for uranium precipitation in the product recovery step, but also calcium for the reduction step if the solvent alloy is recycled.

To be useful in the process, the precipitation step must accomplish the following: (1) appreciably reduce the uranium and plutonium contents of the Zn-Mg solution resulting from the calcium oxidation step (Step V, process flowsheet, ANL-7871, p. 14) of the process and (2) lend itself to phase separation (i.e., the precipitate should separate and be recoverable from the solution). Three types of experiments are in progress or planned. In the first type, the objective is to determine the concentration of uranium still dissolved in a Zn-Mg-Ca melt after equilibration with excess Ca_3N_2 solid phase. In the second type of experiment, the concentration of dissolved plutonium in a Zn-Mg-Ca solution after equilibration

with excess Ca_3N_2 is to be determined. The third type of experiment has the objective of gaining kinetic information, i.e., determining how rapidly the reaction takes place and how completely uranium and plutonium react with solid particles of Ca_3N_2 .

A batch of Ca_3N_2 was prepared for these experiments by heating 6-mesh calcium metal nodules in 1-atm nitrogen at 900°C for 4 hr. Sieve analysis of the Ca_3N_2 in the as-prepared condition showed that 88.5% of the particles were -6 +10 mesh (-0.132 +0.0787 in.) and the remaining 11.5% were -10 +60 mesh (-0.0787 +0.0098 in.). A sample of the particles was submitted for X-ray diffraction analysis. The diffraction pattern indicated that only Ca_3N_2 was present and had a bcc structure of the Mn_2O_3 type with $a = 11.42\text{\AA}$. This is the same crystal structure as that of U_2N_3 , for which $a = 10.70\text{\AA}$.

When Ca_3N_2 (solid) is contacted with a Zn-Mg-U solution, two reactions are possible:

It is not known at present which of these two possible uranium nitrides is formed.

In an experiment (SPR-7) to determine the concentration of uranium in equilibrium with excess Ca_3N_2 solid phase in a Zn-Mg system, the charge consisted of 100 g of uranium metal, 1000 g of magnesium, and 8800 g of zinc. Dissolution of the uranium in the Zn-Mg solution was conducted at 750°C . A 5 1/2-in.-ID baffled tungsten crucible was used in a tilt-pour furnace having an argon atmosphere. The melt was agitated at 500 rpm for 2 hr with the agitator blades located about 1 1/2 in. above the crucible bottom. The Mo-W agitator had two blades pitched at a 45° angle pushing downward and measured 2 1/2 in. in dia and 3/4 in. high.

After the dissolution of uranium, 104 g of Ca_3N_2 was added to the melt in the form of -60 mesh (-0.0098-in.) particles. This quantity of Ca_3N_2 was about 236% in excess of the stoichiometric amount required for reaction 1 and 122% in excess of that for reaction 2.

Next, the melt temperature was increased to 800°C and the melt was agitated at 500 rpm with the agitator blades about one inch below the top of the melt. Filtered samples of the melt were obtained 2 and 3 1/2 hr after Ca_3N_2 addition. The temperature of the melt was then decreased to 750°C , and the melt was held overnight without agitation.

Filtered samples of the melt were obtained the following morning (approximately 20 hr after the Ca_3N_2 had been added). The melt temperature was increased to 800°C again and the melt was agitated to 500 rpm with the agitator blades still about 1 in. below the top of the melt. The melt was sampled again about 22 hr after the Ca_3N_2 addition.

Following these latest samplings, the agitator was lowered until the blades were 1 in. above the crucible bottom. The melt was agitated

at 500 rpm for an additional 2 hr, and the final samples for the experiment were obtained (about 24 hr after the Ca_3N_2 addition). The melt was allowed to settle without agitation for 2 1/2 hr. Then the bulk of the Zn-Mg supernatant solution was tilt-poured from the crucible into a graphite mold.

The furnace was opened, and a cluster of fine Ca_3N_2 particles was observed adhering to the crucible sidewall just above the melt level. Precipitated material was also found on the bottom of the crucible.

Fluorophotometric uranium analyses* of the filtered samples of the Zn-Mg-U solution after Ca_3N_2 addition in this experiment are tabulated below.

Time after Ca_3N_2 Addition, hr	Uranium Content of Melt, wt %
0	1.0 (Based on charge weights)
2	0.074
3.5	0.006
19.75	0.002
24.5	0.002

The 16.5-hr period between the 3.5-hr and the 19.75-hr samples represents an overnight period when the melt was not agitated.

The analyses indicate that 99.8% of the uranium reacted with the Ca_3N_2 and that the equilibrium uranium concentration of the melt was at least as low as 0.002 wt %. Since a significant quantity of the -60 mesh Ca_3N_2 particles added in this experiment was not intimately mixed with the melt, it is possible that the system was depleted of Ca_3N_2 . If this occurred, the final uranium concentration of 0.002 wt % is higher than the true equilibrium value. If these results are applied to the present flow-sheet, in which the uranium concentration in the product solution is about 10 wt %, conversion of at least 99.98% of the uranium to precipitate is predicted.

To identify the form of the uranium precipitate from Experiment SPR-7, samples of the residue remaining in the tungsten crucible were placed in a small tantalum crucible and retorted at 925°C and <1 Torr to distill off residual Zn, Mg, and Ca. By X-ray diffraction analyses** of retorted samples of the products recovered in Experiment SPR-7, the major phase was identified as uranium mononitride (UN). The diffraction pattern of the sample showed that a minor unidentifiable phase possibly was present. Anderson et al.^{2,3} reported that in the presence of excess nitrogen, uranium sesquinitride (U_2N_3) is formed at temperatures below 1475°C and that UN is formed above this temperature. Since our experiment was conducted at 750-800°C, the uranium may have precipitated as U_2N_3 . The major phase in the

* Unless otherwise indicated, analyses discussed in this section of the report were performed by E. Kucera, Z. Tomczuk, and F. Williams of the Analytical Services Group.

** Performed by R. Schablaske of the Analytical Services Group.

retorted samples may have been UN because of decomposition of U_2N_3 to UN at the temperature and pressure used in retorting.

Since uranium was completely stripped from the product solution in a short time, the second and third types of experiments discussed above are being undertaken.

2. Recycle of Reduction Salt Waste (L. Anastasia, T. Cannon)

In the head-end scheme for processing short-cooled LMFBR fuel, the reduction step is followed by the addition of $MgCl_2$ to oxidize to $CaCl_2$ the calcium metal that has not reacted with the fuel oxide to form CaO (Step V, flowsheet, ANL-7871, p. 14); CaO is produced in the salt by the conversion of UO_2 to uranium during the oxide reduction step (Step IV) of the process. The CaO is removed from the process vessel in the waste salt. In the conceptual process, the volume of waste salt (containing about 15 wt % or 27 mol % CaO) is about 60 ft³ per metric ton of U-Pu. It appears desirable to decrease the volume of waste.

The volume of salt waste might be reduced by applying equilibrium phase-separation methods to recover part of the salt for recycle. This scheme is based on the phase changes shown in Fig. I-1. First, solid $CaO \cdot 2CaCl_2$ is heated above 835°C, where it separates into a solid rich in CaO and a liquid containing ~20 mol % CaO . The solid is separated from the liquid and becomes the bulk of the process waste. Next, the liquid is cooled to a temperature slightly above 750°C, where it forms a liquid phase (the eutectic containing 6.5 mol % CaO) and solid $CaO \cdot 2CaCl_2$. The liquid is separated from the solid and blended with fresh $CaCl_2$ to form the feed salt for the reduction step. The scheme for processing the salt is shown diagrammatically on Fig. I-2. The volume reduction achievable is dependent on the purity of the CaO phase separated when the temperature is increased above 835°C. Initial experiments suggest that the volume of waste salt can be reduced by a factor of 3 to 4. Work on this separation scheme is reported below.

In an initial laboratory experiment to determine whether CaO can be separated from a molten salt, 1.28 kg of 33.3 mol % CaO in $CaCl_2$ was prepared in a stainless steel vessel by heating $CaCl_2$ and CaO in the required proportions for 5 hr with agitation at 900°C in an argon atmosphere. Following this mixing period, the molten salt was allowed to equilibrate for 41 hr while the temperature and inert atmosphere were maintained. The furnace was then rapidly cooled to ambient temperature and the salt ingot was removed by cutting away the stainless steel vessel. A distinct layer of separated material was evident on the bottom of the salt ingot. Analysis of this layer indicated that it contained 60 mol % CaO . In this initial attempt to separate CaO solid from molten salt, ~90 g CaO out of a theoretically possible 125 g of CaO separated by simple gravitational settling at 900°C. In a subsequent experiment, essentially the same result was obtained with a 5-hr equilibration and settling time.

The following step in the separation process is to lower the temperature of the equilibrium liquid phase of CaO in $CaCl_2$ (18 mol % CaO in $CaCl_2$) to 760°C in order to separate a second liquid phase containing ~6.5 mol % CaO from a solid phase of $CaO \cdot 2CaCl_2$. The theoretical proportions

FIG. I-1. CaO-CaCl₂ Phase Diagram [based on D. A. Wenz, I. Johnson, R. D. Wolson, J. Chem. Eng. Data, 14(2), 250, Fig. 2 (April 1969)]

FIG. I-2. Conceptual Salt Separation Scheme

in the salt after cooling are 1 mole of liquid phase to 1 mole of solid phase. Experiments using a simple settling procedure such as that described above did not result in separation of the solid phase, $\text{CaO} \cdot 2\text{CaCl}_2$. Preliminary experiments have indicated that separation can be effected by filtration. Filtration is attractive since the solid being filtered ($\text{CaO} \cdot 2\text{CaCl}_2$) can be decomposed by raising the temperature; thus, in the event of a filter plug, raising the temperature would clear the filter, allowing its continued use.

B. Melt Decladding (L. O. Winsch, J. Kincinas, R. Clark).

The Fuel Cycle Branch of RDT requested ANL to evaluate melt decladding as a possible method of removing stainless steel components of a fuel assembly from oxide fuel. Results of some melt decladding experiments and a conceptual decladder design were reported in ANL-7841, pp. 18-20. Evaluation has been completed and a topical report is being issued. Results of recent experiments in this program are given below.

Small-scale experiments were done for the purpose of gaining further information on the feasibility of melt decladding of LMFBR fuel assemblies. Simulated fuel assemblies and sections of stainless steel rod were held in a crucible and inductively heated in an argon atmosphere. The crucible containing the stainless steel was fabricated of MgO or Al_2O_3 and had holes in its base. This crucible was positioned vertically over a second crucible to allow the liquid stainless steel to drain from the UO_2 pellets into the crucible below (Fig. I-3).

In an initial run using a magnesia crucible (2.5-in. dia by 3 in.) with seventeen 9/32-in.-dia holes in the bottom, the stainless steel did not flow through the holes. The stainless steel thoroughly wetted and bonded to the MgO crucible.

In run SSMD-27, an alundum crucible (2 1/8-in. dia by 3.5 in.) with seven 5/32-in. holes in its base was charged with a simulated fuel assembly composed of 116.3 g of stainless steel and 196 g of UO_2 pellets. The charge was heated to 1600°C and held at temperature for a period of 2 hr. Examination of the crucible showed that ~76% of the stainless steel charged had flowed into the bottom crucible.

A magnesia crucible (2.25-in. OD by 3.5 in.) with seven 5/32-in. holes in the base was used in run SSMD-28. A simulated fuel assembly (196 g of UO_2 , 116 g SS) was heated in the crucible at 1472 - 1523°C for a period of 1.5 hr. Examination after the run showed that 44.7% of the stainless steel charged had flowed into the lower crucible.

In run SSMD-29, the alundum crucible used in run SSMD-27 was charged with a stainless steel rod weighing 444 g. It was held at 1540°C for 2 hr. After the run, it was found that 72.4% of the stainless steel had flowed into the bottom crucible. In run SSMD-30, the alundum crucible containing the stainless steel heel (122 g) from run SSMD-29 and an additional 444 g of stainless steel rod were charged to the furnace and heated at 1523 - 1556°C for 2 hr. At the end of this run, the bottom crucible was found to contain 72.9% of the stainless steel charged.

FIG. I-3. Typical Stainless Steel Meltdown Apparatus

These results suggest that the hydrostatic head of the melted stainless steel in the top crucible is the important factor in determining the separation of stainless steel from UO_2 pellets.

In another series of experiments, a different method of effecting phase separation between the molten stainless steel and the oxide pellets was investigated. Type 304 stainless steel tubing (0.25-in. dia by 3 in. long) loaded with UO_2 pellets (0.21-in. dia by 0.25 in.) was charged into an inductively heated alundum crucible, which was heated to 1514-1548°C in an argon atmosphere for a period of about one hour. The crucible, containing melted stainless steel tubing and UO_2 pellets, was then tilted to 15° above horizontal to pour off the stainless steel into a zirconia receiver; the UO_2 remained in the crucible. Table I-1 shows the charges and results for the three runs.

The results indicate that stainless steel can be more effectively separated from UO_2 pellets by the pouring technique than by drainage through holes in the bottom of the crucible.

TABLE I-1. Melt Decladding Runs

Run	Charge, g		Poured, % of charge	
	SS	UO_2	SS	UO_2
SSMD-33	91.3	153.4	77	0
SSMD-34	186.0	314.0	90	0.45
SSMD-35	184.2	310.0	91.6	0.45

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1. S. Lawroski et al., Chemical Engineering Division Summary Report, April, May, June 1963, ANL-6725, pp. 63-66.
2. R. N. Anderson, N. A. D. Parlee, and J. M. Gallagher, Applications of Nitride-Forming Reactions to Reprocessing of Spent Nuclear Fuels, Nucl. Technology 13, 29-35 (Jan. 1972).
3. R. N. Anderson and N. A. D. Parlee, Continuous Removal of Fission Products in a Nitride-Fueled Reactor, Nucl. Technology 13, 297-300 (March 1972).

II. CONTINUOUS CONVERSION OF U/Pu NITRATES TO OXIDES (N. M. Levitz, D. E. Grosvenor, S. Vogler, F. G. Teats)

In the nuclear fuel cycle, uranyl nitrate and plutonium nitrate solutions must be converted to powdered oxides suitable for the fabrication of fuel shapes. For LMFBR fuels and other applications, large quantities of plutonium will have to be processed, and the attendant problems of nuclear criticality, intrinsic radiation, and safety in shipping serve as an incentive for developing high-capacity, low-holdup continuous denitration processes.

A conversion process based on fluidized-bed technology developed in earlier ANL fluidization work¹ has a high potential for producing an oxide powder that is homogeneous with respect to plutonium oxide distribution in the uranium oxide matrix, as well as meeting other process requirements. Basic process steps include fluidized-bed codenitration of uranyl nitrate-plutonium nitrate solutions to $\text{UO}_3\text{-PuO}_2$ powder followed by fluidized-bed reduction of the $\text{UO}_3\text{-PuO}_2$ with hydrogen to $\text{UO}_2\text{-PuO}_2$, which is the required chemical form for fuel manufacture. The process appears to be applicable over the entire concentration range of uranium-plutonium nitrate solutions and to plutonium nitrate alone. An integrated laboratory and pilot-engineering program is in progress. Initial emphasis is on the denitration step.

The laboratory-scale preparation and preliminary characterization of small quantities of $\text{UO}_3\text{-PuO}_2$ powder, $\text{UO}_2\text{-PuO}_2$ powder, and $\text{UO}_2\text{-PuO}_2$ pellets produced by successive drop-denitration, reduction, and pelletizing steps have been reported in earlier reports in this series. Other earlier laboratory studies carried out in support of the engineering program included development of a dissolution procedure for $\text{UO}_3\text{-PuO}_2$ (ANL-7735, pp. 49-50) and a study of solubility limits for U/Pu nitrate solutions (ANL-7841, pp. 24-26).

Engineering-scale investigations are being conducted in a pilot plant (ANL-7735, p. 54) housed in a 3-by-4-module glovebox approximately 14 ft long, 10.5 ft high, and 3.5 ft wide. The pilot-plant components include a 4-in.-dia fluidized-bed denitrator, a feed make-up system, and associated equipment and instrumentation; the equipment is fabricated of stainless steel, except for a dissolver fabricated of Pyrex glass. For criticality safety, vessels that normally contain solution and have diameters greater than 5 in. are filled with boron-glass Raschig rings as a nuclear poison. Instrumentation includes appropriate temperature and pressure sensors with local and panelboard readouts, controllers, recorders, and an automatic data logger.

Shakedown of the pilot plant was completed using uranyl nitrate feed solutions. Certain equipment modifications were made to satisfy the criticality safety review. Recently, runs with mixed U/Pu feed solution were initiated (ANL-7902, p. 23).

During the current report period, denitration with U/Pu feed solution was continued; successful tests were made of an *in situ* jet grinder mounted in the cone bottom of the denitration reactor. Examination with an electron microprobe of $\text{UO}_3\text{-PuO}_2$ powder product was initiated, and difficulties with the oxide powder dissolution procedure were resolved.

A. Pilot-Plant Denitration Run with U/Pu Feed Solution

A 9-hr denitration run (U-18-Pu) was performed using operating conditions that differed from those used in the previous runs with U/Pu feed solutions. The changes included a higher operating temperature (375°C instead of 325°C), a lower feed rate (40 cc/min instead of 80 cc/min), and a higher initial fluidizing-gas velocity (1.4 ft/sec instead of 1.0 ft/sec). All of the changes were expected to reduce the tendency of particles to agglomerate in the bed.

The feed solution contained 1.62M uranium and 0.05M plutonium in 2.56M HNO_3 . The starting bed was ~8300 g of $\text{UO}_3\text{-PuO}_2$ powder from the previous run, sieved through a 20-mesh sieve. The average particle size was 368 μm .

The run was characterized by an overall increase in the average size of the product (Fig. 11-1), as determined from sieve analyses of hourly blend samples. After 5 hr of smooth operation, erratic readings from bed Δp and temperature monitors (often an indication of bed agglomeration) were observed, and the fluidizing velocity was increased from 1.4 to 1.6 ft/sec. Smooth operation resumed. The fluidization velocity was further increased incrementally during the final 4 hr to 2.2 ft/sec to compensate for additional "growth" of the bed particles. Incremental changes in gas velocity were required to maintain fluidization, but a practical limit for gas input was being approached. The run was, therefore, terminated after 9 hr. The final average bed particle size was 549 μm , about 1.5 times the average starting-bed particle size.

In other aspects, the run was operationally good. Product flowed freely via the overflow take-off line to the product receivers; the column pressure remained stable; and no agglomerates larger than 10 mm were found in the final bed.

B. Jet Grinder

In anticipation of particle growth problems, a "jet grinder"^{2,3} had been built into the base of the reactor in the cone section. A jet of air issuing from a 0.040-in.-dia orifice is directed at a fixed target plate that is normal to the air jet. The distance between the nozzle and target is adjustable. An exploratory grinding test was made at room temperature with the jet supply pressure at 90 psig. The charge was 2 kg of $\text{UO}_3\text{-PuO}_2$ product of mixed particle sizes. The powder was fluidized at about 0.4 ft/sec. Significant attrition of the powder was achieved: the quantity of +20 mesh was reduced 40%, and the quantity of +40 mesh was reduced 15%; there was an approximately threefold increase in -200 mesh material.

In subsequent jet-grinder tests, the entire final bed from Run U-18-Pu was treated to produce a quantity of material of a size needed for the next run. The jet was positioned 1/2 to 1 1/2 in. from the target. The results indicated that a spacing of less than 1 1/2 in. must be used for effective grinding. No significant difference in grinding rate was noted for powder charges of 2 to 6 kg, with a fluidizing-gas velocity of ~1.0 ft/sec, and a grinding period of 45 min per kilogram of charge.

FIG. II-1. Changes in Mean Particle Diameter, Run U-18-Pu

The jet grinder will be used in the next denitration run while denitration is in progress. The duration of the grinding periods will be dictated by particle size changes, which will be determined by sieving hourly grab samples of the product.

C. Electron Microprobe Examination of $\text{UO}_3\text{-PuO}_2$ from Run U-18-Pu

Three powder samples from Run U-18-Pu were examined with the electron microprobe analyzer. The powders were cast in PolyLite* resin to form a 1-in. cylinder. The samples were handled in the usual manner by grinding with ever-finer paper including 600 grit paper. The final polish was with 1- μm diamond paste. The surface was then coated with a thin film of aluminum to prepare the samples for microprobe examination.

The samples were first examined with a defocused ($\sim 15\ \mu\text{m}$) beam scanning across the particles, with plutonium and uranium count rates continually recorded on a chart. Samples of the starting bed, final bed, and the sixth-hour sample were examined. In a second approach, quantitative measurements were made on one of the particles from the sixth-hour sample. In this case, a fine (0.5 μm) beam was focussed on a spot and the emitted uranium and plutonium X-rays were counted simultaneously. Three 20-sec measurements were made at each spot, and the average value was used for computation. Nine different measurements were made across the face of a particle. The background above and below the peak was measured, and one half of the average of these values was subtracted from the measured peak count. Standard $\text{UO}_2\text{-PuO}_2$ samples were also measured. All of the results distinctly show a center core of uranium oxide surrounded by two layers of a plutonium-bearing oxide of differing concentrations. The difference in plutonium concentrations in these layers is explained by the fact that the plutonium content of the feed for Run U-Pu-18 was 11.75 mg/ml while that for the earlier runs was 16 mg/ml.

Overall, the results show a layering effect produced by the drying of liquid on seed particles. Within any one layer, the plutonium distribution is quite uniform. No separation of uranium from plutonium was observed in the plutonium-bearing layer.

D. Dissolution of $\text{UO}_3\text{-PuO}_2$ Denitration Product

Dissolution of the $\text{UO}_3\text{-PuO}_2$ denitration product, though not a requirement of the denitration process, minimizes the plutonium inventory requirements in the glovebox. Dissolution in the pilot plant is conducted in a 4-in.-dia, 5-ft-tall Pyrex glass dissolver. Early pilot-plant efforts to dissolve the mixed oxide in nitric acid resulted in incomplete dissolution of the plutonium.

The pilot-plant dissolution procedure is to first treat successive batches of $\text{UO}_3\text{-PuO}_2$ powder with dilute (4M) nitric acid. This dissolves the bulk of the UO_3 and a fraction of the plutonium. The undissolved residue is mainly PuO_2 . The residues from several batches accumulate in the dissolver and are subsequently attacked with concentrated nitric acid, using several strikes of fresh acid. Between acid strikes, the residue is allowed to settle and the supernatant solution is pumped to the feed-storage vessel.

A relatively large amount of UNH solution remains associated with the residue. The addition of an evaporation step could avoid significant dilution

* Product of Reichold Chemical Co.

of the first concentrated nitric acid added. In a test of the dissolution procedure, recently prepared $\text{UO}_3\text{-PuO}_2$ was divided into two batches of 4.5 and 4.7 kg, and the batches were successively processed through the dilute acid dissolution step. The residue was subjected to an evaporation step and one concentrated nitric acid dissolution step. A plutonium concentration of 32 g/liter was achieved, which is significantly below the concentrations obtained in the small-scale experiments using a similar procedure. Reasons for the difference are being sought. Meanwhile, the residue will be treated with one or more strikes of concentrated nitric acid to prepare feed solution for the next denitration run.

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III. IN-LINE ANALYSIS IN FUEL FABRICATION (J. G. Schnizlein, T. Gerding, and M. J. Steindler)

Rapid, precise, and accurate in-line analytical methods are expected to decrease costs and to lead to automated procedures for the fabrication of LMFBR fuels. In this evaluation of proposed analytical procedures, the initial criteria are the specifications for preirradiated fuel properties and the associated precisions (ANL-7735, p. 59) for the Fast Fuel Test Facility (FFTF) project.

A. Plutonium-Uranium Ratio in Fuels

The evaluation of X-ray fluorescence (XRF) for in-line analysis of U/Pu in LMFBR oxide fuel has continued. In the originally defined specification for plutonium content, the required precision was 0.5% relative standard deviation (RSD), which remains our goal; but more recent specifications¹ have eased the required precision to 1% RSD.

An in-line method for plutonium analysis should be applicable at as early a step in the fabrication process as possible. This is, if powder analysis is sufficiently accurate, this will allow adjustments for off-specification uranium or plutonium content to be made most easily. The steps that are next most advantageous as control points are preslugging and green pellet formation. Least desirable would be applying the XRF method to sintered pellets, because then it would be necessary to dissolve off-specification material in an acid solution unless the material could be recycled to the preslugging step. These considerations have influenced planning of the experimental program.

To avoid plutonium hazards and facilitate study of important variables in the analysis, ThO_2 - UO_2 mixtures are being utilized as a stand-in for UO_2 - PuO_2 . This substitution is practical because of the identical relationship of the atomic numbers and thus of the relevant properties (ANL-7755, pp. 45-50) for each pair of elements.

Initially in this program, instrumental and inherent limitations of the XRF method were demonstrated to be adequately low--the relative precision due to the XRF method was less than 0.5% for measurement of uranium and thorium in pellets and thorium-30% uranium powder (ANL-7841, pp. 31-36). Currently being evaluated are the limitations imposed by material effects (i.e., particle-size distribution, density, and sample shape) on analysis of powders, green pellets, and sintered pellets in commercial equipment. Use of the XRF method to analyze pellets is based on the assumption that the surface (to a depth of less than 100 μm) is representative of the entire pellet.

1. Effect of Particle Size of $(\text{Th,U})\text{O}_2$ Microspheres on X-ray Fluorescence Intensity

In studies of powder samples, heterogeneity and particle-size effects have prevented a relative precision of 0.5% being demonstrated for the XRF analysis. Early experimental results (ANL-7841, p. 35) suggest there is a variability of ~3% between analyses of powder samples of a

ThO₂-30 wt % UO₂ mixture. This 3% variability has been attributed largely to mixing and sampling errors and to the unusual particle size distribution of the thorium used. No fundamental reasons are known that would prevent this variability from being lessened by better mixing, control of particle size distribution, and control of the density of the examined surface.

In other earlier work (ANL-7871, pp. 30-33), the XRF intensity for samples of pure UO₂ with narrow particle size distributions was measured at different degrees of compaction, i.e., at bulk densities ranging from 24 to 36% of theoretical density (T.D.). The relative intensity* data for each particle size cut at 25, 30, 35, and 40% of T.D. were compared with values calculated from fundamental parameters by J. W. Criss² (ANL-7902, pp. 27-30). Although the curves for the observed decrease of relative intensity with the logarithm of particle size had a sigmoid shape similar to the curve for the calculated results, the measured relative intensity was markedly higher at lower densities than the calculated values. The experimental relative intensity for 10-20 μ m particles was greater than 0.95 at 40% of T.D. and about 0.92 at 30% of T.D.; in contrast, Criss' calculation indicated a relative intensity of 0.7 for 15- μ m particles at both 30 and 50% of T.D. The model for the calculations apparently includes a greater particle-size effect and a smaller density effect than is appropriate for urania.

In other experimental work (ANL-7902, pp. 30-31), it was observed that the relative XRF intensities for urania microspheres of narrow particle-size distributions (10-20, 20-30, and 37-44 μ m) at the natural packing density of about 60% of T.D. are similar to those of the same narrow distributions of irregular powder at about 27% of T.D. This indicates that increased bulk density alone does not eliminate particle-size effects.

X-ray fluorescence intensities have been measured for microspheres of solid-solution thorium-uranium of narrow particle size distributions (with diameters of 10-20, 20-30, and 37-44 μ m) at their natural packing densities. Figure III-1 shows that the thorium and uranium count rates (relative to the count rates of the respective metals) are affected by particle size. The heavy-metal XRF signal fraction, $I_U/(I_U + I_{Th})$, differed for samples of different particle sizes, but the ratio obtained by dividing the mean heavy-metal XRF signal fraction by the chemical analysis fraction for the same particle size fraction was the same for all particle size fractions. These data, which are also presented in Table III-1, indicate that adequate precision is achieved for solid-solution microspheres.

2. Green Pellets

a. Effect on X-ray Fluorescence Intensity of Dishing and Original Particle Size of UO₂ Green Pellets

Because current FFTF specifications require pellets with dished ends, it was necessary to verify that XRF analysis is not affected

* Relative intensity, I/I_{std} , for uranium is the ratio of the intensity of the U-L α from uranium oxide to that from uranium metal at the same exciting intensity.

FIG. III-1. XRF of (Th, ~0.25U)O₂ (solid-solution microspheres)

TABLE III-1. XRF of Solid Solution Microspheres $(\text{Th,U})\text{O}_2$ Metal standards: $I_{\text{Th}} = 9312$, $I_{\text{U}} = 9842$

Particle Diameter, μm	$I_{\text{Th}} \pm \sigma$, cps	$I_{\text{U}} \pm \sigma$, cps	Signal Fraction, $I_{\text{U}}/(I_{\text{U}} + I_{\text{Th}})$	Chemical Analysis Fraction	Signal Fraction
					Chemical Analysis Fraction
10-20	5677 ± 122 (2.1%) ^a	2253 ± 45 (2.0%)	0.2842 ± 0.0007 (0.25%)	0.2612	1.088
20-30	5426 ± 59 (1.1%)	2119 ± 26 (1.2%)	0.2809 ± 0.0002 (0.07%)	0.2574	1.091
37-44	5111 ± 116 (2.3%)	2011 ± 42 (2.1%)	0.2823 ± 0.0004 (0.14%)	0.2574	1.097
					Avg., 1.092 ± 0.0051 (0.5%)

^aNumbers in parentheses are values of the relative standard deviation.

by the dished surface. Green pellets were formed from UO_2 having a narrow particle size range, 10-20 μm . Five pellets were formed with flat ends and five with ends dished proportionally to the maximum extent allowed by FFTF specifications, i.e., a dish 0.005 in. deep. Their density was 65% of T.D.

Each pellet was counted three times, and the means and variances of the flat and dished pellets were compared. The count rates (cps) obtained were 10230 ± 54 for pellets with flat ends and 10273 ± 53 for dished pellets; these count rates are not statistically different.

The relative intensity for uranium in pellets formed from 10-20 μm urania powder in the dishing experiments was 1.045 ± 0.006 . This is in good agreement with the relative intensity of 1.040 for a flat pellet obtained by pressing irregular 37-44 μm urania powder to about 65% of T.D. (ANL-7902, pp. 30-31). This indicates that pelletizing to a density of about 60% of T.D. avoids particle size effects on the XRF signal.

b. Effect of Density and Surface Treatment on X-ray Fluorescence Intensity for Green ThO_2 - UO_2 Pellets

The FFTF specifications for fuel pellets allow density to vary by $\pm 1\%$ of T.D. Considerable effort has been devoted to evaluating the effect of density on the XRF of green pellets and to determining whether the resultant variation of the signal fraction is enough to interfere with the precision of analysis of composition.

It was desired to determine whether or not the density of the surface, that is, the material seen by the exciting X-rays and contributing to the XRF signal, is represented by the bulk density (determined from weight and dimensions). The process of pressing or re-pressing (similar to preslugging) or polishing of the surface results in greater changes of the signal fraction than do variations of the bulk density associated with a particular kind of surface. Both for as-pressed surfaces over a density range from 64 to 69% of T.D. and for polished samples over the density range from 52 to 69% of T.D., the relative variation of signal fraction appears to be less than 0.1% per % of T.D. However, the signal fractions for different preparation treatments differ widely (Table III-2). This makes it extremely doubtful that the bulk density is representative of the surface density and that the effect of density is acceptably small. Clark³ attributes a large variation of rate of intensity change with percent theoretical density for MgCO_3 , TiO_2 , Cr_2O_3 , and ThO_2 to unusual density gradients developed during pressing.⁴

Because the reproducibility (RSD) of the signal fraction for "polished re-pressed" surfaces (0.12%) is significantly lower than the RSD of the uranium and thorium count rates (1.0%), association of the count rates for these two elements is presumed to be due to re-pressing. In a practical process, preslugging and mill-mixing would be expected to produce a similar effect. This will be verified with U-Pu oxide pellets fabricated at WADCO.

TABLE III-2. Heavy Metal Signal Fraction $[I_U/(I_U + I_{Th})]$
for Various Surfaces of Green Pellets

Treatment	Densities, % of T.D.	Signal Fraction $\pm$ SD	(RSD)
as pressed	64.2-69.0	0.2492 ± 0.0027	(1.1%)
polished	66.0-68.8	0.2402 ± 0.0039	(1.6%)
re-pressed	69.6-70.2	0.2624 ± 0.0019	(0.71%)
polished and re-pressed	68.4-69.4	0.2471 ± 0.0003	(0.12%)

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IV. ADAPTATION OF CENTRIFUGAL CONTACTORS IN LMFBR FUEL PROCESSING (G. J. Bernstein, N. Quattropani)

Development and testing continue on the stainless steel centrifugal contactor having a 4-in.-ID rotor with a 12-in.-long settling zone and a 15-in. overall length (Fig. IV-1). The ANL contactor is unique in that the settling length-to-diameter (L/D) ratio is 3, whereas in other contactors of similar type the L/D ratio is about 1.4. The contactor is being evaluated to determine its suitability for use in Purex-type solvent extraction processing of LMFBR fuel having high plutonium concentrations. Criticality hazards caused by high plutonium concentrations in the process streams will be controlled in the ANL design by limiting the diameter of the contactor to a geometrically favorable dimension. Expected advantages of centrifugal contactors are (1) reduced radiation damage to the solvent as a result of brief residence time in the contactor and (2) improved ease of operation (including rapid flushout at the end of a processing campaign).

The ANL contactor is a modification of the large centrifugal units in use in the Savannah River (SR) plant. Two modes of operation are possible with the ANL contactor. In the mode used in Savannah River units, aqueous and organic phases are fed into a tee at the bottom of the contactor and then up into a mixing chamber where they are mixed with a paddle mounted on an extension of the rotor shaft. The mixture exits through peripheral slots at the top of the mixing chamber and is then directed through a nozzle into the hollow rotor. The rotor separates the mixed phases by centrifugation as it pumps the liquids up the inside of the rotor. At the top of the rotor, weirs direct the two streams through separate discharge ports into appropriate collector rings.

To operate in the second mode, the ANL contactor is converted into an alternative design in which the mixing chamber and paddle are eliminated. The phases are fed through the side of the casing and are mixed by skin friction as they flow downward through the annulus between the spinning rotor and stationary casing. The mixture is directed into the hollow rotor for phase separation as in the other mixing mode. A contactor operated in the annular mixing mode offers distinct advantages in ease of fabrication, operation, and remote maintenance.

The performance of the contactor in both the SR and annular mixing modes is being studied. The study encompasses determination of phase-separating capacity, hydraulic flow characteristics, the effects of entrained solids, effects of variations in mixing intensity, and measurements of mass-transfer efficiency.

During this quarter, additional tests of separating capacity and hydraulic stability were made with the contactor operated in both mixing modes. Exploratory tests were also made to evaluate the behavior of solids entrained in the aqueous feed.

A. Contactor Operation with Mixing in Bottom Chamber (SR Mixing Mode)

The effect of modifications of the mixing paddle and mixing chamber on

FIG. IV-1. Centrifugal Contactor, Savannah River Mixing Mode

separating capacity* was measured. The aqueous phase was 0.5M HNO_3 and the organic phase was 30% tri-n-butyl phosphate (TBP) in n-dodecane diluent. Three different sizes of four-bladed paddles were used, and the configuration of the mixing chamber was modified by inserting or removing a stainless steel spacer ring or "doughnut." The three paddles used were identified as "B," 3 1/4-in. dia by 5/8 in. high (used in preceding tests); "C," 3-in. dia by 7/8 in. high; and "D," 2 1/2-in. dia by 1 3/8 in. high. The spacer was a stainless steel block with a 4-in. dia, 3/4- or 7/8-in. thickness, and a 1-in.-dia axial passage. It was used to evaluate the effects of reduced mixing-chamber volume upon pumping and mixing characteristics. In these tests, A/O ratios varied from 0.25 to 8, and rotor speeds ranged from 2000 to 3500 rpm.

With the spacer present or absent, separating capacities with the "C" or "D" paddles were essentially the same as those reported earlier for the same unit using the larger diameter "B" paddle (see ANL-7902, pp. 38, 41). In general, hydraulic performance was more stable with the smaller diameter paddles and in the absence of the spacer. This confirms our earlier conclusion that flow surging is primarily caused by excessive pumping capacity in the mixing chamber. Small-diameter paddles operating in the larger mixing chamber have lower pumping capacities than do large-diameter paddles in the smaller mixing chambers.

Hydraulic stability was also tested under conditions of flow ranging from well below ($\sim 25\%$) maximum separating capacity up to the maximum. It was found that proper throttling of the casing drain line (Fig. IV-1, bottom left) to control the rate of air bleed into the mixing chamber was more critical for stable operation at low flow rates and high pumping capacities. In the absence of the spacer and with the "D" paddle, operation was stable at all speeds and throughputs tested when the casing drain line valve was wide open. This mixing chamber-paddle combination appears to be suitable for a broad range of operating conditions. However, it should be emphasized that no single paddle and mixing chamber configuration is likely to give optimum performance for all flow ratios, mixing speeds, and throughputs.

In our test unit, input streams are essentially free of entrained air. Because of the absence of air in the inlet streams in these tests, the contactor is sensitive to the amount of air admitted to the mixing chamber through the casing drain line. However, in a bank of operating contactors, input streams will normally have entrained air, which will tend to reduce the excess pumping capacity of the mixing chamber.

In Purex flowsheets of interest, the A/O ratio is expected to be within a fairly limited range of 0.25 to 2 rather than the extremes of 0.25 to 8. In production operations, contactors are operated at ~ 60 -70% of maximum separating capacity. Therefore, matching of a contactor to very specific operating conditions will not be necessary. However, the good performance of the ANL contactor at A/O ratios beyond the range of Purex flowsheets demonstrates the versatility of the unit.

* Separating capacity is arbitrarily defined as the sum of the flow rates of the organic and aqueous phases when entrainment of one phase in the outlet stream of the other phase reaches a maximum of 1 vol %.

B. Contactor Operation in the Annular Mixing Mode

In the previous report in this series (ANL-7902), it was stated that the contactor body was being modified to permit use of a new bottom section and provide a larger annular gap--0.55 in. instead of 0.275 in. The changes have been made and the new bottom section has been installed. In this configuration, inlet streams enter the casing tangentially about 6 in. above the bottom of the unit (the inlets are lower than in the earlier version). The modified contactor is shown in Fig. IV-2.

The bottom baffle plate is removable to permit changes in baffle configuration. Two different baffle arrangements were tested; the first had four straight radial baffles; the second had four curved baffles arranged to direct the swirling liquid toward the rotor orifice. The second appeared to be somewhat more effective in that liquid level in the annulus was lower. Also, a small, four-bladed paddle was installed in the threaded opening at the bottom of the rotor shaft. This paddle serves to place radial vanes in the region just above the orifice so that liquid entering the orifice is quickly directed toward rotor vanes and then to the periphery of the rotor.

A limited number of separating-capacity tests were made, using 0.5M HNO_3 as the aqueous phase and 30% TBP in n-dodecane as the organic phase. Rotor speeds ranged from 2000 to 3500 rpm and A/O ratios from 0.25 to 4. Results are shown in Fig. IV-3. At A/O = 0.25, separating capacity ranged from ~7 to ~10 gpm at rotor speeds of 2000 to 3500 rpm. At A/O = 2, capacities ranged from ~4.5 to ~7 gpm. At A/O = 4, capacities ranged from ~8 gpm at 2000 rpm to ~14 gpm at 3500 rpm. These last separating capacities were observed with uranium present in both streams, as noted in Fig. IV-3. Separating capacities were increased as a result of the larger annular gap. Except at the highest throughputs at A/O = 4, capacities were not limited by flow restriction in the annulus as had been true with the earlier design. In general, capacities were about the same as those found when the unit was operated in the SR mixing mode, except that the minimum capacities were found at A/O = 2 rather than at A/O = 1.

A characteristic of the annular mixing mode was that the nature of the emulsion formed was somewhat different from that formed in the SR mixing mode. It appeared to be easier to separate dispersed aqueous phase from the bulk organic phase than to separate dispersed organic phase from the bulk aqueous phase. Thus, when operation was near maximum capacity, it was possible to shift the position of the emulsion band (by adjusting the weir air pressure) so that organic phase effluent could be obtained which was entirely free of aqueous entrainment; however, it was not possible to reduce the organic entrainment in the aqueous phase below 0.4%. The relative ease of separation of the two phases was also confirmed by allowing a sample of the emulsion mixed at 3500 rpm to settle under 1 gravity. (The sample was taken from a tangential tap on the annulus.) After 10 sec, the organic phase had cleared except for a very slight milkiness; the aqueous phase did not start to clear until 20 sec had elapsed, and an additional 20 sec were required for complete separation.

Static and dynamic pressures at various points were measured through pressure taps in the contactor casing. Two taps were located near the bottom

FIG. IV-2. Centrifugal Contactor, Annular Mixing Mode

FIG. IV-3. Separating Capacity of 4-in.-dia-Rotor Centrifugal Contactor. Annular Mixing Mode. Aq. 0.5M HNO_3 ; Org. 30% TBP in n-dodecane; 1% Entrainment (Note: Capacities at A/O = 4 were obtained with an aqueous phase of $\sim 0.3\text{M}$ U and 0.3M HNO_3 in 30% TBP-n-dodecane.)

of the casing just above the baffles; one was installed perpendicular to the circumference to measure static pressure, and the other was installed tangentially to measure the kinetic energy of the fluid spinning in the annulus when converted to pressure head. The third tap was located in the bottom plate just below the rotor orifice to measure the net pressure of the fluid entering the orifice. These taps were connected to polyethylene standpipes to permit observation of pressure heads. A fourth plastic standpipe was connected to one of the original side inlets to indicate the level of fluid in the annulus.

Observation of the standpipes during the various runs showed that (1) the static head was slightly greater than the height of fluid in the annulus and (2) the tangential pressure was about twice as great. The pressure head developed below the rotor orifice was about equal to the height of fluid in the annulus. It had been anticipated that the pressure below the orifice would be higher than the static head due to conversion of some of the kinetic energy of the fluid into pressure by the baffles on the bottom of the casing. The lower-than-expected pressure at the rotor orifice may in part be due to skin friction between the bottom surface of the rotor and the emulsion, causing the part of the emulsion above the baffles to rotate and to develop a centrifugal force that throws the fluid away from the orifice.

The level of liquid in the annulus must be prevented from rising too high to avoid (1) overflow into the organic phase collector ring and (2) over-mixing. Although increased mixing effectiveness at increased flow rates is desirable to maintain high stage efficiency, excessive mixing might inhibit phase separation and prevent the contactor from operating at its highest potential capacity.

Since the static pressure is used to drive the fluid through the rotor orifice, it would be expected that the level of emulsion in the annulus would rise as the pressure drop through the orifice increases with higher flow rates. Another factor causing emulsion level in the annulus to rise is that vigorous agitation in the annulus causes air to be whipped into the emulsion, resulting in a lower fluid density. The net effect of the aforementioned flow characteristics is to cause the fluid level in the annulus to rise as the throughput or the rotor speed increases. Although excessive liquid levels are not anticipated in normal operation, these factors causing excessive levels apparently contributed to limiting the capacity at 3000 and 3500 rpm and $A/O = 4$.

In an effort to reduce the height of fluid in the annulus, a small paddle was mounted inside the rotor just above the orifice to remove fluid from that region and assist the flow of fluid into the rotor. Curved radial vanes were also installed in the bottom of the casing to improve the conversion of kinetic energy to pressure head. Both of these changes resulted in a slight drop in annular fluid height and a slight increase in separating capacity.

It appears desirable that the elevation of the inlet lines in the present design be lowered further, since very vigorous mixing takes place in the annulus. Another change incorporated in the present design was to install

a tangential take-off line near the bottom of the casing to permit bypassing some of the fluid from the annulus directly to the bottom of the casing below the rotor orifice. In this way, more of the kinetic energy developed in the annulus can be used to force fluid through the orifice. The net effect was to reduce the height of fluid in the annulus and reduce the tendency to overmix at high rotor speeds. This feature could make the annular contactor design adaptable to a greater range of flow ratios and solution compositions than are likely to be encountered in Purex-type process flowsheets. The overall simplified construction of the annular contactor offers significant advantages over the SR design with respect to fabrication costs, operation, and maintenance.

C. Tests of Effect of Solids in the Feed Stream

Concern is often expressed that, in the operation of centrifugal contactors, solids in the feed stream will accumulate in the rotor and ultimately fill the rotor to the extent that the unit will become inoperable. Solids likely to appear in feed streams are of two kinds--fine, heavy particulate solids carried over from the dissolver, and solids resulting from solvent decomposition products, generally called "interface crud." Since it is the usual practice in plants processing fuel by solvent extraction to clarify the dissolver solution by centrifuging to remove undissolved particulate solids, heavy solids are not likely to constitute an operating problem.

At Savannah River,¹ the effect of solids in the aqueous feed was evaluated by using feed solutions containing various quantities of manganese dioxide. The MnO_2 tends to be quite flocculent and thus settles very slowly in an aqueous medium. However, it will separate more readily in a centrifugal contactor than will true "interface crud," which normally tends to float at the aqueous-organic interface in other types of contactors. Because the amount of MnO_2 that will collect in a rotor is sensitive to its physical form, widely varying amounts can accumulate during tests of a centrifugal contactor. Thus, in a multistage test¹ of a 10-in.-dia contactor using feed containing 5000 ppm of MnO_2 , approximately 2 kg accumulated in each unit when steady state conditions had been reached, whereas only 25 g of MnO_2 had collected in similar single-stage tests. The presence of 2 kg solids in the rotor did not interfere with the hydraulic performance of the contactors.

Four tests with MnO_2 at concentrations up to 2600 ppm were made with the ANL contactor. The MnO_2 was prepared by adding NH_4OH to a solution of $KMnO_4$. Various concentrations of MnO_2 in the feed were used, and all tests were made at an A/O ratio of 1, using 0.5M HNO_3 plus MnO_2 as the aqueous feed and 30% TBP in n-dodecane as the organic feed. Two tests were made with the contactor operated in the annular mixing mode and two in the SR mode. For each mode, a run was made at 2000-rpm rotor speed and 4-gpm total throughput, and another run was made at 3500 rpm and 7-gpm throughput.

It was noted that MnO_2 appeared immediately in the aqueous effluent stream, indicating that at no time was all of the suspended material deposited in the rotor. The relative concentration of MnO_2 in the aqueous effluent stream was determined periodically by centrifuging 120-ml samples and observing the level of settled solids. After about 30 min of operation, the

quantity of MnO_2 in the effluent stream levelled off and was apparently equal to the quantity in the feed solution. After ~1 hr, 1-liter samples of the feed solution and the aqueous phase effluent stream were taken, filtered, dried, and weighed to establish that an equilibrium condition had been achieved. No MnO_2 solids were observed in the organic phase effluent stream under any test conditions.

Following each test, the MnO_2 accumulated in the rotor was removed by flushing with water followed by flushing with oxalic acid and nitric acid. Test results are tabulated in Table IV-1. These results show that even with the very high solids loading in the feed, little material was retained in the rotor. No operating difficulties were encountered in these runs and it is quite reasonable to assume that the much lower concentration of less dense "interface crud" likely to be found during Purex-type processing would cause no difficulties.

D. Planned Extraction of Uranium in Centrifugal Contactor

Preparations have been completed for measuring the extraction efficiency of the contactor using natural uranium. A number of runs will be made under extraction and stripping conditions with the contactor operated in the SR and annular modes.

TABLE IV-1. Contactor Runs with MnO_2 Solids

	Runs			
	123A ^a	123B ^a	124A ^b	124B ^b
MnO_2 conc. in aqueous feed, ppm	1600	1400	2600	2400
Total flow rate (A/O = 1), gpm	4	7	4	7
Rotor speed, rpm	2000	3500	2000	3500
Running time, min	75	45	70	85
Total aqueous throughput, gal	150	155	140	300
Retained MnO_2 , g	53	50	83	105

^aAnnular mixing mode.

^bSR mixing mode.

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ERRATUM

In the preceding report in this series (ANL-7902), the curves in Fig. IV-2 are incorrectly keyed. In that graph, the top curve represents data for 3500 rpm, the second curve data for 3000 rpm, the third curve data for 2500 rpm, and the bottom curve is keyed correctly.

V. ELECTROLYTIC REDUCTION AND REOXIDATION
OF PLUTONIUM IN PUREX PROCESSES
(M. Krumpelt, J. J. Heiberger, M. J. Steindler)

In Purex processes, the valence of plutonium is alternated between the tetra- and the trivalent states. Currently, reduction and reoxidation are accomplished by chemical means. An electrolytic valence adjustment is more direct, more easily controllable, and waste-free. Development of an on-stream electrolytic method is confronted with the requirements that reduction rate be adequate and that interference from nitric acid be avoided.

In the past, the major effort of the work was to investigate the prerequisites for an adequate reduction rate, judged from a process standpoint. An equation relating the highest possible current density, the so-called limiting current density, to various process parameters was developed (ANL-7799, p. 57). Two empirical constants needed for the equation were determined experimentally with a stand-in electrolyte for plutonium (ANL-7871, pp. 42-52). The equation was then used to estimate the "half-reduction time" for Pu(IV) as a function of flow velocity, characteristic electrode dimension, and other parameters.

More recently, a new electrolytic cell (ANL-7902, pp. 48-49) was designed to measure the rate of reduction with various combinations of parameters and to reconcile the measurement with the derived equation. Briefly, the cell consists of a recirculating catholyte, flowing at various speeds through a wire-screen cathode. Two symmetrically placed anodes are separated from the catholyte by two diaphragms (presently, fritted glass). Differently shaped and dimensioned cathodes can be used. Voltage control is potentiostatic. In a typical experiment, the catholyte is sampled periodically during an electrolysis and later analyzed for plutonium valence composition.

A. Plutonium Valence Analysis

The plutonium valence analysis is performed by absorption spectroscopy. A Cary 14 spectrophotometer is used. The analytical procedure is as follows: A sample from the electrolytic cell is diluted and transferred into a 1-cm spectroscopic cell, which is placed in a Plexiglas holder equipped with quartz windows. The holder serves as both positioner and liquid-tight secondary container and is placed in the spectrophotometer for recording of the spectrum. The spectrum is evaluated using the molar absorptivities reported by Schmieder *et al.*¹

A Pu(III) nitrate standard, prepared from a weighed amount of plutonium metal, was analyzed and evaluated spectroscopically by Schmieder's method and also by Hagan and Miner's² method. Table V-1 shows that at least for Pu(III), the plutonium concentrations obtained by both methods agree exceptionally well with each other and also with the nominal concentration. Schmieder's method, which defines the effect of nitric acid on the spectra more accurately, is preferred.

TABLE V-1. Analysis for Plutonium in a Nitrate Standard Solution (mol/liter)

Evaluation Method	Pu(III)	Pu(IV)	Total	Nominal
Schmieder <u>et al.</u>	0.0344	0.0005	0.0349	0.0351
Hagan and Miner	0.0343	0.0002	0.0345	0.0351

B. Limiting Current Density

The new recirculating electrolytic cell was installed in the glovebox and used for the first time with plutonium nitrate electrolyte. The electrolyte was prepared by diluting a stock solution obtained from the Hanford reprocessing plant. A spectrochemical analysis indicated that 200 ppm of iron was the major metallic impurity. The electrolyte contained 15.1 g/liter plutonium in 0.5M HNO_3 . The valence composition of the plutonium indicated by spectrophotometric analysis was 10% Pu(III), 87% Pu(IV), and 3% Pu(VI). The catholyte volume was 1 liter. The electrolytic cell was the same as that described in ANL-7902, except that the impeller and orifice plate holder were stainless steel and not gold-plated. The cathode consisted of a circular piece of 45-mesh platinum screen having a wire diameter of 0.20 mm and was coated circumferentially with a polyester resin. The total cathode area was 11.7 cm^2 . Two platinum discs were used as anodes in a 0.5M HNO_3 anolyte. The current was regulated by a Wenking potentiostat; the cell was operated in a thermostatic bath at 30°C.

Current-versus-voltage curves in a plutonium nitrate electrolyte were measured at three different flow velocities, 0.78, 1.27, and 2.41 cm/sec. The objective of this phase of the experiment was to help select a proper cathode potential and flow velocity for the subsequent reduction experiment. The results should be considered preliminary, particularly since the current was allowed to stabilize for only 2-3 min after each change of potential. (This duration may not be sufficient to attain a steady state.) Also, the concentration of Pu(IV) decreased by 3-4% during each of the three measuring periods.

Figure V-1 shows that the current densities were relatively steady in the region between -0.05 and +0.5 V. The level of these plateau-like regions increased with increasing flow velocity, indicating that the electrode reaction is diffusion-controlled. These results, though tentative, may be compared with current densities calculated from the previously derived equation (ANL-7871, p. 51)

$$i_L = N F c D_{jk}^{0.66} v^{0.3} \nu^{0.03} L^{-0.7}$$

where i_L = limiting current density, A/ cm^2

F = Faraday constant, A-sec/equiv

D_{jk} = diffusion coefficient, cm^2/sec

v = linear flow velocity, cm/sec

ν = kinematic viscosity of electrolyte, cm^2/sec

FIG. V-1. Current Densities at Various Cathode Potentials for Three Flow Velocities

FIG. V-2. Relation Between Limiting Current Density and Flow Velocity

- c = concentration of electroactive species, mol/cm³
 L = characteristic electrode dimension, cm
 N = electric equivalents per mole of ions

For the diffusion coefficient, D , the value of 5.8×10^{-6} cm²/sec determined by Peters and Shultz³ was used. The kinematic viscosity, ν , was estimated to be 9×10^{-3} cm²/sec. The calculated and experimental limiting current densities are plotted as functions of flow velocity in Fig. V-2. The experimental points at a voltage of +0.1 were taken from Fig. V-1 and were normalized for a concentration of 0.0486 mol Pu/liter. The experimental data confirm the prediction that the exponent for the flow velocity in the above equation is 0.3, but demonstrate lower-than-expected absolute values for the limiting current densities.

C. Reduction Experiments

In the next phase of this experiment, the cell was operated for 5 hr at a fixed cathode potential of +0.14 V (standard H₂) and a flow velocity of 1.3 cm/sec while the electrolyte was periodically sampled and analyzed. The current passing through the cell was recorded. The purpose of this phase of the experiment was to relate the observed changes in composition to the amount of current passed. In an electrolysis in which only Pu(IV) is reduced and the electrolysis is diffusion-limited, the logarithm of the concentration should change linearly with time. Figure V-3 indicates that the reduction of Pu(IV) in nitric acid does not follow this simple model. As Pu(IV) is being depleted, the reduction becomes less efficient. A measure of the efficiency is the ratio of the amount of transformed plutonium to the integrated current. The ratio can be calculated from Fig. V-4, which shows these two quantities expressed as Faradays and plotted against time. The overall current efficiency decreased as electrolysis proceeded and was less than 25% for this run.

The medium in this reduction experiment was 0.5M HNO₃. Nitric acid can be reduced electrolytically by a very complex mechanism involving nitrous acid (ANL-7871, p. 52). The low current efficiency in this experiment was attributed to nitric acid reduction and/or reoxidation of Pu(III) by nitrous acid.

Consequently, in the next reduction experiment, hydrazine was added to the catholyte (0.5M nitric acid containing 15 g/liter plutonium) as a scavenger for nitrous acid. The amount added made the electrolyte 0.005M in hydrazine; however, upon the addition of hydrazine, considerable gas evolution was observed (as occurs when hydrazine reacts with nitrous acid) and probably lowered the quantity of hydrazine in the electrolyte. In this 3-hr reduction experiment, the current efficiency was 100%, which confirms the hypothesis that nitrous acid plays a decisive role in the electrolysis.

FIG. V-3. Electrolyte Composition during Electrolysis

FIG. V-4. Current Utilization

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VI. DISPOSAL OF TRITIUM AND NOBLE GASES

(L. E. Trevorrow, R. L. Jarry, M. J. Steindler)

An evaluation is being made of the disposal of tritium and noble-gas fission products from the nuclear generation of electrical power. At present, all tritium and noble gases produced at nuclear facilities are diluted in water or air, usually until their concentrations are much below the recommended limits, and discharged to the environment. Recent concern about biological effects of discharging low-level radioactivity has stimulated proposals to lower the permissible concentrations in discharges from light-water reactors.¹ Even where discharges meet local requirements, concern about the accumulation of 12.62-yr tritium and 10.76-yr ⁸⁵Kr in the biosphere may eventually lead to the requirement that tritium and noble gases be separated from the effluent streams of reactors and fuel-reprocessing plants and isolated from the biosphere.

The purpose of this project is to help ensure that procedures for disposal that isolate these gases from the biosphere are available if they are required. It is planned initially to evaluate procedures and later to do experimental testing of problematic stages of procedures.

This program is related to a number of activities sponsored by the USAEC and other bodies to minimize the effects of nuclear power generation on the environment. The related activities have included (1) evaluation of the significance of an increasing environmental inventory of tritium and krypton-85,²⁻⁸ (2) monitoring for tritium and noble gases in the effluent streams of nuclear facilities,⁹⁻¹⁷ (3) development of reactor management practices that would decrease radioactive discharges,¹⁸⁻²¹ (4) development of processes for the separation of noble gases from effluents,^{8,22} (4) development of processes for the separation of noble gases from effluents,^{8,22} and (5) studies of methods of storing noble gases.^{8,22,23} The question of the significance of buildup of tritium in the environment has been debated extensively in the past few years, but relatively little attention has been given to methods of collecting tritium and isolating it from the environment^{24,25} should this become required.

A necessary foundation for this work is information characterizing the streams that carry tritium and noble gases. Therefore, information is being surveyed on the behavior of these wastes in the types of facilities most likely to play major roles in U. S. electric utility systems.

Three types of reactors are in this category: boiling-water reactors (BWRs), pressurized-water reactors (PWRs), and liquid-metal fast-breeder reactors (LMFBRs). All three reactor types produce by the fission process a number of isotopes, both stable and radioactive, of xenon and krypton. The only radioactive isotope of a noble gas that requires long-term storage is 10.76-yr ⁸⁵Kr. The other noble-gas isotopes, many of which are formed in high relative abundance, have short half-lives. Noble-gas fission products are contained in the plant effluent streams as a complex mixture of xenon and krypton isotopes, with a composition that changes rapidly with time. Thus, although estimates of production rates of ⁸⁵Kr and stable isotopes may be readily predicted from fission yields and reactor power level, if separation of noble-gas fission products is required, the estimates of

processing rates of shorter-lived isotopes are strongly dependent on arbitrary assumptions of the decay period before processing.

In all three types of reactors, tritium is generated by fission and by neutron activation of boron, lithium, and deuterium. The tritium generation rates by neutron activation reactions differ greatly for the three types of plants.

This report summarizes information on the behavior of tritium and noble-gas fission products in a PWR, a BWR, and a LMFBR, each of 1000-MW(e) capacity, wherever such information is available. The discussion includes a description of each type of reactor and associated components, estimates of the rates of waste generation, estimates of the release of wastes at the reactor site, and a consideration of the paths of these wastes in the reactor system. These topics were chosen to portray the primary sources of the wastes, the total waste-disposal load, and the problems and quantities related to collection of wastes at the reactor site.

The chemical forms of wastes at a reactor site and the nature and concentrations of accompanying materials differ from those at a fuel-reprocessing site. Therefore, problems related to the processing and the ultimate storage of wastes may also differ for the two types of facilities.

A. Behavior of Tritium and Noble Gases in Boiling Water Reactors

A recent listing of the numbers and power ratings of U. S. civilian BWR power stations shows that BWRs are expected to make an important contribution to electric power production with over 35,000-MW(e) installed capacity by 1980.²⁶

The production and emission of tritium and noble gases at a 1000-MW(e) BWR must be based on calculations and projections because BWRs of this size have not been observed in full-power, routine operation. The generation rates of wastes can be estimated from known fission yields and from projections of specific power, fuel loadings, and exposure times. Emission data, indicative of the disposal loads if wastes are collected at the reactor, are available in detail only for small, first-generation BWRs. Full characterization of releases from a large BWR must await further operation and surveillance. Design estimates of emissions for large BWRs are listed in the Preliminary Safety Analysis Reports for reactors in the 1000-MW(e) range, usually 1100-MW(e) reactors,²⁷⁻²⁹ but these design estimates are conservative; expected emissions are much lower than the estimates.

1. The BWR System; Reactor and Radwaste Flow

A typical BWR system can be described^{30,31} in terms of the components relevant to the behavior of tritium and noble-gas fission products as follows: The reactor vessel is usually situated in an air-ventilated chamber termed the Drywell. Inside the reactor vessel, coolant water is circulated through a core consisting of sintered pellets of slightly enriched UO_2 in Zircaloy tubes. Passage of the steam-water mixture from the core through steam separators and dryers contained in the head of the reactor vessel reduces the moisture content to 0.3 percent maximum. The steam enters the high-pressure turbine casing at 1050 psi, flows through additional moisture

separator units, and into the low-pressure casings of the turbine. From the turbine, the steam flows into the main condenser. The condenser is maintained at a vacuum, and since the seals on the system are not perfect, air leaks into it. Some large BWR systems^{27,29} have been designed to accommodate an air leak up to 60 cfm, but efforts are made to minimize the leak rate, and the expected value is about 20 cfm. This air and any other noncondensable gases are removed from the system by a steam jet ejector that vents to a smaller condenser and the stack. The condensate from the main condenser passes through filters, demineralizer beds, and heaters, and then returns to the reactor.

The reactivity-control system is the locus of generation of a major fraction of the total tritium produced by a BWR. Part of the reactivity control in BWRs has customarily been effected by neutron absorption [^{10}B ($n, 2\alpha$) ^3H] in rods consisting of powdered B_4C contained in stainless steel cladding.³⁰ BWRs do not use boron dissolved in the primary coolant for reactivity control. Although relatively large amounts of tritium are produced in control rods in a BWR, there is no conclusive evidence at present that control rods release significant quantities of tritium at the BWR site.

Figure VI-1 shows a simplified scheme of a typical BWR off-gas system; only the components important in the behavior of tritium and noble gases at the BWR site are included. The main condenser exhaust is the most important gas stream with respect to discharge of noncondensable radioactive gases. This stream is delayed 20-30 min, then pumped through filters to the stack. The purpose of this holdup is mainly to permit sampling before discharge; the decay of some of the short-lived isotopes during holdup is an incidental benefit.

A large steam turbine will contain a number of gland seals to prevent steam leaking along the rotor.^{32,33} Seals of the labyrinth type usually consist of stationary circular blades, their planes positioned normal to the rotor axis. Process steam has customarily been supplied to these glands to prevent steam leaking from the ends of each turbine casing. Part of the steam supplied to the glands flows into the turbine, and the remainder flows into the gland exhaust system.

The turbine gland-seal exhaust is of secondary importance in the discharge of radioactive gases. This gas stream is held up for 2-3 min to permit the decay of 7.13-sec ^{16}N and 26.8-sec ^{19}O , formed by neutron activation of air and water in the core. The main condenser exhaust and the gland-seal exhaust should carry the same radioactive constituents, but because only a small amount of the primary steam enters the gland-seal system, the release rate of radioactive gases from the gland-seal system to the environs⁹ will be approximately 0.1% that from the main condenser off-gas system.

Plans for operation of large BWRs of the near future²⁸ include the use of a steam source independent of the primary cycle, thereby eliminating radioactive emissions from the gland-seal exhaust.

Figure VI-2 shows a simplified scheme of a typical BWR liquid radwaste system. Only the minimum details necessary to illustrate the path of tritium release into liquids are shown. The scheme that has been

FIG. VI-1. Typical 1000-MW(e) BWR Off-Gas System

FIG. VI-2. Typical BWR Liquid Radwaste System

used for most BWRs involves segregation into two internal streams on the basis of their radioactivity and dissolved-solids content (as indicated by ionic conductivity). "Clean waste" (of high radioactivity and low conductivity), collected mainly from equipment drains, is filtered, demineralized, and recycled. "Dirty waste" (of low radioactivity and high conductivity), collected mainly from floor drains, is unsuitable for demineralization because of its high content of dissolved solids and is therefore filtered and discharged.

2. Tritium Generation in a BWR

Sites of tritium generation in a BWR are numerous. They include fuel (light-particle emission in fission), control rods (neutron activation of boron), primary coolant (activation of naturally occurring deuterium), and structural materials (neutron activation of lithium and boron impurities). The last site is of minor importance. The generation rates of tritium in a 1100-MW(e) BWR, based on GE design figures,³⁴ are summarized in Table VI-1. These values will vary for different burnups and management of fuel and control rods.

TABLE VI-1. Generation Rate of Tritium
from Various Sources in a 1100-MW(e) BWR

<u>Source</u>	<u>Generation Rate</u>	
	<u>μCi/sec</u>	<u>Ci/yr</u>
Fission	820	25,000
Deuterium Activation, $^2\text{H}(n,\gamma)^3\text{H}$	0.43	14
Boron Activation (control rods) $^{10}\text{B}(n,2\alpha)^3\text{H}$ $^{10}\text{B}(n,\alpha)^7\text{Li}; ^7\text{Li}(n,\alpha)^3\text{H}$	330	10,400

3. Appearance of Tritium at the BWR Site

The problem of disposal of tritium at the reactor site originates with its appearance in the primary coolant. The appearance rate of fission-product tritium in BWR effluent streams depends strongly on the integrity of fuel cladding. If the cladding has no defects, the most important source of tritium in effluents consists of relatively small amounts formed by neutron activation of naturally occurring deuterium in the coolant.³⁴ Although large amounts of tritium are formed in control rods, it has not been established whether tritium penetrates their stainless steel cladding.^{34,35}

It is commonly assumed that tritium escaping through fuel-cladding defects as atomic or molecular tritium is converted rapidly to THO in the primary coolant because of the highly active nature of reactor water in the radiation field.¹¹ GE design features³⁴ indicate that about 17 Ci/yr of tritium is expected to appear in the reactor water of a 1100-MW(e) BWR;

however, experience at the 237-MW(e) KRB Gundremmingen plant³⁴ indicates that up to 1% of the tritium produced by fission might appear in either liquid or gaseous effluents. If this occurs in a 1000-MW(e) plant, 250 Ci/yr could appear in gaseous or liquid streams.

In past and present operation of BWRs, tritium appearing in the primary coolant has been released to the environs in both liquid and gaseous discharges. Observed quantities of tritium discharged in liquids at individual BWR sites in recent years²⁰ have ranged from <1 to 50 Ci/yr. Although the concentration of tritium in most plant fluids may be 10^{-2} to 10^{-3} $\mu\text{Ci/ml}$,⁹ liquid wastes are usually diluted with the main condenser coolant before discharge, and the concentration in discharge canals has been in the range of 20 pCi/liter²⁰ on the basis of experience for the years 1967-1969. This concentration is extremely low in comparison to the guide level in drinking water 3×10^6 pCi/liter²⁰ and also is low in comparison to the proposed¹ guide level of 5×10^3 pCi/liter.

Surveillance at Dresden I reactor showed⁹ that of all tritium discharged at the site, about 10% was in gaseous effluent and 90% was in liquid effluent. However, only the gaseous tritium in the delay line of the condenser exhaust was measured. The surveillance report recommended that the stack effluent be monitored in future work, implying that the total THO released in gases may have been greater than that in the condenser exhaust. In future operation of large BWRs, a greater fraction of the total tritium released will appear in the gaseous streams because of efforts to increase recycling of primary coolant; perhaps 50% will be released in gaseous effluents and 50% in liquid effluents.³⁴ Figure VI-3 summarizes the probable paths of tritium in a 1000-MW(e) BWR.

Perhaps the most difficult aspects of the problem of separating tritium from BWR effluents are due to the large volume of the water-vapor-bearing effluents and the low concentrations of THO in H_2O .

Recent reports differ in identifying the main pathways for gaseous THO in a BWR. One report²⁰ identifies the exhaust from the main condenser and the gland seal as the major carrier of gaseous THO ($\text{THO-H}_2\text{O}$ vapors). However, the quantities of water leaving the reactor via these exhaust streams are probably too small, since they both flow through condensers, to account for all tritiated water leaving the reactor. For example, although the release of primary coolant in the main condenser exhaust of Dresden I was only 3 ml/sec or about 0.26 ton/day, the total release of process water as moisture from a BWR may be higher by a factor of 10^2 . A subsequent report³⁴ identifies the building ventilation streams that join in the stack as the major carriers of gaseous THO released at the reactor. The THO is said to enter the ventilation streams through numerous equipment leaks and by evaporation from pools of process water.

Thus, unless the tritium in gaseous effluents can be assigned to a stream of lesser volume, the gas stream that must be considered in any separation process is the stack exhaust. This stream will contain a large volume of air, a relatively large volume of H_2O , and a low ratio of THO to H_2O . As an example, the stack exhaust of the KRB Gundremmingen plant carries about 100 tons of moisture per day, of which 1/10 to 1/3 is process water.³⁴ If the process water contains 10^{-2} to 10^{-3} $\mu\text{Ci/ml}$, the stack exhaust should contain 6×10^{-5} to 200×10^{-5} ppb THO in H_2O .

See Fig. VI-2 for system of disposing of liquid wastes in equipment and floor drains.

* Experience at Dresden I reactor⁹ indicates tritium concentration in the fuel storage pool will be similar to that in primary coolant, $\sim 10^{-2}-10^{-3}$ μ Ci/ml.

FIG. VI-3. Probable Flow Pattern of Tritium in a 1000-MW(e) BWR

A total of 8.5 to 250 Ci will flow through the major liquid pools in a BWR in a year. This liquid will be processed if separation or storage of tritium is required. These pools are the primary coolant, the equipment drain system, the floor drain system, and the fuel storage pool. Although the radioactivity and dissolved solids content of these pools differ, the concentration of tritium can be expected to be about the same in all pools, 10^{-2} to 10^{-3} $\mu\text{Ci/ml}$ or 6×10^{-3} to 6×10^{-4} ppb THO in H_2O .^{9,34}

4. Generation of Noble-gas Fission Products at a BWR

The noble gases xenon and krypton are generated in significant quantities by fission within the fuel assemblies and in relatively insignificant quantities by fission of tramp uranium on the surface of fuel assemblies.

Because of their short half-lives, the generation rates of many noble-gas fission-product isotopes are inconsequential in relation to long-term disposal problems. The generation rate of 10.76-yr ^{85}Kr , the isotope of most importance to long-term disposal considerations, was calculated to be about 3.8×10^5 Ci/yr in a 1000-MW(e) or 3000-MW(t) BWR from listed yields³⁶ for the fission of ^{235}U by thermal neutrons.

5. Appearance of Noble Gases at the BWR Site

Except for the relatively insignificant amounts of noble gases released by the fission of tramp uranium, noble gases are emitted at the reactor site by diffusion through small cladding defects into the coolant and thence into the main condenser where the steam jet ejector sweeps out noncondensable gases.

The composition of the noble-gas mixture emitted at the reactor site varies with the irradiation history of the fuel and the cladding leak rate. Three models for noble-gas mixtures to be found at the reactor site have been defined;^{20,37} (1) the recoil mixture gases removed from the core soon after fission, (2) the equilibrium mixture gases present in fuel after one month of irradiation; all isotopes except ^{85}Kr are in radioactive equilibrium, and (3) the diffusion mixture gases that leak from UO_2 fuel through defective cladding. The mixture escaping from small defects would approach the diffusion mixture, whereas the mixture escaping from large defects would have the spectrum of the recoil mixture superimposed. Calculations of the composition of noble-gas fission-product mixtures as a function of decay time³⁷ indicate that ^{85}Kr is a minor constituent at short decay times, but becomes a major constituent after decay times of 3 to 60 days. The main condenser off-gas after the normal 30-min holdup of this stream would consist of a mixture of roughly equal parts of xenon and krypton.

The predicted maximum quantities of noble-gas radioisotopes emitted from a BWR of 1100-MW(e) capacity (Table VI-2) are available from a design estimate;²⁷ no results of surveillance for routine operation of a reactor of this size are available. The estimates are based on the release of a diffusion mixture with a total noble-gas emission rate of 10^5 $\mu\text{Ci/sec}$ or 3×10^6 Ci/yr. These estimates are understood to be conservative; emissions during operation are expected to be at 2% of these rates or 6×10^4 Ci/yr; the highest observed emissions to 1969 are about 20% of the estimated rates. The amounts (Table VI-2) are the maxima that might be emitted in the absence

of any removal or decay treatment other than a 30-min holdup. The decay scheme for ^{85m}Kr indicates that 19% of its disintegrations result in ^{85}Kr ;³⁶ therefore, 19% of the ^{85m}Kr separated from reactor effluents will constitute a small additional quantity of gas that requires long-term storage.

TABLE VI-2. Predicted Maximum Amounts^a of Radioactive Noble-gas Isotopes Emitted Annually by an 1100-MW(e) BWR

Isotope	Half-Life	Ci/yr	mol/yr
^{89}Kr	3.2 m	1.1×10^4	1.9×10^{-7}
^{137}Xe	3.8 m	2.9×10^4	6.0×10^{-7}
^{135m}Xe	15.6 m	2.7×10^5	2.2×10^{-5}
^{138}Xe	14 m	8.2×10^5	7.4×10^{-5}
^{87}Kr	76 m	4.92×10^5	2.0×10^{-4}
^{83m}Kr	1.86 h	9.5×10^4	5.5×10^{-5}
^{88}Kr	2.8 h	5.4×10^5	4.8×10^{-4}
^{85m}Kr	4.4 h	1.6×10^5	2.3×10^{-4}
^{135}Xe	9.2 h	5.77×10^5	1.7×10^{-3}
^{133m}Xe	2.3 d	6.3×10^3	1.1×10^{-4}
^{133}Xe	5.27 d	1.7×10^5	6.9×10^{-3}
^{131m}Xe	11.9 d	3.8×10^2	3.5×10^{-5}
^{85}Kr	10.76 y	2.6×10^2	7.8×10^{-3}

^aCalculated from design values for a diffusion mixture, based on a total emission rate of 100,000 $\mu\text{Ci/sec}$ (3×10^6 Ci/yr) after 30-min holdup. This is a conservative estimate. Operating values may be 2% of these; observed maximum values (to 1969) in smaller BWRs were 20% of these.²⁷

The estimated total emission rate (3×10^6 Ci/yr) of noble gases from an 1100-MW(e) BWR can be compared with observed emission rates for plants of lower power ratings. Preliminary reports of emissions in 1970 at Oyster Creek, 540 MW(e); Tarapur 1 & 2, 420 MW(e); and Tsuruga, 331 MW(e), ranged from 2×10^4 to 8×10^5 Ci/yr.²⁰

If separation of noble gases from effluents of a BWR is required, the exhaust from the main condenser is the stream of primary importance since it contains about 99.9% of all noble gases released into the primary coolant and contains smaller amounts of air than the stack exhaust (which also carries building ventilation air).

Table VI-3 shows the predicted total annual amounts of xenon and krypton in the main condenser exhaust stream of an 1100-MW(e) BWR, having air inleakage of 20 cfm. The total annual amounts of xenon and krypton radioisotopes are about 9×10^{-3} mol each, rather small quantities in spite

of corresponding large numbers of curies. The concentrations of xenon and krypton in the exhaust stream are not significantly higher than the normal concentrations of xenon and krypton in air, 0.087 and 1.14 ppm,³⁸ respectively.

TABLE VI-3. Predicted Amounts^a of Total Xenon and Krypton Isotopes in Exhaust from Main Condenser of 1100-MW(e) BWR

Source	Xenon		Krypton	
	mol/yr	liters (STP)/yr	mol/yr	liters (STP)/yr
Air Leaking into Equipment ^b (stable xenon and krypton)	1.2	28	15	340
<u>Fission Products Leaking from Fuel</u>				
Radioactive Isotopes ^c	9×10^{-3}	0.2	9×10^{-3}	0.2
Stable Isotopes	9×10^{-1}	20	1×10^{-1}	2

^aAfter 30-min holdup.

^bValues based on 20-scfm air inleakage; for other design of BWRs of this capacity, values of air leaks range from 1 to 60 scfm.

^cBased on a total emission rate for all radioactive noble gas isotopes of 100,000 $\mu\text{Ci/sec}$; anticipated operating values are 2% of this, and maximum values experienced in 1969 were 20% of this emission rate.

Figure VI-4 is a simplified diagram of the flowpath of noble gas fission products in a BWR and indicates the estimated quantity of ^{85}Kr vented to the stack, 260 Ci/yr [~ 0.2 liter(STP)/yr].

The main condenser exhaust stream will also carry 154 cfm of H_2 and 77 cfm of O_2 from radiolysis of reactor water, but these two gases will be eliminated by catalytic recombination (to be used in several modern large BWRs). The stream also will contain the activation product, ^{13}N , and the fission product, ^{131}I . Nitrogen-13 is expected to appear at a rate of $3.4 \times 10^2 \mu\text{Ci/sec}$ ²⁹ (after a 30-min holdup), corresponding to 11,000 Ci/yr or 5.7×10^{-7} mol/yr. The rate of evolution of ^{131}I in gaseous form from the 210-MW(e) Dresden I reactor at the time of a thorough surveillance⁹ was $9.2 \times 10^{-4} \mu\text{Ci/sec}$, corresponding to 3.0×10^{-2} Ci/yr, or 18×10^{-10} mol/yr.

B. Behavior of Tritium and Noble-gas Fission Products in Pressurized Water Reactors

PWRs installed by 1980 are expected to make the largest contribution to U.S. nuclear power generation in the near future, over 61,000-MW(e) capacity.²⁶ Since the behavior of tritium and noble gases in a 1000-MW(e) PWR has not been fully characterized by observation, their behavior must be inferred from design data for large plants and experience from smaller plants.

*This number is based on Preliminary Safety Analysis Estimates²⁷ of the emission of total noble gases at a rate of 10^5 μ Ci/sec.

FIG. VI-4. Simplified Path of Noble Gas Fission Products and Estimated Quantities of ^{85}Kr in a 1000-MW(e) BWR

1. PWR System

Pressurized-water reactors are distinguished from boiling water reactors by several characteristic differences. The two most obvious differences are (1) the coolant system in the PWR is operated at higher pressure, 2250 instead of 1050 psia, and (2) the reactor coolant cycle and the working fluid cycle are separate in the PWR, whereas in the BWR the reactor coolant is also the working fluid.

In a typical PWR system, the main components of the coolant cycle and the working-fluid cycle are as follows.^{21,30,31} The coolant cycle consists of the reactor, the pressurizer to maintain the water system in a nonboiling condition at the operating temperature, the recirculating pump, and the reactor-coolant side of the heat exchanger. The working-fluid cycle consists of the steam-operated turbine, the steam condenser, the feedwater pump, and the working-fluid side of the heat exchanger.

Reactivity control in PWRs has customarily been effected by regulating the concentration of boron dissolved in primary coolant. In a conventional chemical-shim control system, the boron content of the coolant water is adjusted by adding either demineralized water or concentrated boric acid. In an advanced PWR concept, the concentration of boron in the coolant is regulated by controlling the temperature of an ion-exchange resin in which boron is either absorbed from or released to the coolant. Another novel feature of the advanced PWR is that a low level of carrier gas is maintained in the waste-gas system by using a hydrogen purge and subsequently removing the hydrogen from the system by combination with oxygen to form water. The hydrogen purge continuously strips fission-product gases from the primary coolant.

2. Tritium Generation in a PWR

Tritium is formed in a PWR by fission, by neutron activation of the boron dissolved in the coolant, and by neutron activation of naturally occurring deuterium in primary coolant. If the tritium-generation rate is 0.013 triton per 100 fissions,³⁹ a 1000-MW(e) or 3000-MW(t) reactor should produce about 18,500 Ci/yr, equivalent to about 1.9 g or 0.6 mol/yr. An additional 500 to 1000 Ci/yr would be produced by neutron activation of boron in the coolant.* The yield of tritium in fission is a function of both the neutron energy and the identity of the fissioning nuclei; the thermal neutron yield from ^{239}Pu exceeds that from ^{235}U by a factor of about 2. As burnup increases, the fraction of fissions from ^{239}Pu and hence the rate of generation of tritium increases slightly.

Tritium production in a PWR from control rods (containing B_2O_3) would be important only during the initial cycle, when control rods are used to maintain a negative moderator temperature coefficient. Metals such as silver-indium-cadmium alloy are used as control rods during subsequent operation of the reactor, and these metals do not produce tritium under neutron irradiation.³⁵

*The total coolant volume of a large [1100-MW(e), Zion] PWR is 12,760 ft³ or 361,360 liters.

In Westinghouse PWRs, lithium is employed for pH adjustment of the reactor coolant. A maximum level of 2.2 ppm lithium is maintained by adding ${}^7\text{LiOH}$ and by a cation demineralizer that will remove any excess of lithium produced in the ${}^{10}\text{B}(n,\alpha){}^7\text{Li}$ reaction.⁴⁰

The ${}^6\text{Li}(n,\alpha){}^3\text{H}$ reaction is controlled by using 99.9 at. % ${}^7\text{Li}$ to limit the ${}^6\text{Li}$ impurity in the LiOH used in the reactor coolant and in the lithium-form demineralizers.⁴⁰

Since the amount of naturally occurring deuterium in water is less than 0.015 at. %, the tritium produced from this neutron activation of deuterium is in the range of <10 Ci/yr.⁴⁰

3. Generation of Noble Gases in a PWR

The noble gases krypton and xenon are produced in a PWR solely by the fission processes: about 1.1×10^{-5} mol of ${}^{85}\text{Kr}$ and 6.1×10^{-5} mol of ${}^{133}\text{Xe}$ are generated in each thermal megawatt-day of operation.³⁶ The noble-gas mixture produced by nuclear reactor operations contain several isotopes, both radioactive and stable, of each element. Four stable isotopes of krypton (82, 83, 84, 86) and seven stable isotopes of xenon (128-132, 134, 136) are produced. The stable isotopes constitute most of these elements, about 94% for krypton and more than 99% for xenon.

Of the hundreds of millions of curies of krypton and xenon activity in the nuclear fuel of a 1000-MW(e) reactor at zero decay time, relatively little remains in the fuel discharged after 60 days of cooling. The radioisotopes that require consideration after a 60-day cooling period are ${}^{85}\text{Kr}$ and ${}^{133}\text{Xe}$. For a 1000-MW(e) PWR at a steady state after three years of operation (with 1/3 of the core replaced each year), the ${}^{85}\text{Kr}$ production rate would be about 3.84×10^5 Ci/yr, corresponding to 11.44 mol/yr, and the production rate for ${}^{133}\text{Xe}$ would be about 10.06×10^7 Ci/yr, corresponding to 4.07 mol/yr. After about 60-day cooling, the ${}^{85}\text{Kr}$ activity would have decreased by about 2%, while the ${}^{133}\text{Xe}$ activity would have decreased by about three or four orders of magnitude.

4. PWR Radwaste Systems

Tritium and the noble gases appear in different PWR streams. Tritium that escapes through fuel cladding will be rapidly incorporated into the coolant mass because of its rapid exchange with normal hydrogen in water, but krypton and xenon, because of their inert chemical behavior, will almost certainly remain in the gas phase. The amounts of noble gases that will appear in the reactor pressure vessel will depend on the number of failed fuel elements. On the other hand, the appearance of tritium in the reactor vessel is dependent in part on fuel cladding failure and in part on migration through stainless steel cladding. Tritium released from the fuel matrix is essentially all absorbed by Zircaloy cladding (forming the tritide),^{11,40} which will probably be the only cladding used in future installations. Whichever cladding is used, the major fraction of the tritium and noble gases formed in fuel will be carried to the reprocessing plant. A discussion of the path of tritium and the noble gases in a PWR system requires a description of both the gaseous- and liquid-waste handling systems.

a. Conventional PWR Waste Management

In conventional PWR operation, noble-gas fission products such as ${}^{85}\text{Kr}$ have been maintained under pressure in the circulating primary coolant.

Gases were released from the primary system when coolant was withdrawn or when there was leakage from the circuit. The ^{85}Kr flow path in a conventionally managed 1000-MW(e) PWR is shown in Fig. VI-5. The radioisotopes and hydrogen were separated periodically from the water by a nitrogen strip and then combined in a header with gases (principally the nitrogen cover gas) from tank vents, equipment vents, and sampler vents. The gases were compressed, passed through moisture separators, and collected in decay tanks where they were retained (60 to 120 days for the Yankee-Rowe reactor) until they could be released at a controlled rate through absolute filters to the atmosphere.³⁷ It is estimated that for a typical PWR the discharge from the gas-decay tanks will consist of less than 20,000 ft³/yr of N₂, containing 3200 Ci of ^{85}Kr and 800 Ci of ^{133}Xe . From 50,000 to 300,000 cfm of ventilation air and containment building air may be combined with reactor gases for release through the stack.³⁷

Liquid wastes from various drains and from resin regeneration, which contain tritium and relatively large amounts of dissolved salts, are collected in holdup tanks and then treated by evaporation (Fig. VI-6). The evaporator overheads may be either passed through mixed-bed demineralizers and returned to the plant or mixed with condenser coolant and discharged. The evaporator bottoms are mixed with cement and put into drums for off-site disposal. Coolant discharged from the primary circuit contains boric acid that is usually recovered. This stream is passed first through a gas stripper and then to an evaporator. The boric acid may be reused after filtration and demineralization. This same line of equipment is used to process so-called "clean wastes" of very low dissolved solids content. It is estimated that 200,000 gal of waste containing about 0.2 Ci of activity, exclusive of tritium, will be discharged annually. An additional 3900 Ci of tritium will be discharged each year in the liquid wastes.³⁷

b. Improved PWR Waste Management

Improved PWR gaseous and liquid waste-handling systems designed for concentration and long-term storage with minimum release to the environment have been described by Westinghouse.²¹ The new waste-gas handling system (Fig. VI-7) provides for continuous stripping of fission gases such as ^{85}Kr from the coolant by a hydrogen purge. Gas compressors direct the waste gas stream through the hydrogen recombiner to gas decay tanks, or shunt part of the gas back to the volume control tank. This waste-gas handling system has the advantages of low residual gas volumes (because the purge gas, H₂, is recombined to form water), greatly facilitating storage of radioactive gases for the life of the plant. If a 40-yr plant life and 1% defective fuel pins are assumed (the actual percentage of defective fuel should be smaller), the total activity of gases after 40 yr of accumulation would be less than twice the activity present (mainly from ^{133}Xe) during operation with any batch of fuel with 1% defects.²¹ For a 1000-MW(e) PWR, the amount of ^{85}Kr that would have to be dispersed or contained would be 58,600 Ci, i.e., 1.8 mol or 40 liters (STP).

With the improved system of PWR waste management,⁴⁰ during recycle of primary coolant over the lifetime of a 400-MW(e) plant, unpreventable losses of tritium of <100 Ci/yr (probably as THO vapor) are expected to occur. The losses would occur in "containment purging" and "unrecoverable plant leakage". The total tritium accumulated during the lifetime of a

FIG. VI-5. Simplified Scheme of ^{85}Kr Flow in Gas Phase in a 1000-MW(e) PWR (Conventional Waste Management)

FIG. VI-6. Simplified Scheme of Tritium Flow in Liquid Waste in a 1000-MW(e) PWR (Conventional Waste Management)

FIG. VI-7. Improved Scheme for Handling ^{85}Kr in a 1000 MW(e) PWR
(Improved Waste Management)

400-MW(e) PWR is expected to have an activity of $3.3 \mu\text{Ci/cc}$ in a total volume of perhaps $67,800 \text{ ft}^3$ (if the fuel storage pool is excluded). About 30 yr of operation is required to reach this equilibrium concentration. These figures correspond to a total of $6.3 \times 10^3 \text{ Ci}$ of tritium at a concentration of 2 ppb THO in H_2O .

The conceptual, improved system for liquid waste is shown schematically in Fig. VI-8. The various plant process streams and collection drains are segregated to maintain separation of tritiated or highly radioactive fluids from nontritiated water. The system has been designed to insure that all tritiated liquids are recycled as much as possible. The principal methods of removing any activity present are still conventional evaporation, filtration, and ion exchange. Ultimate disposal of the radioactive materials collected in the waste evaporators, spent resins, and filters is accomplished by drumming and shipping offsite.

C. Behavior of Tritium and Noble Gas Fission Products in Liquid Metal Fast Breeder Reactors

Information on the behavior of tritium and noble-gas fission products in a large commercial LMFBR is limited to projections since production of commercial electric power by a 1000-MW(e) LMFBR is not expected to occur before the early- to mid-1980's.⁴¹ Construction of a 1300-MW(e) LMFBR in England and a 1000-MW(e) LMFBR in France is scheduled to begin in 1974.⁴² Forecasts indicate that the contribution of LMFBRs to electric power production in the U.S.^{43,44} will be about 50,000 MW(e) by the year 2000. For the present survey, the behavior of tritium and noble gases in a large LMFBR has been inferred from design data of 1000-MW(e) LMFBRs of General Electric (GE),^{45,46} Combustion Engineering (CE),⁴⁷ Westinghouse (W),⁴⁸ Babcock & Wilcox (B&W),⁴⁹ and Atomics International (AI)^{44,50} and also from experimental data from smaller, sodium-cooled fast-fission facilities.

In an earlier review⁵¹ of the transport of gaseous fission products from an LMFBR, the emphasis was on transport following an accident. The present discussion concerns transport of tritium and noble-gas fission products during normal operation.

1. LMFBR System

Although there are a number of uncertainties in the choices of design and materials, fuel for the first large LMFBRs in commercial utilities is expected to be as follows: The core fuel pins will probably consist of pellets of a UO_2 - PuO_2 mixture clad in stainless steel and will be surrounded by an axial blanket and a radial blanket of UO_2 pellets clad in stainless steel.

Vented fuel pins of various designs^{48,52,53} that would permit volatile fission products to escape (after interim holdup for decay of short-lived isotopes) into the primary coolant, the cover gas, or a plenum have received much consideration. However, vented fuel pins will probably not be employed in first-generation LMFBRs.

The flow pattern of coolant and working fluid in a large LMFBR will involve heat transfer from the core and blankets to a primary coolant

FIG. VI-8. Improved PWR Waste Liquid System²¹

of liquid sodium, heat transfer from the primary coolant to a secondary coolant (also liquid sodium), and finally heat transfer from the secondary coolant to the working fluid, water/steam. Heat transfer from the primary coolant to the secondary coolant will occur in an intermediate heat exchanger; heat transfer from the secondary coolant to the working fluid will occur in an evaporator, a superheater, and a reheater.

Two arrangements for the positioning of the intermediate heat exchanger and primary coolant pump are being considered. In the Pot System, the primary coolant pump and the intermediate heat exchanger are both located within the reactor vessel and are thus immersed in the primary coolant; in the Loop System, the pump and heat exchanger are located outside the reactor vessel.

Liquid sodium coolants will be protected from atmospheric moisture by a cover gas, probably argon.

2. Tritium Generation in LMFBR

Tritium will be generated in an LMFBR as a result of (1) the fission of a number of actinide nuclides, ^{235}U , ^{238}U , ^{239}Pu , and ^{241}Pu and (2) neutron activation of lithium and boron. Estimates of tritium generation rates as a result of fission are inaccurate because of uncertainties in the fission yield of tritium. Estimates of the generation rate of tritium by neutron activation, obtained for the present purpose from products of average values of flux and cross sections, are inaccurate mainly because of incomplete information on the neutron spectrum as a function of radial distance from the core center.

a. Tritium Generation by Fission

Most of the fission-generated tritium will originate inside the fuel and blanket rods; the contribution to the waste disposal load from the tramp fissile material in a 1000-MW(e) LMFBR is expected to be negligible compared to the contribution from other sources. The rate of generation of tritium in a 1000-MW(e) LMFBR can readily be estimated from tabulations of tritium contents of fuel discharged from the AI Reference Oxide LMFBR.⁴³ The average generation rate of tritium in core and blankets of this reactor is calculated to be 22,000 Ci/yr or 0.76 mol/yr, based on yields that are apparently those for thermal fission. Actual values, however, may be about twice as large (i.e., 44,000 Ci/yr) since yields of tritium in fast fission are about twice as large as those in thermal fission.^{54,55}

b. Generation of Tritium by Reaction of Neutrons with Boron

The total generation rate of tritium by neutron activation in an LMFBR will be greatly affected by whether tantalum or B_4C is chosen for burnup control. No tritium is formed in the reaction of neutrons with tantalum, $^{181}\text{Ta}(n,\alpha)^{182}\text{Ta}$. On the other hand, the absorption of neutrons by B_4C produces tritium by the reaction $^{10}\text{B}(n,2\alpha)^3\text{H}$. Boron control rods are specified for the AI Reference Oxide Reactor⁵⁰ and also for the Fast Flux Test Facility,⁵⁷ but tantalum control rods have been specified in the follow-on concepts of AI,⁴⁴ B&W,⁴⁹ GE,⁴⁷ GE,⁴⁶ and W.⁴⁸ Some concepts specify tantalum for burnup control and B_4C for scram. The amount of tritium

produced in B_4C rods used only for scram is difficult to predict since their exposure to the neutron flux is uncertain.

(1) Tritium Generation Rates in B_4C Rods Employed for Burnup Control

Although the follow-on concepts specify tantalum for burnup control, B_4C has not been ruled out. The amounts of tritium produced in a 1000-MW(e) LMFBR as a result of using boron for burnup regulation would probably be larger than from any other source. In light-water reactors, it is not certain that the tritium formed in stainless steel-clad B_4C rods diffuses through the cladding; this is in contrast to the observed diffusion of tritium through stainless steel-clad fuel rods.^{34,35} In LMFBRs, however, the temperature of control rods will be higher than in LWRs (500-600°C compared to 300-400°C). Hence, the tritium is expected to diffuse out of stainless steel-clad B_4C control rods into the sodium primary coolant.

The rate of tritium generation in boron used for burnup regulation can be estimated by assuming a ratio for tritium produced from boron control to tritium produced from fission. The amounts of tritium produced by fission and in boron have been estimated for two fast-fission facilities, EBR-II and FFTF.⁵⁷ The ratios in these estimations are about 2.4 for 300-MW(t) FFTF and about 2.7 for 62.5-MW(t) EBR-II. If a similar ratio (~2.5) is assumed for a 1000-MW(e) LMFBR, the production of tritium in B_4C control rods would be 55,000 to 110,000 Ci/yr, i.e., 2 to 4 mol/yr. Other calculated ratios⁵⁸ of tritium formed in B_4C control rods to tritium formed by fission in FFTF are as high as 7 to 1, which would imply an even greater production rate in a 1000-MW(e) LMFBR.

The rate of tritium generation in boron used for burnup regulation can also be calculated by estimating tritium yield per unit weight of ^{10}B in the fast neutron flux, and from assumptions of the number of control rods and the weight of boron in each rod. If it is assumed (1) that 1300 Ci of tritium is produced by irradiation of 1 kg of ^{10}B in a fast flux of 10^{15} n cm⁻² sec⁻¹ for 6 months, (2) that each control rod contains 1.3 kg of ^{10}B ,⁵⁹ and (3) that a large LMFBR has 19 control rods,⁵⁰ the amount of tritium formed in control rods would be 64,000 Ci/yr, which is in the range of the first estimate.

(2) Tritium Generation Rate from Activation of Boron Impurity in Sodium Coolant

The tritium generated by neutron activation of boron impurity in the sodium coolant, estimated from design values for the conceptual reactors, is a small fraction of the total tritium generated in an LMFBR. If the average fast flux is 10^{13} n cm⁻² sec⁻¹ in the primary coolant, the coolant volume is 55×10^3 ft³ (pot reactor),⁶⁰ the boron concentration* is a maximum of 25 ppm,⁶¹ and the average cross section for the reaction $^{10}B(n,2\alpha)^3H$ is 30 mb,^{57,62} then the tritium generation rate is 70 Ci/yr.

*The boron concentration in sodium in an operating LMFBR will probably be lower than the purchase specification of 25 ppm; concentrations of 2 ppm in SEFOR⁶² and <0.05 ppm in EBR-II⁶³ have been reported.

The amount of tritium formed by the same mechanism in the secondary coolant of a pot reactor should be smaller, since the sodium inventory ($12 \times 10^3 \text{ ft}^3$)⁶⁰ and the exposure to the neutron flux will be smaller. Also, in the primary and secondary systems of a loop reactor, which has lower sodium inventories and shorter neutron exposure times, less tritium will be produced than in the primary coolant of a pot system.

(3) Tritium Generation Rate from Activation of Boron Impurity in Fuel

Some tritium will be generated as a result of neutron activation of the boron impurity in core and blanket fuels. In this estimate, it is assumed that the neutron fluxes and fuel loadings are those of the AI Reference Oxide Reactor.⁴³ For the core, the loading is 12.6 metric tons of uranium-plutonium mixture with a plutonium fraction of 0.22, and the flux is $5 \times 10^{15} \text{ n cm}^{-2} \text{ sec}^{-1}$. For the radial blanket, the loading is 26.7 metric tons of uranium, and the flux is $1.35 \times 10^{15} \text{ n cm}^{-2} \text{ sec}^{-1}$. For the axial blanket, the loading is 7.32 metric tons of uranium, and the flux is $9.7 \times 10^{14} \text{ n cm}^{-2} \text{ sec}^{-1}$. If the boron concentration is 10 ppm^{64,65} and the cross section is 30 mb,^{57,62} the tritium generation rate is 370 Ci/yr in the core, 200 Ci/yr in the radial blanket, and 40 Ci/yr in the axial blanket, a total of about 600 Ci/yr.

c. Tritium Generation in LMFBR by Neutron Activation of Lithium Impurity in Coolant, Core, and Blankets

The rate of lithium generation in a 1000-MW(e) LMFBR by neutron activation of the lithium impurity in the primary coolant is likely to be small. For this estimate, it was assumed (1) that the volume of primary coolant (in a pot reactor) is $55 \times 10^3 \text{ ft}^3$,⁶⁰ (2) that below 1 MeV, the average cross section is 900 mb⁶⁶ and the neutron flux in the coolant is $4 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$,⁶⁰ and (3) that above 1 MeV, the average cross section is 100 mb⁶⁶ and the neutron flux in the coolant is $1 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$.⁶⁰ The estimated rate of tritium generation is about 85 Ci/yr. As in the case of boron activation in the coolants, tritium generation by lithium activation in the secondary coolant will be at a lower rate than in the primary coolant. Also, the generation rates in both the primary and secondary coolants of a loop reactor will be lower as a result of their lower sodium inventories and lower neutron exposures.

The rate of tritium generation by neutron activation of lithium impurity in core and blanket fuel was estimated, assuming the neutron fluxes and fuel loadings for the AI Reference Oxide Reactor listed above⁴³ and a maximum lithium concentration of 10 ppm in UO_2 and PuO_2 .^{64,65} The calculated generation rates are 720 Ci/yr for core, 390 Ci/yr for radial blanket, and 290 Ci/yr for axial blanket. The total is about 1400 Ci/yr of tritium formed by neutron activation of lithium impurity in core and blankets.

3. Tritium Distribution in an LMFBR System

A large fraction of the tritium formed by fission in an LMFBR can be expected to migrate out of stainless steel-clad fuel. This conclusion is supported by calculations of the permeability of stainless steel by tritium,⁶⁷ by analyses of tritium distribution in EBR-II⁶⁸ and SEFOR,⁶² and

by analyses for tritium in irradiated fuel.⁶⁹

Analyses for tritium at various locations in the EBR-II system have been obtained, expressed as percentages of the total calculated to have been produced by fission.^{68,70} The percentages were based on values for thermal fission yields of tritium and should be amended since the fast fission yields are greater, perhaps by a factor of 2.⁷⁰ If tritium transport in EBR-II is assumed to be similar to tritium transport in an LMFBR system,* the analyses** indicate that a high percentage of the tritium formed in fission will pass into the primary coolant, that the largest fraction of tritium entering the primary coolant will be removed in the primary cold trap (presumably as sodium tritide), that small percentages will migrate through the primary containment to appear in the secondary coolant system, that smaller fractions will penetrate the secondary containment to appear in the water/steam system, and that very small fractions will appear in the cover gas. It should be noted, however, that the distribution of tritium in an LMFBR may depend on the type of fuel material; the distribution in an oxide-fueled LMFBR may differ from that found in EBR-II, which contained a metallic fuel at the time of this analysis.

The amounts of tritium found in primary sodium of SEFOR were almost equivalent to the total amounts of tritium calculated to have been formed by fission.⁶² Although the calculations were apparently based on the thermal fission yield of tritium, they do support other indications that a large fraction of fission-generated tritium escapes from fuel assemblies into the primary coolant.

Results of analyses for tritium in irradiated fuels and for tritium in coolants are in accord with the conclusion that a high percentage of fission-generated tritium escapes from fuel assemblies. LMFBR stainless steel-clad oxide fuels that had been irradiated to burnups of 1.8 to 3.0 at. % generally contained less than 5% of the calculated amounts of tritium formed by fission.⁶⁹

The tritium distribution in FFTF⁷¹ was calculated from projected tritium production rates, volumes and flow rates of coolant, cold trap efficiencies, areas and thicknesses of walls, and diffusion coefficients. The observed distribution of tritium in EBR-II and the calculated distribution in FFTF were used to estimate the tritium flow path and distribution in a 1000-MW(e) LMFBR,[†] as shown in Fig. VI-9.

* Tritium transport in EBR-II may not be a good model for tritium transport in a large LMFBR because of differences in design and the lower (300-350°C) operating temperature of EBR-II.

** Additional uncertainties may be caused by migration of tritium to the surfaces of samplers on cooling.

† An estimate of tritium distribution in an LMFBR, derived from semiquantitative analogy to EBR-II and FFTF, must be considered a rather gross approximation. More accurate distributions would be obtained from diffusion calculations based on an LMFBR design.

FIG. VI-9. Probable Flow Path of Tritium and Estimates of Distribution in Ci/yr for 1000-MW(e) LMFBR

*Quantities generated when B_4C is used for burnup control. Other values are for tritium generation with other control rods.

4. Summary of Tritium Behavior in 1000-MW(e) LMFBR

Of the 22,000 to 44,000 Ci/yr of tritium formed by fission, 70-95% may leave the fuel pins in the reactor. Most of this (20,000 to 40,000 Ci/yr) would be collected in the primary sodium cold trap, and a smaller portion (perhaps 1,000 to 2,000 Ci/yr) in the secondary cold trap. If the species collected is sodium tritide, its weight will total about 17 to 35 g of NaT in the primary cold trap and about 9 to 18 g of NaT in the secondary cold trap. These totals may be about a factor of three greater if B_4C is used for burnup control. The contents of the cold trap may also include, based on an analysis of a FERMI-I cold trap,⁷² a large amount of Na_2O . The amount would depend on the integrity of the cover-gas seal and the resulting air leak (moisture). The trap would also contain lesser amounts of carbon, hydrogen, and nitrogen compounds. Analyses of EBR-II sodium⁷³ indicate that other possible materials in the cold trap are sodium and its activation products (^{22}Na and ^{24}Na); activated corrosion products (^{60}Co , ^{55}Fe , ^{59}Ni , ^{124}Sb , ^{182}Ta); fission products (^{137}Cs and ^{144}Ce);⁴⁸ and a number of metallic and nonmetallic impurities in minor concentrations. Less than 1% (200-400 Ci/yr) of the total tritium may eventually appear in the steam system. The sources and distribution of tritium in a 1000-MW(e) LMFBR are summarized in Table VI-4.

5. Generation of Noble-gas Fission Products in LMFBRs

Noble gases will be generated at the interior of fuel pins and blanket pins in sufficiently large volumes in LMFBRs to necessitate planning for disposal or storage. The amounts of noble gases generated by fission of tramp heavy elements on the exterior surfaces of assemblies will be negligible. The estimated generation rate of ^{85}Kr in the AI Reference Oxide Reactor is about 285,000 Ci/yr³. Estimated activities in the cover gas of the GE conceptual LMFBR imply a generation rate of about 430,000 Ci/yr. The difference presumably stems from a difference in specified burnup.

6. Noble-gas Distribution in the LMFBR System

Some noble-gas fission products can be expected to be released from the fuel at the reactor site as a result of escape from vented or leaking fuel pins; the remainder will be transported to the fuel reprocessing plant. Noble-gas fission products collected at the reactor will be accompanied by some of the cover gas, argon or helium, and by relatively large amounts of short-lived noble gas isotopes and their daughters.

For stable isotopes and 10.76-yr ^{85}Kr , the generation rates are a good measure of the amounts that enter into long-term disposal or storage operations. For shorter-lived isotopes, on the other hand, the amounts to be collected and disposed of will be much smaller than the amounts generated. Moreover, for some of the shortest-lived isotopes, although the amounts generated will be large, those encountered in separation and disposal operations will be negligibly small owing to decay during transit from the generation site to the separation or disposal site. In-transit decay will greatly affect not only the total amounts of noble gas isotopes at the collection or disposal point, but also the composition of the mixture because of the variation in half-lives. Examples of in-transit times are an assumed

TABLE VI-4. Summary of Tritium Sources and Estimated Distribution
in a 1000-MW(e) LMFR Reactor

Source	Ci/yr	mol/yr	Distribution	Ci/yr	mol/yr	Concentration
<u>Reactor Using Ta Control Rods</u>						
Fission	4.4×10^4	1.5	Fuel	2.2×10^3	7.6×10^{-2}	
Activation of B_4C	0.0	0.0	Primary Sodium	1.3×10^3	4.5×10^{-2}	
Activation of B in Na	7.0×10^1	2.0×10^{-3}	Primary Cold Trap	4.0×10^4	1.4	
Activation of B in Core & Blanket	1.2×10^3	4.0×10^{-2}	Primary Cover Gas	4.0×10^{-1}	1.4×10^{-5}	1.6×10^{-9} mol/mol ^a
Activation of Li in Na	85	2.8×10^{-3}	Secondary Sodium	4.4×10^2	1.5×10^{-2}	
Activation of Li in Core & Blanket	1.4×10^3	4.7×10^{-2}	Secondary Cold Trap	1.7×10^3	5.8×10^{-2}	
			Secondary Cover Gas	4.0×10^{-2}	1.4×10^{-6}	1.6×10^{-10} mol/mol ^a
			Water/Steam	4.4×10^2	1.5×10^{-2}	1.4×10^{-3} μ Ci/liter ^b
<u>Reactor Using B₄C Control Rods</u>						
Fission	4.4×10^4	1.5	Fuel	2.2×10^3	7.6×10^{-2}	
Activation of B_4C	1.1×10^5	4.0	Primary Sodium	4.6×10^3	1.6×10^{-1}	
Activation of B in Na	7.0×10^1	2.0×10^{-3}	Primary Cold Trap	1.4×10^5	4.8	
Activation of B in Core & Blanket	1.2×10^3	4.0×10^{-2}	Primary Cover Gas	1.5	5.2×10^{-5}	6.0×10^{-9} mol/mol ^a
Activation of Li in Na	85	2.8×10^{-3}	Secondary Sodium	1.5×10^3	5.2×10^{-2}	
Activation of Li in Core & Blanket	1.4×10^3	4.7×10^{-2}	Secondary Cold Trap	6.2×10^3	2.1×10^{-1}	
			Secondary Cover Gas	1.5×10^{-1}	5.2×10^{-6}	6.0×10^{-10} mol/mol ^a
			Water/Steam	1.5×10^3	5.2×10^{-2}	4.7×10^{-3} μ Ci/liter ^b

^a Mol/mol of argon if cover gas volume is $6,830 \text{ ft}^3$ (ref. 52).

^b Assumes that all tritium entering the water system is eventually discharged into once-through condenser cooling water flowing at 160,000 gpm (ref. 6). The estimated concentrations for a tantalum-controlled reactor and a boron-controlled reactor have the same order of magnitude and are slightly less than that specified in the suggested amendment to 10 CFR Part 50 regarding discharges from LWRs. The suggested amendment states that the concentration of tritium prior to dilution in a natural body of water should not exceed $5 \times 10^{-3} \text{ } \mu\text{Ci/liter}$ (ref. 1).

10-min holdup in leaking fuel pins and an assumed 5-day holdup in vented pins.^{48,52}

The holdup of noble gases in sodium should be small; the solubility of ⁸⁵Kr in sodium is considered negligible, and de-entrainment is thought to consist largely of mechanical separation.⁷⁴ The average time for disengagement of noble gases from sodium in SEFOR was found to be about 5 min,⁷⁵ but disengagement should take longer in the larger sodium pool of a 1000-MW(e) LMFBR. Estimates of the de-entrainment of noble gases from primary coolant in the 1000-MW(e) reactor of GE indicate that at any time, a maximum of $2 \times 10^{-4}\%$ of the gas released from defective fuel elements is "entrained in the coolant".⁵²

The amounts of short-lived isotopes to be collected or disposed of will depend strongly on cover-gas management. One management scheme specifies operation with a continuous purge with or without interim holdup in tanks for decay before discharge.⁴⁸ Another scheme provides no purge but rather the replacement of cover gas at each 6-month refueling.⁵² Operation without a purge would result in fission products accumulating in the cover gas; whether this mode of operation is possible would depend on the integrity of the cover seal since the level of radioactivity in the reactor building atmosphere must be kept below MPC.

The fraction, F , of a gaseous radioactive isotope released from fuel has been expressed as a function of the release fraction of a stable isotope of the same element and the half-life of the radioactive isotope.⁵²

$$F = F^0 e^{-\lambda t} = \text{observed release fraction of radioactive species}$$

F^0 = observed release fraction of stable species

λ = decay constant

t = apparent holdup time

Observed releases of noble gases from irradiated oxide fuel pellets have varied from a few percent to almost 100 percent of the amounts generated.^{76,77}

Equilibrium gamma activities in the cover gas of the GE 1000-MW(e) LMFBR⁵² were estimated for defective pins and vented pins, based on 6-month accumulation without purge, 1% of the fuel pins defective, a release fraction of 0.35 for stable isotopes, and holdup times of 10 min for a leaking pin and 5 days for a vented pin. The assumption of 1% of the fuel pins having defects is understood to be extreme; in actual operation, the percentage of defective fuel would be expected to be much lower. These estimates were used to calculate the annual load in curies and the volumes and concentrations in the cover gas for various isotopes if stagnant gas were processed semiannually (Table VI-5). Thus 0.15 MCi/yr or 10^5 cc(STP)/yr of ⁸⁵Kr and 55.2 MCi/yr or 5×10^4 cc(STP)/yr of ¹³³Xe would be collected if the cover gas of a reactor using vented fuel pins were processed at 6-month intervals. The Westinghouse concept offers similar estimates;⁴⁸ from their predictions it can be calculated that 0.169 MCi/yr or 1.14×10^5 cc(STP)/yr of ⁸⁵Kr and 37.6 MCi/yr or 3.4×10^4 cc(STP)/yr of ¹³³Xe would be released at the Westinghouse reactor if vented fuel is used, based on a release fraction of 0.5 for stable isotopes.

TABLE VI-5. Radioactive Noble Gas Fission Products
in Cover Gas of a 1000-MW(e) LMFBR^a

Isotope	t 1/2	MCi/yr	cc(STP)/yr	mol/mol Cover Gas ^b
<u>Leaking^c Pins</u>				
⁸⁹ Kr	3.2 m	0.232	0.0880	0.0228x10 ⁻⁸
¹³⁷ Xe	3.8 m	0.144	0.0668	0.0173x10 ⁻⁸
^{135m} Xe	15 m	0.177	0.0322	0.00834x10 ⁻⁸
¹³⁸ Xe	17 m	0.564	1.14	0.295x10 ⁻⁸
⁸⁷ Kr	1.3 h	0.382	3.56	0.922x10 ⁻⁸
^{83m} Kr	1.86h	0.069	0.918	0.238x10 ⁻⁸
⁸⁸ Kr	2.8 h	0.546	10.9	2.82x10 ⁻⁸
^{85m} Kr	4.4 h	0.225	7.24	1.88x10 ⁻⁸
¹³⁵ Xe	9.2 h	0.950	62.0	16.1x10 ⁻⁸
^{133m} Xe	2.3 d	0.0245	9.87	2.56x10 ⁻⁸
¹³³ Xe	5.3 d	0.996	902.	234x10 ⁻⁸
^{131m} Xe	12 d	0.003	6.36	1.65x10 ⁻⁸
⁸⁵ Kr	10.7 y	0.0015	1000.	259x10 ⁻⁸
<u>Vented^d Pins</u>				
¹³⁵ Xe	9.2 h	0.0105	0.684	0.177x10 ⁻⁸
^{133m} Xe	2.3 d	0.572	230.	59.6x10 ⁻⁸
¹³³ Xe	5.3 d	55.2 ^e	50,000. ^e	12,900x10 ⁻⁸
^{131m} Xe	12 d	0.230	474.	123x10 ⁻⁸
⁸⁵ Kr	10.7 y	0.150 ^f	100,000. ^f	25,900x10 ⁻⁸

^aCalculated for values listed for GE concept, ref. 52, based on semiannual processing of accumulated activities in nonpurged cover gas.

^bBased on cover gas volume of 6,830 ft³ of argon with twice-a-year replacement, ref. 52.

^cAssuming release fraction of 0.35 for stable isotopes and 1% of the fuel pins defective; the actual percent of defective fuel pins is expected to be lower.

^dAssuming a release fraction of 0.35 for stable isotopes.

^eThe predictions for ¹³³Xe release in the Westinghouse concept (assuming that the release fraction is 0.50 for stable isotopes from vented fuel) are 37.6 MCi/yr and 34x10³ cc(STP)/yr; these values are calculated from values listed in ref. 48.

^fPredictions for ⁸⁵Kr release in the Westinghouse concept (assuming that the release fraction is 0.50 for stable isotopes from vented fuel) are 0.169 MCi/yr and 114x10³ cc(STP)/yr, calculated from predicted yields in ref. 48.

Radioactive noble gases collected for storage will be accompanied by relatively large volumes of stable noble-gas fission products. The volumes of stable isotopes produced in a 1000-MW(e) LMFBR are readily approximated from tabulated fission-product yields for the AI Reference Oxide Reactor at 0.85 load factor.⁴³ If these volumes are reduced by factors of 0.01 to represent leaking fuel or by 0.35 to represent vented fuel, they become comparable with the volumes of radioactive isotopes calculated to be released at the GE reactor. The volumes of stable isotopes and the volume of ⁸⁵Kr are summarized in Table VI-6 to indicate the volumes of gases destined for long-term storage.

TABLE VI-6. Volumes of Fission-Product Gases Requiring Long-Term Storage
[Noble Gases Released from 1000-MW(e) LMFBR]

	Leaking Pins ^a		Vented Pins ^b	
	Liters (STP)/yr	Mol/Mol Cover Gas ^c	Liters (STP)/yr	Mol/Mol Cover Gas ^c
⁸⁵ Kr ^d	1	2.59×10^{-6}	100	2.59×10^{-4}
Stable Isotopes ^e	64.6	1.67×10^{-4}	6462	1.67×10^{-2}
Sum ^f	65.6	1.70×10^{-4}	6562	1.70×10^{-2}

^a Assuming that the release fraction of stable isotopes is 0.35 and that 1% of the fuel pins are defective; actual operation should involve a smaller percentage of defective fuel pins.

^b Assuming that the release fraction of stable isotopes is 0.35.

^c Assuming that the cover gas is 6,830 ft³ of argon, ref. 52.

^d Calculated from yields predicted for the GE conceptual reactor, ref. 52.

^e Calculated from weights of fission products tabulated for the AI Reference Oxide reactor, ref. 3.

^f Sums may be greater than the values listed since some cover gas (depending on the collection process and its efficiency) will accompany the noble-gas fission products.

If noble gases are collected at the reactor site for long-term storage, some decay would occur before final packaging. Table VI-7 summarizes the quantities of noble-gas fission products present in cover gas of a 1000-MW(e) LMFBR. The cover gas had been removed after 6-month accumulation in a reactor and 30-day cooling.

If cover gas is to be processed for removal or concentration of noble-gas fission products, the volumes of gases collected will vary with the rate of processing and the efficiency of the process. An ORNL study⁷⁸ of the processing of cover gas of a 1000-MW(e) LMFBR through a cascade of permselective membranes showed that the total quantity of concentrated gas collected in standard N₂ cylinders at 2200 psi increased from 1 to 50 cylinders per week as the product take-off rate increased from 0.02 to 1 scfm for a

TABLE VI-7. Major Noble-Gas Fission Products in Cover Gas
after 6-Month Operation and 30-Day Cooling^a

Radioactive Isotope	Defective Fuel Pin			Vented Fuel Pin		
	MCI	Mol	Mol/Mol Cover Gas ^b	MCI	Mol	Mol/Mol Cover Gas ^b
^{133m} Xe	1.8×10^{-6}	3.1×10^{-8}	3.6×10^{-12}	4.1×10^{-5}	7.4×10^{-7}	8.6×10^{-11}
¹³³ Xe	9.6×10^{-3}	3.9×10^{-4}	4.5×10^{-8}	5.3×10^{-1}	2.2×10^{-2}	2.6×10^{-6}
^{131m} Xe	2.7×10^{-4}	2.5×10^{-5}	2.9×10^{-9}	2.0×10^{-2}	1.9×10^{-3}	2.2×10^{-7}
⁸⁵ Kr	7.5×10^{-4}	2.2×10^{-2}	2.6×10^{-6}	7.5×10^{-2}	2.2	2.6×10^{-4}
Stable Noble-Gas Fission Products ^c		1.44			144	

^a Assuming that cover gas management consists of removal of accumulated gases from 1000-MW(e) GE reactor (ref. 52) after 6 mo of non-purge operation, then cooling 30 days before processing for final storage.

^b Argon cover gas in most concepts. Volume = 6,830 ft³ for GE concept, ref. 52.

^c Calculated from tabulated values for 1000-MW(e) AI Reference Oxide Reactor (ref. 43).

constant feed rate of 10 scfm with various assumed numbers of stages, membrane area, cascade volume, and pressures.

7. Conclusions on Behavior of Noble Gases in a 1000-MW(e) LMFBR

A total of 0.3 to 0.4 MCi/yr of ^{85}Kr will be generated in a 1000-MW(e) LMFBR; some will be released into primary coolant and pass quickly into the cover gas, and the remainder will appear at the fuel reprocessing plant. Less than 1% of the ^{85}Kr should appear in the cover gas as a result of leakage from defective fuel, but 35 to 50% or more may appear in the cover gas if vented fuel pins are used. Larger quantities of other radioactive isotopes of krypton and xenon than of ^{85}Kr are generated, but owing to their short half-lives, many will decay before they reach a collection point. Holdup times of 10 min for leaking fuel and 5 days for vented fuel have been assumed. Thus, for vented fuel, the only isotopes to be considered if a collection process is used at the reactor are ^{135}Xe , ^{133m}Xe , ^{133}Xe , ^{131m}Xe , and ^{85}Kr . If 1% of the fuel pins are defective (a conservative specification based on a release fraction of 0.35 for stable isotopes and semiannual reprocessing of cover gas), about 1500 Ci/yr or 1 liter (STP)/yr of ^{85}Kr , 996,000 Ci/yr or 0.9 liter (STP)/yr of ^{133}Xe , and 66 liters (STP)/yr of stable xenon and krypton isotopes would be collected at the GE reactor. For vented fuel, if a release factor of 0.35 for stable isotopes is assumed along with semiannual processing of cover gas, about 150,000 Ci/yr or 100 liters (STP)/yr of ^{85}Kr , 55,200,000 Ci/yr or 50 liters (STP)/yr of ^{133}Xe , and 6600 liters (STP)/yr of stable xenon and krypton isotopes would be collected at the GE reactor.

Noble-gas fission products collected at the reactor would be accompanied by a quantity of reactor cover gas--argon or helium. The quantity would depend on the collection process used and its efficiency. The possible flow paths for transport of noble gases in an LMFBR are summarized in Fig. VI-10, where the distribution of ^{85}Kr is shown in Ci/yr. The distribution of shorter-lived isotopes is subject to uncertainties related to varied in-transit decay.

FIG. VI-10. Possible Flow Path of Noble Gas Fission Products and Estimated Distribution of ^{85}Kr (Ci/yr) for a 1000-MW(e) LMFBR (*Quantities for nonvented pins)

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