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THORIUM FUEL CYCLE DEVELOPMENT PROGRESS REPORT

OCTOBER 1969

No. 3

Compiled by

The Staff of the Chemical Technology

and

Metals and Ceramics Divisions

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CHEMICAL TECHNOLOGY DIVISION
METALS AND CERAMICS DIVISION

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No. 3

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R. E. Brooksbank, J. R. Parrott

OCTOBER 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 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 still in progress.

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 ± 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, and forming ThO_2-UO_3 gel microspheres to dense ThO_2-UO_2 in good yield.

1.1 Sol and Microsphere Preparation Development

(P. A. Haas)

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.

<u>CPDL Microsphere Preparation</u> (C. C. Haws)

Chemical analyses for the 43 kg of ThO_2-UO_2 spheres prepared during the demonstration run are now avilable, and are given in Table 1.1. These results demonstrate:

1. A good, low O/U ratio was obtained.
2. Nearly theoretical densities, much better than > 95% of theoretical, were obtained.
3. Gas release values as low as any sol-gel products from routine operation.
4. Very good carbon contents -- lower than we expected.

Table 1.1. Chemical Properties of ThO_2-UO_2 Product Batches from CPDL Demonstration Run

Calciner Batch Number	O/U Ratio	Mercury Density, 15000 psi	Gas Release, cc/g	Carbon, ppm	Surface Area, m^2/g
1	2.004	10.17	0.026	40	0.017
2	2.010	10.19	0.009	40	0.005
3	2.011	10.11	0.030	30	0.122
4	2.015	10.22	0.019	40	0.009
Specification:	< 2.03	9.67[1]	≤ 0.3	< 500	- - -

[1] Theoretical density = 10.18 g/cc.

1.2 Preparation of Test Materials

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

Operation of the Solex Development Laboratory was discontinued after two additional sol forming runs (1 kg HM each) were completed. This makes a total of 3.5 kg of Th + ^{235}U ($Th/^{235}U$ = 4.18/1) sol produced for the preparation of fuel for irradiation testing as set forth in the National HTGR Recycle Development Program draft.

The two runs were made with a 15% reduction in the extractant (Amberlite LA-2 in n-paraffin) flow rate reported last month. The resultant sol contained a NO_3^-/metal mole ratio of 0.1. The system has now been flushed free of residual thorium and uranium and decontamination was initiated to permit the installation of additional equipment for preparation of LMFBR fuel for testing in EBR-II.

Microsphere forming with the above sol was performed in the Cell 4 facility. However, after prolonged operation, the transfer of gel microspheres became difficult, indicating insufficient drying in the column. A new column with a smaller throat diameter and a taper designed to give a higher alcohol velocity was installed. Initial operation of this column with 0.1% Ethomeen S/15 surfactant gave excellent results in forming 500 μ diam gel spheres. The particle residence time was 45 min, which is ample.

Operation was terminated when a small crack in the column was detected. A new column is being fabricated.

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 which is 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 development, although some work was done on particle handling and inspection.

2.1 Particle Coating

The 5-in.-diam prototype remotely operated coating furnace is designed to be used for both pyrocarbon and silicon carbide coating of microspheres. We are currently testing and modifying the equipment.

The furnace has been successfully tested to 1650°C, a temperature sufficiently high for both low temperature pyrocarbon coating and silicon carbide coating. For this test, the furnace heating element was shielded with two molybdenum reflectors. Approximately 55% of the 100 kw of power that is available was required. However, only a 6-in.-cone length had a temperature variation of less than 50°C. We believe that extreme temperature variations will lead to the deposition of soot layers in the pyrocarbon coatings, so we have designed and are having fabricated a 9 1/2-in. extension for the furnace. With this extension, the constant temperature heat zone should be more than doubled.

We completed a series of tests on the exhaust system. Initially, we found errors in the operation of the back-pressure control valves. These errors were corrected. We also discovered that the water-sealed furnace exhaust pump will back water into the absolute filters when it is shut down with the valves in normal operating position. Fortunately,

we have found that manually shutting the exhaust-pressure control valve prevents the backflow of water, and we have incorporated this technique into our operating procedures.

The exhaust system now operates correctly except for the alarm circuits, which do not give reliable alarms. This situation is currently being investigated.

We were concerned about water carryover from the scrubber used in silicon carbide coating to the absolute filters. However, sustained flow of 5 cfm argon or helium through the scrubber system did not adversely affect the absolute filters downstream from the scrubber.

The combustible gas alarms have been tested and are working correctly. However, we found that no combustible gas alarm lines went to the exhaust, thereby preventing adequate tests of our procedures for purging the exhaust after coating operations. This oversight will be corrected by the installation of a valve to allow exhaust gas to flow to both the oxygen and combustible gas meters.

The oxygen meter did not contain a pump or flow meter. This equipment has been obtained and will be installed next month.

As mentioned last month, we are improving our laboratory 5-in.-diam coating furnace. The installation of an exhaust connection to the prototype furnace exhaust pump is now complete. Installation work of the new furnace top section, vacuum system, particle loading system, and reconnection of the gas and cooling water supply continues. This construction should be completed next month.

2.2 Particle Handling

We have modified a SWECO[1] gyratory screen for use in hot cells. Previously, each screen, frame, and self-cleaning unit had to be assembled piece by piece in place. We have modified the design so that these parts can be assembled into a module. Only one assembly for each desired screen size need be handled in the hot cell. We have also eliminated the

[1] Southwest Engineering Company, Los Angeles, California.

clumsy clamp rings used to hold the screen frames together. Thus, in a hot cell, the screens can be changed by releasing toggle action clamps and changing screen modules, actions which can be done with manipulators. We are currently having specially designed gaskets fabricated for the modules.

Also this month, we screened, shape separated, and batched for coating approximately 38 kg of sol-gel $(Th\text{-}U)O_2$.

2.3 Particle Inspection

We investigated typical particle distributions for sol-gel microspheres. Results of particle size analysis on $(^{233}U,Th)O_2$ microspheres production showed that the standard deviation of the particles could vary from 16 to 30 μ from the mean size in batches with a mean diameter of approximately 300 μ. The standard deviation was generally in the 21 to 26 μ range. No special effort was made to control the standard deviations during this production run.

A recent production run of $(^{233}U,Th)O_2$ microspheres had a particle diameter standard deviation of 23 μ in the first half, and after conditions were changed, a standard deviation of nearly 30 μ. Since the changed conditions were undesirable from the standpoint of standard deviation and material reject (21%), we should only consider the first half of the operation. This half of the run produced nearly 20 kg of material of which only 6% was rejected for out-of-roundness. The mean size was only slightly higher (366 μ instead of 350 μ) than that intended. This size control is excellent since the size results were not available in time to make corrections to the process as would be the case in a true production facility.

2.4 Particle Blending

Fabrication of the filler-blender, which will be used for loading particles in carefully controlled ratios, was begun.

III. MATERIALS IRRADIATION

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

Nothing significant to report.

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

During the month six dissolutions of UO_2 powder and salvaged metal were made to recover 3055 g of ^{233}U. One solvent extraction purification run performed on the day shift only resulted in the recovery of 18 kg of ^{233}U containing 6 ppm ^{232}U. The system was flushed extensively and a second run to recover 3 kg of ^{233}U containing 40 ppm ^{232}U was started. This high ^{232}U material had been stored for 2 years in shipping containers. The bulk of the material was received from Australia.

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.

A test was made to determine the efficiency of a small water scrubber in reducing the radiation background in the vessel off-gas line as a result of entrainment while air sparging. Results were similar to those for a silica gel trap test reported last month; that is, the scrubber was not quite as efficient in trapping the uranium and highly radioactive ^{232}U daughters as the paper filters.

The design of revisions to the off-gas system is complete. This design includes an entrainment separator and an SGN Mini-Caisson absolute filter. Piping changes will eliminate the collection of liquids in the line. Items to be purchased were ordered.

3. LWBR Support

As reported last month, at the request of Bettis Atomic Power Laboratory, we submitted a proposal to receive, store and purify approximately 600 kg of ^{233}U for the Navy's Light Water Breeder Reactor Program. This proposal also included the recovery of uranium from scrap generated during the fuel fabrication program.

The second proposal, which consists of converting the uranium to a ceramic-grade oxide suitable for blending with thoria for pellet pressing, has now been submitted.

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