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THORIUM FUEL CYCLE DEVELOPMENT PROGRESS REPORT

December 1969

No. 5

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CHEMICAL TECHNOLOGY DIVISION
METALS AND CERAMICS DIVISION

THORIUM FUEL CYCLE DEVELOPMENT PROGRESS REPORT

December 1969

No. 5

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IV. URANIUM-233 REPROCESSING

R. E. Brooksbank, J. R. Parrott

JANUARY 1970

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DECEMBER 1969

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INTRODUCTION

The thorium fuel cycle development at ORNL is directed almost solely at HTGR fuels. These fuels consist of large blocks of graphite containing coolant channels and fuel and blanket holes. The fuel and blanket are made of microspheres of uranium or thorium compounds separately, or of mixtures of them in a single microsphere. The microspheres are coated with layers of pyrolytically deposited carbon and in some cases silicon carbide. The microspheres are retained in the holes in the graphite blocks in either unbonded or bonded forms.

Development work on all aspects of HTGR fuel recycle is in progress at ORNL. In addition, a major recycle development facility, the Thorium-Uranium Recycle Facility (TURF), has been built at ORNL, and the Coated Particle Development Laboratory (CPDL) has been put into operation in Building 4508. TURF is intended to be used as a development pilot plant for fuel recycle. The CPDL is for engineering development studies leading to design of the pilot plant equipment.

I. HEAD-END REPROCESSING DEVELOPMENT

(R. E. Blanco, W. E. Unger)

The objective of this program is to evaluate head-end processes for converting irradiated HTGR fuels to a form suitable for recovery and decontamination of the thorium and uranium by the solvent extraction process. Small samples of irradiated and unirradiated fuel are processed to determine irradiation effects which affect fuel reprocessing steps and to provide a comparison with metallographic studies. An important objective is the determination of the amount of breakage of coatings and the resultant amount of cross contamination of the fertile Th-^{233}U and fissile ^{235}U components in alternative reprocessing steps. Mechanical systems are being developed for degrading the fuels and providing a material suitable for use in studies of the burn-leach steps using fluidized bed or fixed bed burners. The mechanical and burn-leach engineering development work is carried out using full scale unirradiated fuel and is designed to provide scale-up data for use in the design of pilot or full scale processing plants.

1. Studies with Irradiated Fuels

(V. C. A. Vaughen, J. H. Goode, G. Davis)

Evaluation of the data from the crush-burn-leach experiment on Dragon fuel is being carried out as time permits.

2. Head-End Engineering Studies

(C. D. Watson, R. S. Lowrie)

The head-end engineering studies are comprised of two principal areas of investigation — mechanical and burn-leach. The present general approach involves the mechanical dissection by sawing of full-sized graphitic blocks containing fuel sticks followed by comminution to size fractions suitable for the downstream burn-leach process. However, recent decisions leading to the possible use of loose fuel particles rather than fuel sticks may alter this approach quite drastically in future work.

There is nothing to report in this area this month.

II. REFABRICATION DEVELOPMENT

1. Particle Preparation

(R. G. Wymer - Coordinator)

The fuel material of primary interest for ORNL recycle studies is the ThO_2-UO_2 particle, which has a thorium-to-uranium ratio of about 4.2. The uncoated fuel particles are to be microspheres 350 $\pm$ 100 μ in diameter, made by the sol-gel process. Fuel preparation includes development and demonstration of all process steps involved in making remotely the ThO_2-UO_2 microspheres. The steps include demonstrating a reliable, remote method for reproducibly mixing $Th(NO_3)_4$ and $UO_2(NO_3)_2$ solutions in the desired thorium-to-uranium ratio, preparing the mixed, stable ThO_2-UO_3 sol in concentrations exceeding 1 g-mole of oxides per liter, forming ThO_2-UO_3 gel microspheres, and converting them to dense ThO_2-UO_2 in good yield.

1.1 Sol and Microsphere Preparation Development

(P. A. Haas, R. E. Brooksbank)

Experimental engineering studies of processes and equipment for preparation of sols and microspheres are reported here. The present emphasis is on processes, procedures, and prototype equipment for preparation of oxide microspheres in the Thorium-Uranium Recycle Facility (TURF). Tests of flowsheets and procedures to be used for test materials preparation are also included.

During the past month the critically safe and alpha-contained Solex equipment was used for test runs on a flowsheet for the preparation of ThO_2-UO_3 sol having a thorium-to-uranium ratio of about two. Although we are still not certain that we will proceed with a production run of sol of this type, we want to be aware of problems which may arise in its preparation. This composition of sol, containing enriched uranium, has been requested in connection with fabrication of eight test elements to be tested in the Peach Bottom Reactor. Test runs to date have shown that the solvent extraction process for sol preparation is satisfactory, but that somewhat more effective nitric acid extraction conditions are necessary to

get an appropriately low nitrate-to-metal ratio than are required for the preparation of sols which have a higher thorium-to-uranium ratio. This work is discussed further under Section 1.3.

1.2 Sphere-Forming Column Chemistry

(W. D. Bond, K. S. Warren, K. J. Notz)

Our previous studies have shown that pH, surfactant concentration and water content of 2-ethyl-1-hexanol (2EH) are important variables in the microsphere forming process. We are presently examining methods for improving the control of pH and surfactant concentration during continuous operation of sphere forming columns.

Our present system for controlling the water content is adequate. For water content control, a portion of the used solvent is heated at 150-160°C to remove most of the water, and the desired water content is obtained by mixing this relatively dry 2EH with the remaining wet solvent. However, the removal of nitric and formic acids from 2EH before distillation is desirable (and probably necessary). Nitric acid accelerates solvent and surfactant degradation during the distillation step in which water is removed, and formic acid interferes with long-term column operation with urania sols by promoting clustering. Therefore, the use of ion exchange resins for removing these acids from 2EH is being investigated.

Anion exchange resins are available in several chemical types (e.g., weak base and strong base) and in two physical modifications (macroreticular and gel); varying degrees of refinement exist within these categories. Chemically a strong base resin should be more effective than the weak base type for removing weak acids, such as formic, but regeneration of strong base resins is more difficult than for weak base resins, particularly from the nitrate form. Therefore, both chemical types were tested. Only macroreticular resins were tested initially.

It was found that a weak base resin (Amberlite IRA-93) is almost as effective as a strong base type (Amberlite IRA-900) for the removal of both nitric and formic acids. The nitric acid is, of course, removed in preference to the weaker formic acid and the formic acid breaks through

first as a column becomes loaded by a mixture of both acids. With the macroreticular weak base resin, even formic acid was taken out at a fairly fast rate; at a flow rate of 4 bed volumes per hour, removal was quantitative up to the bed capacity. At 16 bed volumes per hour, removal was still very effective. A flow rate of 10 bed volumes per hour was adopted for subsequent work.

While surfactants (Span 80 and Ethomeen S/15) do not appear to interfere with acid removal, Span 80 is held up on the resin column, and Ethomeen S/15 may be. This problem is being investigated now, along with resin regeneration.

1.3 Preparation of Test Materials

(J. R. Parrott, F. L. Daley, R. J. Shannon)

The sol-forming equipment in the Solex Development Laboratory and the cell 4 Microsphere-Forming Facility were operated during the month in an attempt to make $^{235}UO_2$-ThO_2 microspheres containing a Th-to-U ratio of 2-to-1. This material will be used for high burn-up irradiation tests in Peach Bottom Reactor as a part of the National HTGR Recycle Program. A 2-to-1 ratio of Th-to-U is lower than we have made on a large scale by the solvent extraction process, and we had reason to expect to have to do some preliminary testing.

The first attempt to make UO_3-ThO_2 sol produced sol with a low (.06) NO_3^-/metal ratio which resulted in gelation at a low concentration during evaporation. The NO_3^-/metal ratio was adjusted to 0.12 by the addition of HNO_3 but an attempt to form the resultant sol into microspheres was unsuccessful. Severe "raisin pitting" of the formed spheres was noted in the column during drying.

The second sol-forming run was made with a 15% reduction in the extractant (Amberlite LA-2 in an n-paraffin diluent). The resultant sol was concentrated to 1 M in metal and according to the chemical analysis contained a NO_3^-/metal ratio of 0.146. The sol was formed into microspheres but after approximately 20 minutes drying time in the 2-ethyl-1-hexanol column, cracking became severe. This phenomenon had been observed

previously when forming spheres from a sol with a high nitrate-to-metal ratio. The sol was found to be made up of 25 to 40 angstrom crystallites rather than the 50 to 60 angstrom crystallites usually observed in ThO_2-UO_3 sols made by solvent extraction. Digestion of the sol for several hours at an elevated temperature failed to improve the forming characteristics.

A third run will be made with an increased extractant flow to decrease the NO_3^-/metal ratio.

2. Fueled Graphite Fabrication Development

(F. J. Furman, J. D. Sease, and R. A. Bowman)

We are developing processes and equipment for the refabrication of HTGR fuel as detailed in the National HTGR Recycle Development Program Plan. The fuel consists of microspheres of thorium and/or uranium as the oxide or carbide, coated with multiple layers of pyrolytic carbon and silicon carbide. These particles are loaded into hexagonal graphite logs which contain both fuel and coolant holes.

Our work is divided into particle coating, particle handling and inspection, particle blending, fuel element assembly, and fuel element inspection. Most of the work this month was on particle coating and inspection.

2.1 Particle Coating

We have recently completed construction of a 5-in.-diam prototype remote coating furnace. This furnace is an advanced version of our 5-in.-diam laboratory furnace which has been successfully coating particles for over two years. The improvements incorporated into the prototype furnace are intended to demonstrate remote, production-scale operation and maintenance. Besides being the prototype of a large-scale remote particle coating furnace, this furnace is sufficiently instrumented to be a valuable development tool. The furnace is shown in Fig. 1. Also shown are some of the exhaust handling equipment such as filters, pressure gages, and valves. Figure 2 shows the control panel for the furnace. The entire operation, including the furnace temperature, the exhaust system, and the

Photo 97835-A

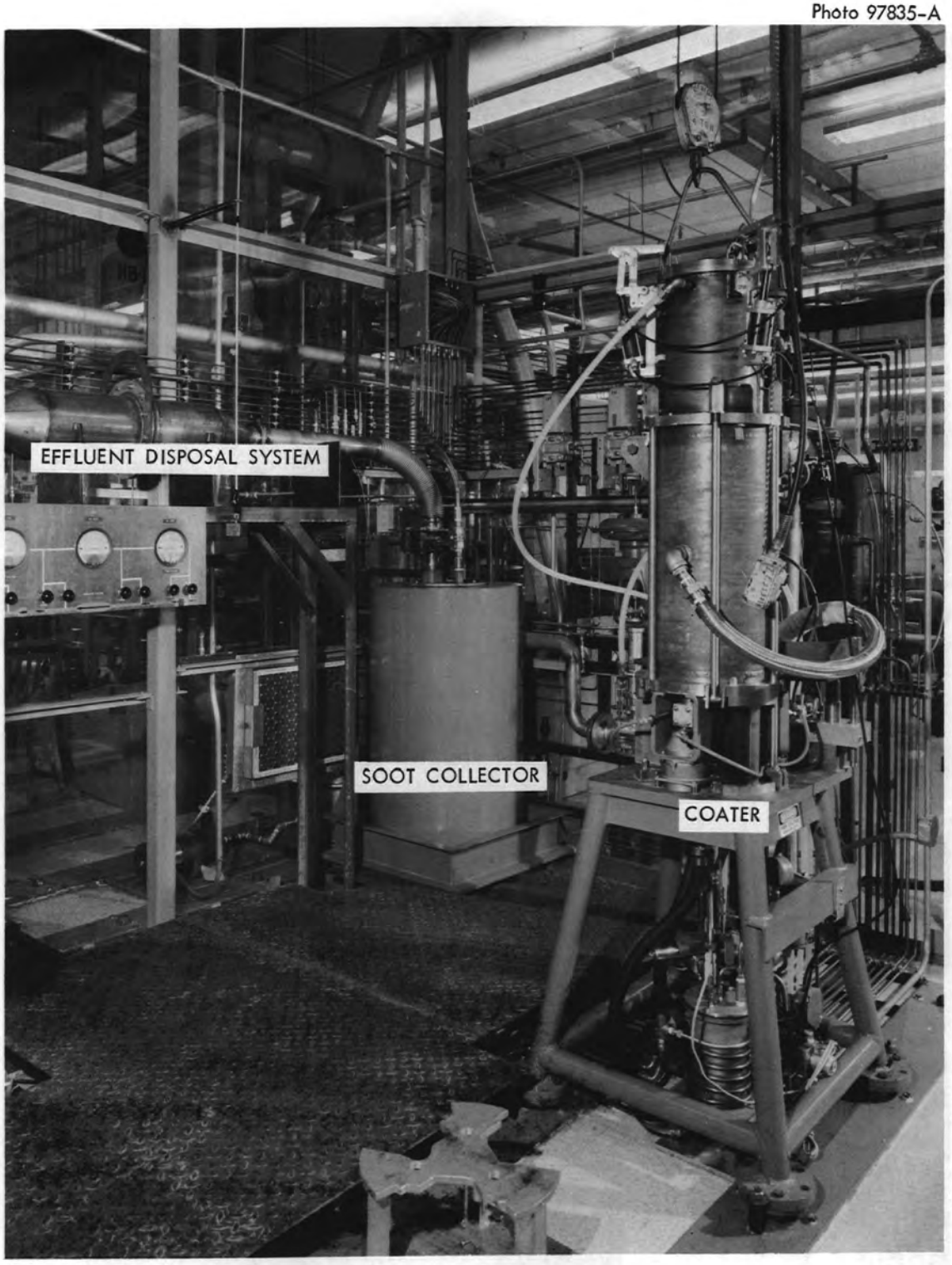

Fig. 1. Prototype 5" Diameter Remote Coater

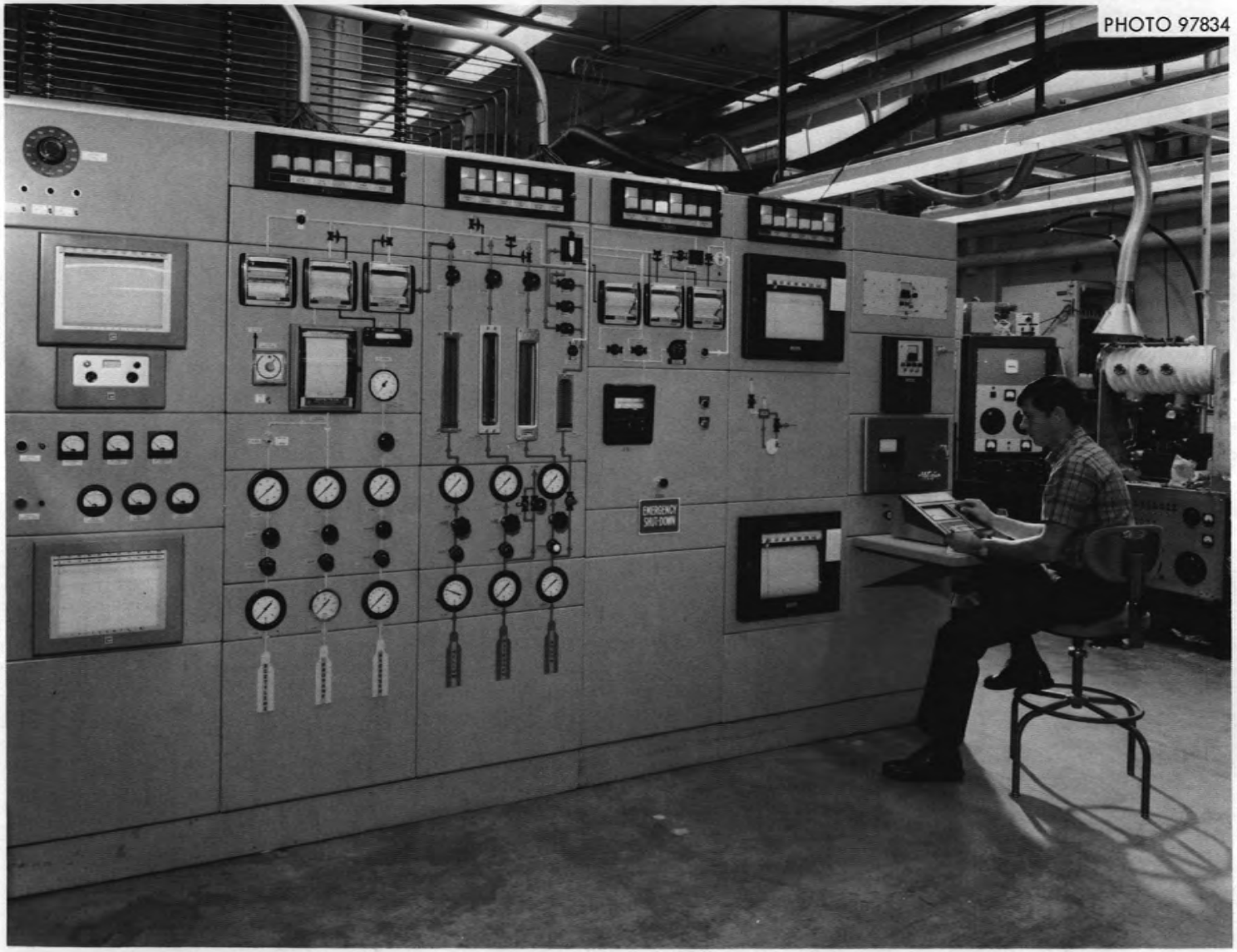

Fig. 2. Control Panel for Prototype 5-in.-diam Remote Coater

gas supply are controlled from this panel. A notable feature of the panel is that no combustible gases are routed through the panel. All combustible gas valves and piping are located elsewhere and controlled by pneumatic methods from the panel. This approach minimizes the danger of combustible gas leaks in the operating area. Also seen in Fig. 2 are the numerous safety alarms along the panel top and the gas analyzers at the right side of the panel. These devices signal unsafe conditions and, if the condition is potentially dangerous, they automatically shut down coating operations.

During the past month we completed the remaining checkout of the furnace and operated it for the first time. During the final checkout phase we repaired the stack O_2 monitor, repaired and modified the furnace exhaust, weather-proofed the exhaust system, and completed the furnace temperature controller.

The stack O_2 monitor, used to ensure complete purging of the furnace and furnace exhaust system prior to coating, failed when a filament burnt out. The unit as-received was calibrated for He as the background gas, and when N_2 was used, the great difference in properties of these gases caused the filament to overheat. After replacing the filament, the instrument was calibrated with N_2.

During the operation of the 5-in.-diam coating furnace in the Coated Particle Development Laboratory, we discovered that at high gas flows, some particles were being blown out the exhaust of the furnace. We installed a baffle in front of the exhaust port to prevent loss of the particles out the exhaust. This baffle was so successful that we also have installed one on the prototype coating furnace.

Work was also completed on the furnace temperature controller sensor. This device is a highly sensitive photoelectric cell sighted on the furnace cone wall through a collimator.

We have also weather-proofed the water sealed H_2 pump used in the exhaust system of the coating furnaces. The pump system which is located on the roof had to be heat-taped and insulated.

After completing the above items, we made several coating runs in the prototype coater using acetylene as the coating gas. Using conditions established in our 5-in.-diam development coater with 1 kg batches of nominal 360 μ ThO_2 microspheres, the coatings obtained appear to be as expected. Detailed analysis of these coating runs are now in progress.

III. MATERIALS IRRADIATION

(A. L. Lotts, T. N. Washburn, J. D. Sease, and J. H. Coobs)

1. Irradiation of Prototype Recycle Fuels

(A. R. Olsen, R. B. Fitts, and F. J. Furman)

Irradiation tests for the HTGR recycle program have a twofold objective: (1) to provide irradiated fuel for head-end process studies, and (2) to provide irradiation proof tests of the processes and of the products of the various stages of process development for the Thorium-Uranium Recycle Facility. The test conditions have been defined as fuel temperatures between 750 and 1300°C with fast fluence exposures from 4 to 8 x 10^{21} neutrons/cm^2 and burnup levels up to 20% FIMA.

A multi-stage program has been proposed, with two stages to be implemented during FY-1970. These two stages involve accelerated capsule tests in the Advanced Test Reactor and eight Recycle Test Elements to be irradiated in the Peach Bottom Reactor.

1.1 Capsule Irradiations

We have just been informed by Idaho Nuclear Corporation that only one "A" position in the ATR is currently unassigned. They are collecting data on this position and four other similar-size test locations so that detailed experimental design work can proceed. If these alternate ATR positions do not have satisfactory flux levels and energy distribution, we will be restricted to a single capsule in the ATR. Because of this limitation we are investigating a possible alternate to ATR irradiations. The alternate approach involves the use of a "partial-element" in the ORR. Detailed designs for these elements, their availability, cost and information on flux energy spectrums and levels have been requested from the ORNL Operations Division.

1.2 Large-Scale Irradiations

Eight test fuel elements will be irradiated in the Peach Bottom Reactor. These elements, designated Recycle Test Element (RTE's), will contain samples of fuels of the types proposed for use in the 1100 Mw(e) HTGR. These tests will serve two purposes.

(1) They will provide fuel with varied irradiation histories for limited scale checkout of head-end reprocessing prior to final design of equipment for TURF.

(2) They will provide thorough testing of the irradiation performance of the candidate recycle and make-up fuels.

A schedule and proposed fuel loading for the test elements have been received from Gulf General Atomic. In this schedule the first two RTE's are discharged after one year of irradiation; two more after two years; and the remaining four after three years in-reactor. The proposed fuel loading places primary emphasis on the irradiation of make-up types of fuel particles (all carbide) with less testing of recycle fuel particles (oxide-carbide combinations). We are presently evaluating this proposal.

IV. URANIUM-233 REPROCESSING

(J. R. Parrott, R. G. Nicol, W. A. Shannon)

ORNL serves as a national distribution center for ^{233}U. The facility, which contains a small batch leacher, a batch dissolver, and a single-cycle solvent extraction system, is capable of purifying ^{233}U at the rate of 25 kg per week. It includes storage systems for liquids and solids, with capacities of 500 and 120 kg of ^{233}U respectively.

1. Dissolution and Purification

The dissolution and purification equipment were not operated during the month. Except for 9 kg of uranium (84% ^{233}U) remaining in the vault, all the scrap has been dissolved and accounted for.

2. Storage and Distribution

The facility presently contains 226 kg of ^{233}U which varies in isotopic purity between 84 and 98% and ^{232}U content between 4 and 250 ppm. No receipts or shipments were made during the month.

We also have a facility (TRUST-Thorium Reactor Uranium Storage Tank) in which we store 1047 kg of highly enriched uranium (76.5% ^{235}U, 9.7% ^{233}U) in the form of a uranyl nitrate solution. This material is the uranium product from the Indian Point reactor fuel, which was purified by solvent extraction at the Nuclear Fuels Services Plant. The solution will be stored indefinitely since the ^{232}U content (120 ppm) prohibits its direct refabrication into fuel elements, and the low ^{233}U content makes it of little interest for reactors demonstrating the thorium fuel cycle.

Results of the analysis of solution removed from storage tank P-25 (TUC-7), after adding more cadmium and gadolinium (soluble neutron poisons) and air sparging for 6 hours, showed the amounts of poisons to continue to be less than that specified in the criticality review, as follows:

	Mole Ratio with respect to U	
Poison	Sample TUC-7	Specification
Cd	0.286	$\geq$ 0.313
Gd	0.0218	$\geq$ 0.0263

The tank was air sparged another 8 hours* and sampled (TUC-8) as before. The results showed the Cd/U mole ratio to be 0.307 and the Gd/U ratio to be 0.0256; these are within the accuracy of measurement.

A new vessel off-gas line for tank P-25 was installed, except for the pressure control valve and associated instrument tubing. The valve is scheduled to be shipped in early December.

3. LWBR Support Program

Funding was received from Bettis Atomic Power Laboratory to support ORNL participation in the Light Water Breeder Reactor Program. ORNL will receive approximately 650 kg of ^{233}U from the production plants, store the material as a solid or solution, purify and convert to ceramic grade UO_2 powder at a rate of 25 kg ^{233}U per week. Operation is scheduled to begin in January, 1971.

Development programs to optimize the purification as well as the oxide forming flowsheets are underway. Detailed design of the additional storage space and modifications to the solvent extraction facility have begun.

*Sparging consisted of eight 1-hour tests because of the high-radiation background created in the vessel off-gas line. The tests were made at 2-day intervals to allow for decay of ^{232}U daughters.

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