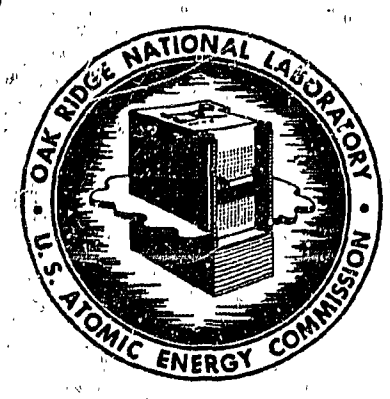

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL- TM- 3032

THORIUM FUEL CYCLE DEVELOPMENT PROGRESS REPORT

May 1970

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CHEMICAL TECHNOLOGY DIVISION
METALS AND CERAMICS DIVISION

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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Compiled by

The Staff of the Chemical Technology and
Metals and Ceramics Division

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 a bonded state.

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 facility for fuel recycle. The CPDL is for engineering development studies leading to design of the equipment to be used in TURF.

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 a solvent extraction process. Small samples of irradiated and unirradiated fuel are studied to determine

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effects of irradiation on fuel reprocessing steps and to correlate 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 for fixed-bed burners. The mechanical and burn-leach engineering development work is carried out using full-scale unirradiated fuel of the type to be used in PSC, 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)

1.1 Procurement of Irradiated Dragon Fuels

We have been in negotiations with the UKAEA for the procurement of 9 irradiated Dragon compacts of the (Th/U)C_2, ThC_2, UC_{10}, UC_{20} and (U/Th)O_2 varieties, and 7 unirradiated controls for our head-end studies. The compacts selected are similar to proposed recycle and makeup fuel particles. For example, there is one type of compact (19M) which includes two types of SiC coated particles, similar to the Ft. St. Vrain Reactor - a large (~1200μ) ThC_2 kernel and a small (~600μ) UC_{10} particle. The types of compacts requested are given in Table 1.

These compacts will be sent before July 1, 1970, if the arrangements and clearances can be completed.

1.2 GGA Fuel Stick Analysis

We have put an old, unirradiated (~2 yr) GGA resin-bonded FSV style fuel stick through our jaw crusher and some of the head-end processing steps. The graphite sleeve broke cleanly away from the fuel stick at a 5/8" jaw opening. Of the original 379.60 g, 256.17 g of large graphite fragments were recovered free of fuel. Sieve analysis of the remaining 123.43 g of fuel and small pieces of graphite gave

Table 1. Requested Dragon Fuel Samples

UKAEA Code	Material	Number of Units Requested		Kernel Diam (μm)	Density, % Theoretical	Coating Type and Thickness
		Irradiated	Unirradiated			
3M	$(10Th,U)C_{2,4}$	2	1	850-1000	60-70	TRISO (50/30/80)
18M	UC_{20}	1	1	422-600	60-70	TRISO (25/30/70)
19M	ThC_2*	2	1	850-1200	60-70	TRISO (25/30/70)
	UC_{10}			422-600	60-70	TRISO (25/30/70)
38M	$(5Th,U)C_{2.4}$	1	1	422-600	60-70	BISO (40/80)
2M4	$(10Th,U)O_2$	1	1	500	~75	BISO (130 total)
2M7	$(10Th,U)O_2$	1	1	500	~75	TRISO (160 total)
2M10	$(10Th,U)C_2$	1	1	500	~60	TRISO (150 total)

*Both of these particle types are in the one compact.

a distribution of 50.7% +4 mesh, 12.5% +9 mesh, 8.5% +20 mesh, 26.1% +42 mesh, 1.18% +60 mesh, 0.36% +100 mesh, and 0.74% -100 mesh fines. Those fractions above 60 mesh were individually split into eight samples and combined to provide eight randomized samples of crushed fuel. The -60 mesh samples were combined for leaching. Leaching results are not yet available.

Two samples were burned at 750°C in a fluidized bed with alumina (T-61). Considerable self-sticking and slight alumina adhesion were noticed for the SiC coated particles from the burner product. This sticking may be the result of an impurity (Na or Li, for example) in the resin reacting with the SiC coatings. Leaching followed by tumbling and several (3-5) screenings appeared to help separate the smaller U particles from the larger Th particles; however, crossover and breakage calculations are still not finished. A considerable amount of screen blinding was observed with the wide range of particle sizes present; however, the screens did not have any self-cleaning action. Final screen analyses after burning were: 8.12% +28 mesh, 42.8% +35 mesh, 6.62% +42 mesh, 25.8% +48 mesh, 14.4% +60 mesh and 2.23% -60 mesh (includes some Al_2O_3 fines) for the R-1 fraction. These results have not yet been interpreted for crossover and breakage.

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 general approach followed has entailed the mechanical dissection, by sawing, of full-sized graphitic blocks containing fuel, followed by comminution to size fractions suitable for the burn-leach process. However, the recent GGA decision to use bonded fuel sticks rather than loose particles as the reference form has necessitated changes in the approach.

Work on the head-end engineering studies program has resumed. Efforts during this report period were primarily directed toward rewriting the National HTGR Recycle Program Plan to reflect changes which have occurred in the overall HTGR program.

The Jeffrey hammer mill was reconditioned and equipped with a new dust collection system. Screen bars for this unit were obtained which will permit material to be crushed as fine as 0.125 in. Comminution tests will be made as soon as fuel blocks become available.

The 2-in.-diam fluidized-bed burner has also been reconditioned, and tests are under way to check out the instrumentation, the off-gas analyzers (for CO, CO_2, and O_2), and to train the technicians in fluidized-bed burning operations.

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 reliable, remote processes 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)

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.

A review and revision was started of the sol-gel sections of the "National HTGR Recycle Devebopment Program Plan." This is part of an effort to bring this program plan up-to-date and to allow application of the Critical Path Time-Cost Scheduling technique to the Recycle Program.

2.0 Fueled Graphite Fabrication Development

(F. J. Furman, W. H. Pechin, and J. D. Sease)

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, and 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, particle bonding, fuel element assembly, and fuel element inspection. This month we continued work on particle handling and coating of fuel material and on fabricating fuel sticks to be used in the Recycle Test Elements (RTE's) being prepared for irradiation in the Peach Bottom Reactor.

2.1 Particle Handling

Prior to any coating operation, the sol-gel microspheres must be sintered to high density and processed to remove over- and undersized and nonspherical particles. All sintering and processing of RTE material was completed this month.

2.2 Particle Coating

We coated four types of microspheres for the RTE's in the prototype remotely operated coating furnace: ThO_2, (Th–20% U)O_2, high spherical (Th–33% U)O_2, and nonspherical (Th–33% U)O_2. During the last month we completed the coating of all particles required for the RTE's. The analysis of this material will be presented in the next section.

2.3 Particle Inspection

The measured diameters on the (Th–20% U)O_2 and (Th–33% U)O_2 are listed in Table 1. The coating properties are listed in Table 2. The gradient density results on the isotropic coatings are not yet available. The chemical analyses on the kernel material are listed in Table 3.

An improvement has been made in the calibration of the split image eyepiece which is used to measure particle diameters from the microradiographs. The eyepiece was calibrated against the stage micrometer at eight different micrometer marks, and the calibration factor was determined as a function of measurement by a least squares fit to a hyperbolic function. This provides a means to account for a significant nonlinearity of the eyepiece calibration and averages out the irregularities in the micrometer scale.

2.4 Development of Bonded Beds of Coated Particles for HTGR Fuel Elements

(J. M. Robbins)

This report period has been devoted entirely to the production of fuel sticks for the Recycle Test Elements (RTE's), and to the fabrication of the spine samples that will be tested with the RTE's in Peach Bottom. The current status of the production of RTE's is shown in Table 4. It is anticipated that all RTE's will be shipped by the end of May 1970.

Some problems are being encountered in the fabrication of the spine samples. The particle bed is the same combination of small UO_2 and large ThO_2 that was used in the "g-type" RTE's. Again, it is difficult or impossible to inject some bonding mixes into the dense particle bed. These difficulties have to be overcome with each individual mix. These spine samples should be complete by May 20, 1970.

Table 1. Diameters on $(Th\text{-}U)O_2$ Particles Coated for Recycle Test Elements

Run Number	Kernel Diameter		Buffer Diameter			Final Diameter		
	Average (μm)	Standard Deviation (μm)	Measured Average (μm)	Standard Deviation (μm)	Calculated Average (μm)	Measured Average (μm)	Standard Deviation (μm)	Calculated Average (μm)
$(Th\text{-}20\%\ U)O_2$ Particles								
54/53	342.1	35.3	511.7	39.5	495.7	657.5	33.4	668.5
55/53	350.4	28.8	511.7	39.5	512.1	677.7	32.7	690.4
56/52	344.2	39.2	517.6	50.5	499.0	770.0	44.2	757.0
57/52	356.6	29.4	517.6	50.5	517.0	784.8	44.7	782.1
$(Th\text{-}33\%\ U)O_2$ Particles								
60/58	354.9	41.8	508.5	50.3	509.7	759.4	52.7	763.7
61/58	351.7	35.0	508.5	50.3	508.7	756.0	40.8	766.6
62/59	375.4	48.6	526.7	47.3	548.2	823.5	60.5	829.7
63/59	379.5	41.2	526.7	47.3	552.5	816.5	50.6	862.5
66/65	339.7	40.3	537.8	38.2	517.8	793.5	34.9	782.7
67/65	341.2	37.1	537.8	38.2	520.1	805.8	40.6	797.6
68/64	366.3	28.7	530.9	37.2	541.9	784.3	47.2	819.3

Table 2. Coating Properties of Particles Prepared for the Recycle Test Elements

Run Number	Buffer Coating				Isotropic Coating		
	Thickness From Measured Diameters (μm)	Standard Deviation (μm)	Thickness From Calculated Diameters (μm)	Density From Mercury Displacement (g/cm³)	Thickness From Measured Diameters (μm)	Thickness From Calculated Diameters (μm)	Density From Mercury Displacement (g/cm³)
54/53	72.0	15.0	76.8	1.106	72.9	86.4	1.941
55/53	72.0	15.0	79.4	1.106	83.0	89.2	1.881
56/52	73.5	15.0	77.4	1.104	126.2	129.0	1.820
57/52	73.5	15.0	80.2	1.104	133.6	132.6	1.840
60/58	76.3	17.1	77.4	1.197	125.5	127.0	1.818
61/58	76.3	17.1	78.5	1.197	123.8	129.0	1.840
62/59	79.8	16.3	86.4	1.227	148.4	140.8	1.832[a]
63/59	79.8	16.3	86.5	1.227	144.9	155.0	1.735[a]
66/65	87.0	16.5	89.1	1.172	127.9	132.5	1.826
67/65	87.0	16.5	89.5	1.172	134.0	138.8	1.733
68/64	76.5	12.7	87.8	1.267	126.7	138.7	1.730[a]

[a]These runs were made using the poorly shaped 2:1 ThU kernels.

Table 3. Kernel Analyses

Kernel Batch	Coating Runs	Wt % Th	Wt % U	O/M	Wt % O[a]	Σ %'s
102-4970	54 thru 57	64.64	16.38	2.104	11.71	92.73
UX 11,12,13 17,18	66 and 67	59.96	27.00	2.067	12.34	99.30
UX 7,8	62 and 63	62.49	26.54	2.063	12.62	101.65
UX 14,15,16	60 and 61	61.51	27.68	2.004	12.28	101.47
UX 5,6,9,10	68	62.33	26.41	2.094	12.76	101.50

[a]Calculated from reported O/M.

Table 4. Current Status of the Production of RTE Fuel Sticks at ORNL

Type Particles	Number of 2.14-in.-Long Sticks Needed			Number Shipped	Number Ready to Ship	Number Remaining to Fabricate
	RTE's 1–4	RTE's 5–8*	Total			
(4.2 Th/U)O_2	96	72		72	26	70
(2 Th/U)O_2 + ThO_2	96	72		72	0	96
(2 Th/U)O_2 + ThC_2	144	168		168	144	0
UO_2 + ThO_2	96	120		120	11	85

*All fuel sticks for RTE's 5–8 (3-yr elements) were made and shipped first.

2.5 Fuel Element Assembly

We are setting up equipment to load two RTE fuel segments. These 15-in.-long graphite blocks containing eight fuel holes will be loaded with coated (Th–20% U)O_2 particles and graphite flour. We are performing this operation because the oxide material is contaminated with < 10 ppm ^{238}Pu, a contamination level too high to allow element assembly in the factory at Gulf General Atomic (GGA). We will assemble the segments in a hood, seal the fuel channels, and ship the segments to GGA for final assembly into the 12-ft Peach Bottom fuel elements.

III. MATERIAL IRRADIATION

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

1.0 HTGR Recycle Fuels Irradiation

(T. N. Washburn, R. B. Fitts, and A. R. Olsen)

The irradiation tests on the HTGR recycle program have two main objectives: (1) to provide irradiated fuel for head-end process studies, and (2) to provide irradiation proof tests of the products of coated particle process development for the Thorium-Uranium Recycle Facility. The test conditions of interest include fuel temperatures between 600 and 1300°C, burnup to 20% FIMA in the $(Th,U)O_2$ particles, and fast fluence exposures up to 8×10^{21} neutrons/cm^2.

The first two stages in this program are being implemented this year. They are: (1) accelerated burnup rate capsule irradiations, and (2) eight test fuel elements to be irradiated in the Peach Bottom Reactor.

1.1 Capsule Irradiation

(A. R. Olsen)

During the past month we have continued to investigate the possibilities of using a thermal neutron shield for an irradiation capsule to be irradiated in an ETR-J8 position. The current investigation revolves around the use of a zirconium-hafnium sleeve around the outside of the stainless steel capsule. A capsule design has been developed as shown in Fig. 1. The physics calculations for this design will be made as soon as 36-group cross sections are available for the ANISN calculations. D. B. Jenkins is currently

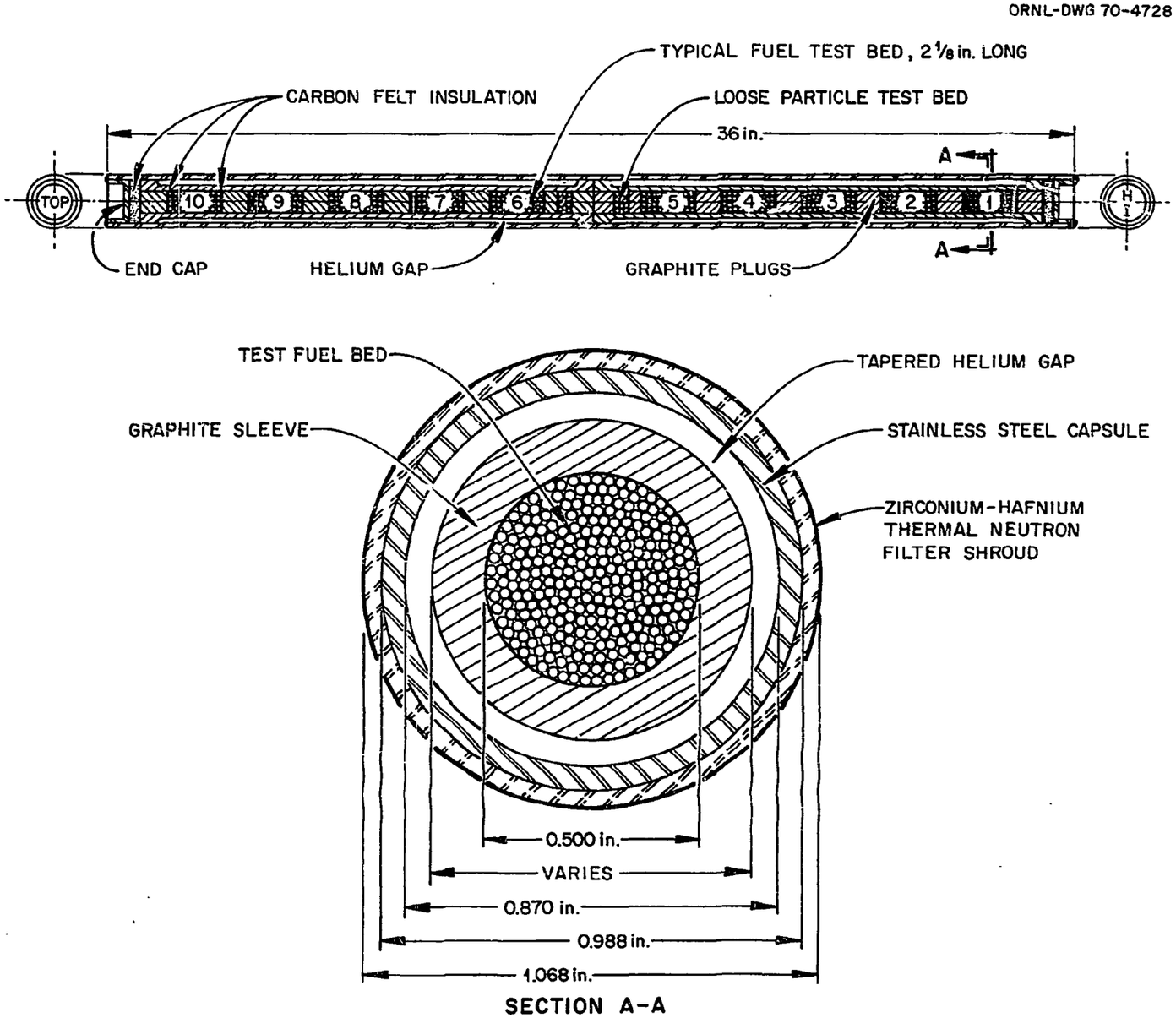

Fig. 1 Schedule of Proposed HTGR Recycle Irradiation Capsule.

assembling the necessary information to generate this cross-section data. Based on similar work at Bettis,[1] thermal neutron flux reductions to a factor of 2 are possible using pure hafnium sleeves 0.040 in. thick. With the cooperation of the local AEC site representatives, we have contacted the AEC Naval Reactors Branch in Washington, and they are currently checking with Bettis to see if they can provide us with sleeves of the hafnium alloys.

In order to proceed without delay when the calculations are completed, we have arrived at a tentative loading schedule for the first two capsules. This current loading plan is given in Table 5.

1.2 Large Scale Irradiation
(R. B. Fitts)

Eight Recycle Test Elements (RTE's) will be operated in the Peach Bottom Reactor starting in June 1970. These fuel elements will contain samples of fuels proposed for use in 1100 Mw(e) HTGR's. The preparation of the ORNL portion of the fuels for RTE's is behind schedule, although not seriously, and is progressing well as outlined below and described in detail as indicated.

The particles of the RTE's have all been coated (Section 2.2 of this report) and all but the last three batches of (Th–20% U)O_2 particles have passed all inspections (Section 2.3 of this report). The bonded stick making effort is progressing despite some routine difficulties.

The RTE's contain two 15-in. fuel bodies loaded entirely with loose (Th–33% U)O_2 coated particles. Since GGA has decided that these bodies cannot be loaded at their factory we have decided that they must be loaded here. Three graphite blocks (one extra) are being shipped to ORNL ready for loading. The calcined petroleum coke filler for this loading will also be shipped here from GGA. These bodies will be loaded and returned to GGA as soon as possible.

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[1]R. M. Lieberman, "A System for Calculation of Fission Power in Irradiated Tests," National Symposium on Developments in Irradiation Testing Technology, Sept. 9–11, 1969, CONF-690910, USAEC-1970, pp. 473–490.

Table 5. Fuel Loadings for HTGR Irradiation Test Capsule H-1 and H-2

Position	Capsule H-1		Capsule H-2	
	Temperature (°C)	Particle Mix[a]	Temperature (°C)	Particle Mix[a]
1	1050	f	950	f
2	1050	g	950	g
3	1050	c	950	c
4	1050	a	950	a
5	1050	f	950	f
LP[b]	1050	a, c	950	a, c
LP[b]	1300	a, c	750	a, c
6	1300	f	750	f
7	1300	a	750	a
8	1300	c	750	c
9	1300	g	750	g
10	1300	g[c]	750	g[c]

[a]Particle mix: a = (4.2 Th, U)O_2 BISO + ThO_2 BISO.
c = (2 Th, U)O_2 BISO + ThO_2 BISO.
f = UC_2 TRISO + ThC_2 BISO.
g = UO_2 BISO + ThO_2 BISO.

[b]LP's are loose particle containers for extensive metallographic examination and performance analysis.

[c]Blended beds (All others are bonded beds).

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 $^{233}UO_3$, which was incompletely dissolved in a solution having a low acid concentration last month, was dissolved in 4 M HNO_3. Since the resulting solution had an acid concentration that was too high for purification by an ion exchange process, the entire batch was transferred to the solvent extraction system for future purification.

The dissolver system is being redesigned and procedures are being rewritten to allow safe operation and to produce a feed solution that is compatible with the ion exchange process.

The solvent extraction equipment was not operated during the month.

2. Storage and Distribution

The facility presently contains 262 kg of ^{233}U which varies in isotopic purity between 84 and 98% and ^{232}U content between 4 and 250 ppm. A total of 1,131 g of ^{233}U was received and 74 g of ^{233}U was shipped 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.

This solution was sparged for 25 hours and sampled to determine the concentration of soluble neutron poisons. The data show that the poisons

are present in the proper concentrations, within the limits of accuracy of measurement.

Neutron Poison	Mole Ratio ($\frac{X}{U}$) Actual	Required* (min)
Cd	0.30	0.31
Gd	0.024	0.026

*J. P. Nichols, "TRUST Facility — Safety Analysis Report," ORNL-CF-68-3-37 March 29, 1968.

Sparging was stopped because of high radiation background at the off-gas filter. It will be resumed after a 2-in.-thick lead shield is installed around the filter.