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ORNL-TM-2765

THORIUM FUEL CYCLE DEVELOPMENT PROGRESS REPORT

November 1969

No. 4

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CHEMICAL TECHNOLOGY DIVISION
METALS AND CERAMICS DIVISION

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I. HEAD-END REPROCESSING DEVELOPMENT

R. E. Blanco, W. E. Unger, V. C. A. Vaughen, C. D. Watson

II. REFABRICATION DEVELOPMENT

R. G. Wymer, A. L. Lotts, R. E. Brooksbank, P. A. Haas
W. D. Bond, J. W. Snider, J. D. Sease

III. MATERIALS IRRADIATION

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

IV. URANIUM-233 REPROCESSING

R. E. Brooksbank, J. R. Parrott

NOVEMBER 1969

OAK RIDGE NATIONAL LABORATORY
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CONTENTS

		Page
Introduction		1
I.	HEAD-END REPROCESSING DEVELOPMENT	
	Studies with Irradiated Fuels	2
	Head-End Engineering Studies	2
II.	REFABRICATION DEVELOPMENT	
	Particle Preparation	3
	Fueled Graphite Fabrication Development	7
III.	MATERIALS IRRADIATION	
	Irradiation of Prototype Recycle Fuels	9
IV.	URANIUM-233 REPROCESSING	
	Dissolution and Purification	11
	Storage and Distribution	11
	LWBR Support	12

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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 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 4.25. 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 cleaned up and made ready for test runs on a flowsheet for the preparation of ThO_2-UO_3 sol having a thorium-to-uranium ratio of two. Although we are not certain at this time that we will proceed with a production run of sol of this type, we want to be ready if called upon. 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.

1.2 Sphere-Forming Column Chemistry

(W. D. Bond, J. W. Snider, P. A. Haas)

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.

In the past, sphere forming columns have been operated continuously by making periodic additions of surfactants to off-set the losses of surfactant caused largely by reaction of the nitric acid (extracted from the sol) with the surfactants during removal of water by distillation. In addition to reactions during distillation, a relatively small amount of reaction occurs in the forming column as evidenced by slow discoloration of the solvent when the forming column is batch operated without a distillation system. The pH or acid contents of the 2EH that have been employed in continuous operation, have been mainly those governed by the amount of acid extracted from the sol which can subsequently be maintained in the 2EH with the distillation system operating. When higher acid contents are required, nitric acid must be added to the 2EH, and reactions with surfactants and 2EH are increased.

Laboratory studies have shown that reactions of nitric acid with 2EH and surfactants during distillation could essentially be eliminated by removal of the acid prior to distillation steps by contacting the 2EH with alkaline solutions. The acid content of the alcohol could then be maintained by adding nitric acid to the alcohol after the removal of water by distillation. We are presently evaluating this procedure as a means of controlling the pH and surfactant concentration of the engineering development sphere forming column during continuous operation. We are also studying a total 2EH purification method in which the 2EH is recovered by distillation; the used surfactants are discarded, and the 2EH is recycled

to the forming column after surfactants, water and nitric acid are added. Studies are continuing on the effect of surfactant and water content and the pH of 2EH on sphere forming using different sols in batch operated laboratory forming columns.

Recovery of 2EH by Distillation

Steam distillation is being examined as a means of recovering 2EH free of surfactants and then recycling the purified 2EH to the microsphere forming column. In the continuous distillations, water and used 2EH containing surfactants were metered into the distillation flask. The volumes of 2EH (free of surfactant) per volume of water added are tabulated below as a function of temperature.

Temperature, °C	Vol of 2EH/Vol of H_2O
120	0.2
165	2
175	4-9

Several stages of distillation are required to obtain pure 2EH from recycled solvent when steam is not used. After 3 stages of distillation the distillate contained detectable surfactant.

1.3 Preparation of Test Materials

(J. R. Parrott, P. A. Haas, F. L. Daley, R. J. Shannon)

Clean-out of the sol-forming equipment in the Solex Development Laboratory was completed during the month. The evaporator recirculation pump failed during flushing and was replaced. The system will be put in operation to make possible preparation of 5 kg of $^{235}UO_3$-ThO_2 sols containing a Th/U ratio of 2/1 (see Sect. 1.2 above).

The $^{235}UO_2$-ThO_2 sol made during the previous program (Th/U = 4.18/1) was formed into microspheres in the cell 4 facility. Operation was excellent with the new column. Several batches of low-nitrate sol, which could not be formed into microspheres previously, were processed successfully this month, suggesting the advantage of aging certain sols prior to forming.

A total of 7,050 g of oxide as calcined product is available for pyrocarbon coating. It is estimated that ~5 kg of this material will be suitable for coating.

The system was cleaned out and placed in standby for the next HTGR program.

Although not as a part of this program, but as a matter of interest to readers of this report, we should report that we finished the preparation of 20 kg of ThO_2 microspheres and shipped them to Los Alamos Scientific Laboratory. These microspheres (44 to 88 μ diam) were prepared using isoamyl alcohol in a column operating without fluidization. The nominal production rate was 500 g ThO_2 per hour and the yield in the 44 to 88 μ size range was 55%.

Sol-gel material on hand from development studies was used to supply the following:

(a) 1900 g of ThO_2 spheres to the Reactor Chemistry Division for use in "ion exchange" studies in molten salt.

(b) 1900 g of ThO_2 spheres to Gulf General Atomic Corporation.

(c) 40 kg of ThO_2-UO_2 spheres to be used in pyrocarbon coating and other studies at ORNL.

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 recycle fuel, as detailed in the National HTGR Recycle Program Plan. The fuel consists of microspheres of thorium and/or uranium as the oxide or carbide. These particles are typically made into a fuel stick and then inserted into a hexagonal graphite log which contains both fuel holes and coolant holes.

Our work is divided into particle coating, particle handling and inspection, particle blending, fuel stick molding and inspection, fuel element assembly, fuel stick carbonization, and fuel element inspection. This month we emphasized particle coating and inspection.

2.1 Particle Coating

The 5-in.-diam prototype remote coating furnace is an advanced version of our 5-in.-diam laboratory furnace which we have successfully operated for over two years. The improvements incorporated in the prototype furnace are designed to allow reliable remote, production-scale operation and maintenance. We are continuing tests on the recently constructed prototype furnace.

The hydrogen supply lines for the silicon carbide coating system have been leak-checked. These hydrogen lines can supply 2 to 3 cfm of dried H_2 or 5 to 10 cfm of H_2 as received from a tank truck.

The pneumatic particle loading and unloading system for the furnace has been installed and tested. This system uses a differential pressure to transfer the particles from a glovebox in through the furnace top. To unload, the particles are dropped through the bottom of the furnace to a cooling chamber and then by differential pressure propelled back to the glovebox. During checkout, only minor difficulties were encountered with this system. These difficulties have since been corrected.

Last month we mentioned that the O_2 monitor for the stack did not have a pump or flowmeter. These items were installed; however, during

testing, a filament in the instrument was burnt out. Since the O_2 monitor is necessary to ensure safety, the coating operations are being delayed until the monitor can be repaired.

We are currently testing an optical sensing device for controlling the furnace temperature. We are experimenting with different collimators to eliminate interference from the heating element which is generally hotter than the area of interest, the furnace cone. We expect to complete the development of the sensor this month.

The alarms and monitors for the effluent exhaust system are now working correctly. In addition to monitoring the temperature to detect fire at a number of sites on the exhaust system, we monitor the power going to the pump and the water circulating to the pump seals.

The 5-in.-diam laboratory furnace in the Coated Particle Development Laboratory has been remodeled and is now in operation. A new top section was installed on the furnace along with new loading and unloading lines, coolant lines, drain line, and gas lines. The major modification was the connection of the exhaust to the effluent exhaust system of the prototype coating furnace.

2.2 Particle Inspection

To economically produce coated particles, the accurate size of the particles must be known immediately before and after coating. We are developing a particle size analysis to provide this information.

We have modified a HIAC Automatic Particle Counter[1] to minimize electronic drift. This drift necessitated frequent recalibration to obtain the 1% accuracy we desire. We replaced the power supply to the thresholds of each channel with a Hewlett Packard 6205B regulated power supply[2] through a choke coil to prevent signal pulses from affecting the supply voltage. We changed the operating lamp power supply to a regulated power supply controlled by a photo diode observing lamp intensity. The photo diode is mounted inside the chassis and receives the signal by fiber optics.

We will resume calibration of the analyzer this month.

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[1] High Accuracy Products Corp., Claremont, California.

[2] Hewlett-Packard, Palo Alto, California.

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 and F. J. Furman)

The HTGR recycle program requires irradiation tests. The twofold objective of these tests is: (1) to provide irradiated fuel for head-end process studies, and (2) to provide irradiation proof tests 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 × 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 test elements to be irradiated in the Peach Bottom Reactor.

1.1 Capsule Irradiations

A preliminary capsule design has been developed and distributed for comments prior to proceeding with the detailed design. Basically the proposal involves a capsule containing four 8-in.-long fuel bed segments. Each segment will contain a loose 0.3-in.-diam bed of coated particles. The bed diameter is limited by the available test space in the Advanced Test Reactor. Two types of particles are to be included: (1) a $(Th,^{235}U)O_2$ recycle particle with a thorium-to-uranium ratio of 4.2:1, and (2) a ThO_2 particle. The coating parameters proposed are the latest available Gulf General Atomic recommendations, and the final fuel bed will have an overall thorium-to-uranium ratio of approximately 12:1.

The preliminary design analysis indicates each segment can be operated at a different central bed temperature. The physics calculations to develop a shell source are incomplete; so final design calculations cannot be completed.

1.2 Large Scale Irradiations

No additional work has been done on the Peach Bottom Reactor tests pending receipt of comments from Gulf General Atomic on the proposals sent to them in August.

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 solvent extraction purification run, **begun last month to recover** 3.0 kg of ^{232}U, was completed (Run No. 9694097). The system was flushed extensively and a second purification run to recover 6.1 kg of ^{233}U containing 6 ppm ^{233}U was made (Run No. 969698). The latter run was made to fill an order that was later cancelled.

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. A sample of each of the solution storage tanks was withdrawn and submitted for analysis to verify the "book" inventory.

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.

Since introduction of the uranyl nitrate solution into storage tank P-25, repeated chemical analyses for cadmium and gadolinium (soluble neutron poisons) indicated that their concentrations were constant but lower than specified by the Criticality Review Committee after a year's storage. (The mole ratios: Cd/U $\geq$0.313 and Gd/U $\geq$0.0263 must be met if

either is to poison the entire amount of uranium in case the tank leaks.) To meet the above requirements, 13 kg of cadmium as nitrate and 3.5 kg of gadolinium as oxide were dissolved and added to the stored solution this month. The solution was then sparged and sampled (TUC-7). Radiation intensity of a 10-ml sample was about 500 mrad/hr at contact with the glass bottle.

Sections of the new vessel off-gas piping for the storage tank P-25 are being fabricated.

3. LWBR Support Program

As a result of a meeting with representatives from Bettis Atomic Power Laboratory, ORNL participation in the Navy's Light Water Breeder Reactor Program is a certainty. Preliminary plans for the receipt, storage, and purification of 600 kg of ^{233}U have been made. Detailed schedules and costs for the above, in addition to conversion to a ceramic-grade UO_2 powder, will be submitted to Bettis in early November. The planned production rate is 17.5 kg of ^{233}U a week for a period of approximately 16 months. The blending of this powder with ThO_2 and subsequent pressing into pellets will be performed by Bettis.

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