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STATUS AND PROGRESS REPORT FOR THORIUM FUEL CYCLE DEVELOPMENT FOR JANUARY 1, 1969 THROUGH MARCH 31, 1970

Compiled by
R. G. Wymer and A. L. Lotts

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

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

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ORNL-4629

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

METALS AND CERAMICS DIVISION

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Compiled by

R. G. Wymer and A. L. Lotts

Edited by

Sigfred Peterson

FEBRUARY 1971

OAK RIDGE NATIONAL LABORATORY
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SUMMARY

1. Process Demonstration and ^{233}U Distribution

The Oak Ridge National Laboratory facility for storing and handling ^{233}U is being augmented by nine wells for storing solids and five tanks for storing solutions. This change increases the storage capacity by 80% for solids and 100% for solutions. A nitrate-to-oxide conversion line with a capacity of 22 kg ^{233}U/week is being installed. The facility received 44 kg of ^{233}U and shipped 7 kg. Experience with the TRUST (Thorium Reactor Uranium Storage Tank) facility showed that using borosilicate glass Raschig rings is practical for criticality control in large tanks of solutions of fissile isotopes.

2. Thorium-Uranium Recycle Facility

The safety analysis was published and accepted, and the maintenance manual was completed. The cell used for LiF-$^{233}UF_4$ preparation was cleaned to permit direct installation of equipment for isolating ^{248}Cm. Improvements were made or sought in the in-cell fire protection system, emergency power, cell outlet filters, and waste systems.

3. Sol-Gel Process Development

Demonstration of Engineering-Scale Production of ThO_2-UO_2 Microspheres

We prepared ThO_2—19% UO_2 microspheres in a continuous, engineering-scale demonstration at 10 kg (Th+U)/day. Sol preparation by amine extraction was routine and reproducible, and 1.6 M ThO_2-UO_3 sol containing 120 kg of ThO_2-UO_3 was produced in 99.5% yield based on the metal nitrate feed. No significant problems are anticipated in adapting sol preparation to fully remote operation. Up to 95% yields (based on sol fed to the system) of product-grade 250- to 450-μm-diam spheres (calcined) could be obtained by using multiple two-fluid nozzles and gelation of the sol droplets in 2-ethyl-1-hexanol (2EH). Addition rates of surfactants required to sustain operation of the sphere-forming column

demonstrated the need for a cleanup and recycle process for the 2EH in long-term operations.

Operation of 20-kg-batch, fixed-bed gel sphere dryers, previously used for drying ThO_2 gel spheres, was unsuccessful with ThO_2-UO_3 because of uncontrollable temperature excursions. With external heating and the instrumentation for measuring bed temperatures we could not carry out the dryings in the required 48-hr turnaround time. After installation of an adequately designed dryer, 20-kg batches of the ThO_2-UO_3 gel spheres were dried successfully in the specified time. No problems were encountered firing 10-kg batches of dried gel spheres in a fixed-bed calciner. The calciner concept tested appears workable.

The microspheres produced met specifications covering size, thorium-to-uranium ratio, roundness, oxygen-to-uranium ratio, gas release, density and carbon content.

CUSP Solvent Extraction Preparation of UO_2 Sol

The CUSP (Concentrated Urania Sol Preparation) process was used in engineering-scale equipment to prepare urania sols containing more than 230 kg of UO_2. High-quality products were consistently obtained in both laboratory and engineering equipment.

During the engineering-scale operations, solvent regeneration was complicated by small quantities of colloidal uranium in the solvent. These particles are not effectively removed by standard treatments with nitric acid, water, and caustic. However, scrubbing with 1 M HNO_3–1.2 M $HC_2H_3O_2$ removed about 96% of the uranium. The solvent is regenerated by scrubbing with a sodium carbonate solution and then with water.

An effective contactor for the extraction of nitrate to form urania sol is a column with a spray header to disperse the aqueous phase into the extractant, Alamine LA-2. This type of contactor is being considered for use with the large engineering-scale equipment.

Gel Sphere Forming Development

The factors important in forming microspheres were studied in factorial experiments. The variables were the concentration in the 2EH of water, acid, and the surfactants, Ethomeen S/15 and Span 80. Analysis of the data showed that the concentration must be properly balanced for good sphere forming with ThO_2-UO_3 sols. When the Ethomeen S/15, Span 80, and acid concentrations were properly balanced, varying the water content from 0.5 to 1.7% had little effect.

We are studying the methods used to recycle the 2EH to the sphere-forming step. Our principal interest is to prevent chemical degradation of the alcohol during water removal as well as to recover totally purified 2EH. Laboratory studies showed that reactions of nitric acid with 2EH and surfactants during distillation could essentially be eliminated by removal of the acid before distillation by contact with alkaline solutions or ion exchange resins.

Scrubbing with an alkaline solution during continuous operation of the sphere-forming column was unsatisfactory because of emulsification and entrainment. Substituting a resin-bed column for the alkaline scrubber in the solvent recycle circuit avoided phase separations and hence avoided emulsion and entrainment problems. The performance of the ion exchange column is being evaluated.

Distillation appears feasible if total purification is required. Pure 2EH was obtained by distillation of water-2EH at 100, 150, and 180°C.

Optimum conditions for forming a sol into gel microspheres change in a complex manner with the properties of the sol. Although understanding is incomplete, especially for urania sols, qualitative conclusions about the effects of some of the variables can be made. Surfactants and acid concentrations can be balanced so that good sphere forming occurs. However, formic acid buildup in the 2EH has prevented continuous operation. Removal of formic acid from the recycle 2EH will be required in continuous operation.

We reported on the design and operation of fluidized-bed columns for gel sphere preparation. Major topics are fluidization requirements, control of alcohol composition, and capacity limitations.

Preparation of gel spheres without fluidization is simpler than preparation in fluidized-bed columns; however, the sol droplets that are introduced into a nonfluidized column must be small enough to gel before they settle to the bottom. The requirements for the nonfluidized procedure were calculated by combining mass-transfer and settling correlations with a computer program. The calculations and experimental results show that sol droplets initially smaller than 300 μm are easily gelled, while larger droplets require long free-fall distances (column heights) when 2EH is used as the drying alcohol and distort when isoamyl alcohol is used.

Preparation of Test Material for Recycle Test Elements

During the past year, microspheres of ThO_2, ThO_2-$^{235}UO_2$ (Th/U atom ratio 4.2), ThO_2-$^{235}UO_2$ (Th/U atom ratio 2), and $^{235}UO_2$ were produced for use in eight Recycle Test Elements (RTE's). The RTE's will be used in hot-cell studies of head-end reprocessing and of the products of fuel fabrication. The ThO_2 microspheres (1300 g) were on hand. Batches of ThO_2-$^{235}UO_2$ microspheres with thorium-to-uranium atom ratios of both 4.2 (1000 g) and 2 (2700 g) were prepared by solvent extraction in engineering-scale sol-gel equipment that had been used previously to prepare 32 kg of ThO_2-$^{233}UO_2$ (Th/U ratio 3). The $^{235}UO_2$ microspheres (300 g) were made from sol prepared by the ORNL precipitation-peptization method. Six RTE's have been fabricated from the above material. The remaining two will be fabricated late in fiscal year 1970.

4. Fueled-Graphite Fabrication Development

Equipment was developed for the remote transfer, shape separation, screening, and blending of fuel particles and the determination of coating anisotropy, density, and size distribution. Remotely operable equipment is described for coating fuel particles with pyrolytic carbon and with silicon carbide. Coating and bonding of fuel for Recycle Test Elements are described. Surface morphologies of carbon coatings are shown and correlated with density.

5. Irradiation of HTGR Fuels

Capsule design and other preparations were made for accelerated testing of coated-particle fuels in the Engineering Test Reactor. Recycle Test Elements, prototypical of full-scale HTGR fuel elements, are being fueled for irradiation in the Peach Bottom Reactor. Several types of coated ThO_2 and UO_2 particles in various combinations will be irradiated to demonstrate performance of products produced by processes proposed for use in TURF, and to provide fuel for reprocessing studies. Good integrity to 6×10^{21} neutrons/cm^2 was shown by bonded beds of coated particles prepared with a pitch binder loaded with 40% graphite or a combination of 29% graphite and 29% carbon black. Blended beds of loose particles shrank during irradiation more than expected from coating densification.

6. Fundamental Sol-Gel Studies

The nitric acid present in gel spheres reacted with the sorbed alcohol during drying in steam. The rate at which the drying temperature is increased must be both slow and uniform in fixed beds so that the chemical reaction rate can be controlled and heat is not liberated at an excessive rate. A purge of steam through the bed of spheres enhances the desorption and vaporization of the organic reactants and thus reduces the quantity of organic materials that are available for reaction with nitric acid. Carbonaceous materials and other volatiles remaining after drying were removed during firing before any appreciable shrinkage or densification of ThO_2-UO_3 gel spheres occurred; thus no problems are encountered in attaining the density and chemical composition specified for calcined products.

7. Thorium Ceramics Data Compilation

Property data on thorium ceramic compounds are being compiled. Collections on oxides and nitrides are being issued; that on carbides has been drafted.

1. PROCESS DEMONSTRATION AND ^{233}U DISTRIBUTION

J. R. Parrott

Storage and Distribution Facility

J. R. Parrott R. G. Nicol J. P. Nichols W. A. Shannon

Oak Ridge National Laboratory serves as a national distribution center for ^{233}U. The facility includes shielded wells for storing up to 168 kg of ^{233}U in solid form and tanks (containing borosilicate glass for neutron poisoning) that can store 500 kg of ^{233}U in uranyl nitrate solutions at ^{233}U concentrations up to 250 g/liter. Also, a shielded interim storage vault (Building 3100) can hold up to 70 kg of ^{233}U or ^{239}Pu in shipping containers. At present, nine wells for solid storage and five tanks for solution storage are being added to increase our capacity for solid by 80% and for solution by 100%. Both new facilities are needed for storage of feed material for the Light Water Breeder Reactor support program, and later the solid storage facility will be required for 200 kg of ^{233}U from the Elk River Reactor after recovery and conversion to oxide at the Italian CNEN Plant.

The storage facility accepts ^{233}U as uranyl nitrate solution or as properly packaged solids. The solids can be metal or compounds that can be dissolved readily and safely in stainless steel equipment.

The purification facilities in the center include a single-cycle solvent extraction system capable of purifying ^{233}U at the rate of 25 kg/week. At present, all ^{233}U processed in the facility is shipped as nitrate solution. The system is being modified to increase reliability and flexibility, and a complete nitrate-to-oxide conversion line with a capacity of 22 kg of ^{233}U per week is being installed for the Light Water Breeder Reactor support program.

Distribution Activities Summary

J. R. Parrott R. G. Nicol W. A. Shannon

During the past year, 18 shipments containing 44 kg of ^{233}U were received by the facility, and 23 shipments containing 7 kg of ^{233}U were sent. The largest single shipment received was 13 kg of ^{233}U (as UO_3) from Nuclear Fuel Services at Erwin for the LWBR support program. The largest single disbursement was 1 kg of ^{233}U [as $UO_2(NO_3)_2$] to Los Alamos. The activity of the facility for each calendar year from 1960 is shown in Fig. 1.1. Table 1.1 shows the present inventory of ^{233}U (exclusive of Consolidated Edison Fuel) in the facility.

The TRUST (Thorium Reactor Uranium Storage Tank) facility was placed in operation last year. The receipt, accountability, radiation exposure during unloading, and other pertinent information have been reported.[1] However, experience gained in the storage of a large volume of fissile solution, using soluble neutron absorbers for criticality control, is felt to be of sufficient interest to the industry to warrant a detailed report of our first year's operation, including all aspects of nuclear safety.

The increase in the number of operating power reactors will result in the reprocessing of spent fuels whose isotopic compositions render them relatively undesirable for immediate recycle; hence, interim storage of large volumes of aqueous nitrate fissile solutions must be provided. In such instances, there is incentive to use soluble neutron absorbers for criticality control. This technique provides for inexpensive storage, and the soluble neutron absorbers can be separated from the fissile material in the solvent extraction purification process.

The facility consists of a charging glove box in the area above the cell, an unloading and sampling facility located in a processing cell, and a 5000-gal (19,000-liter) storage tank in an underground pit adjacent to the building (Fig. 1.2). We presently have 1047 kg of

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[1]Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, pp. 199–202.

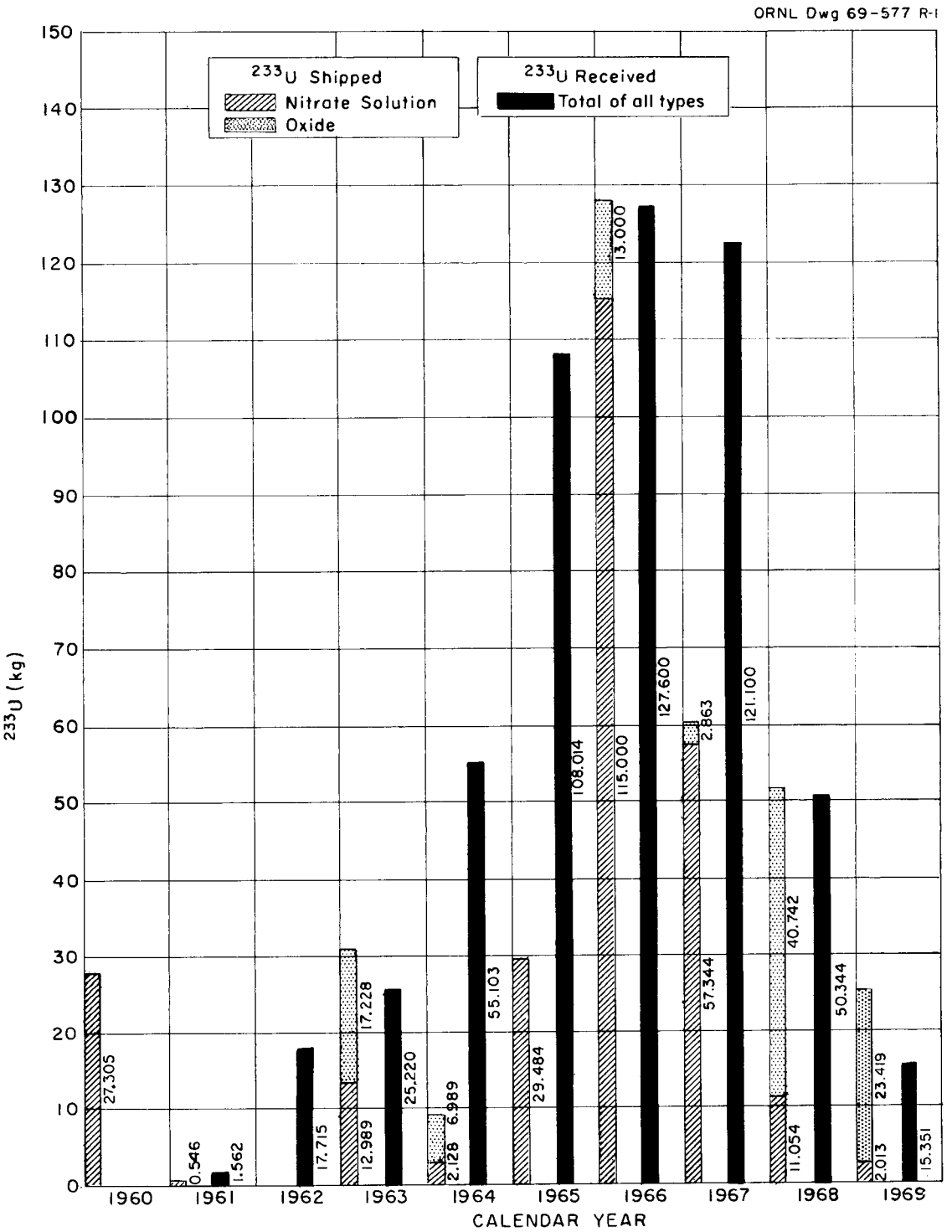

Fig. 1.1. Receipts and Shipments of ^{233}U – Building 3019 Dispensing Facility.

Table 1.1. Inventory of ^{233}U – March 31, 1970

Form	Isotopic Purity (wt %)	^{232}U Content (ppm)	Quantity (kg)
Nitrate	91	13	24.8
	97	5	2.2
	97	9	45.8
	97	42	17.9
	98	6	34.3
Oxide	84	6	7.6
	91	250	61.7
	97	< 5	13.4
	97	50	11.0
	98	6	35.6
Fluoride	91	250	1.9
Metal	98	42	5.1
TOTAL			261.3

uranium (76.5% ^{235}U, 9.7% ^{233}U) stored in the facility. The tank was filled before use with borosilicate-glass Raschig rings to prevent criticality.

Neutron multiplication factors calculated with the ANISN program, a one-dimensional, multigroup neutron transport code using the S_4 approximation and 16-group cross sections, are shown in Table 1.2. The results are for systems of infinite dimensions containing solutions, precipitates, and Raschig rings. The method and geometrical model slightly overestimate the results of two ORNL exponential experiments with solutions of ^{235}U and ^{233}U in vessels packed with borosilicate-glass (Pyrex) Raschig rings.

Pyrex Raschig rings (line 3) with no cadmium or gadolinium in solution keep the neutron multiplication factor from exceeding 0.63 for solution uranium concentrations up to 250 g/liter.

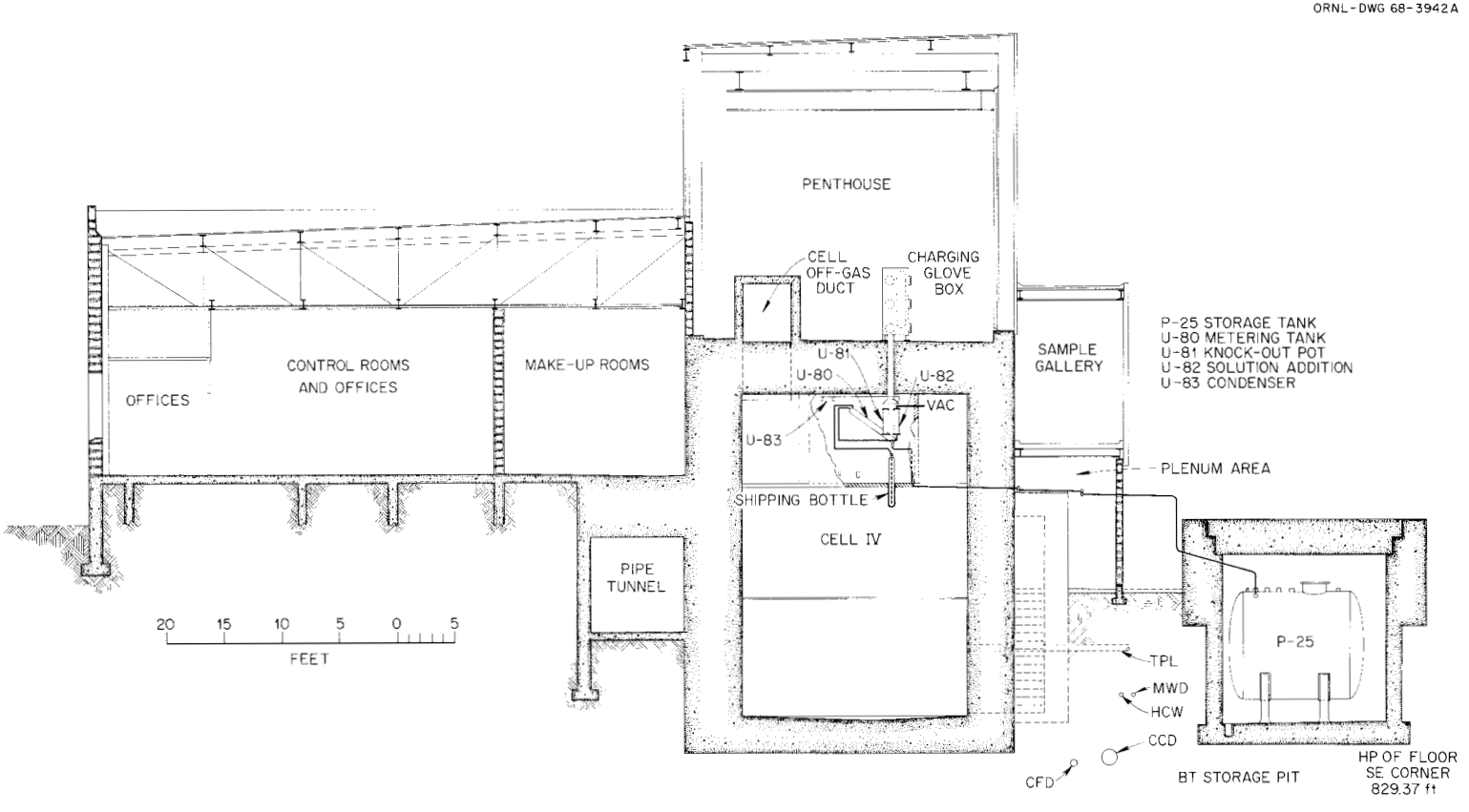

Fig. 1.2. Cross Section of TRUST Facility.

Table 1.2. Multiplication Factors, K_∞, for Systems Containing Uranium Solution or Precipitate and Borosilicate-Glass Raschig Rings

Solution Composition				Volume Fraction, %			K_∞	
Uranium (g/liter)	HNO_3 (M)	$Cd(NO_3)_2$ (M)	$Gd(NO_3)_2$ (M)	Solution	Precipitate[a]	Raschig Rings	Calculated	Experimental
415 (93% ^{235}U)	< 1	0.0	0.0	78	0.0	22	1.04	1.0
330 (98% ^{235}U)	< 1	0.0	0.0	62	0.0	38	0.98	0.97
250[b]	6.5	0.0	0.0	66	0.0	34	0.63	
250[b]	6.5	0.33	0.0	100	0.0	0.0	0.81	
200[b]	6.5	0.0	0.028	100	0.0	0.0	1.00	
0.0	6.5	0.33	0.028	50	16[b]	34	0.56	
0.0	6.5	0.33	0.028	41	25[b]	34	0.76	
0.0	6.5	0.33	0.028	33	33[b]	34	0.91	
0.0	6.5	0.33	0.028	25	41[b]	34	1.03	
0.0	6.5	0.33	0.028	16	50[b]	34	1.14	

[a]Precipitate is $UO_2(NO_3)_2 \cdot 6H_2O$ at 2.807 g/cm^3.

[b]Uranium contains 75% ^{235}U, 12% ^{233}U, and 13% ^{238}U.

The calculated multiplication factor of at most 0.81 (line 4) shows that, with no gadolinium or glass Raschig rings present, 0.33 M Cd is sufficient to assure safe conditions up to a uranium concentration of 250 g/liter.

The multiplication factor calculated on line 5 shows that 0.028 M Gd without cadmium or rings would result in a marginally subcritical system with a maximum uranium concentration of 200 g/liter.

Lines 6 through 10 show that if all the uranium were selectively precipitated and the volume fraction of precipitate does not exceed 40%, an infinite system would remain subcritical. This situation is overly pessimistic because of the following:

1. our experience indicates that a precipitate would deposit uniformly on all the surfaces of the rings;
2. the precipitate would probably carry down gadolinium and cadmium, rendering the mixture subcritical;
3. a precipitate would form slowly and be detected well before 40% of the column became occupied with it;
4. a concentrated precipitate near the bottom of the tank would have enough neutron leakage to reduce the multiplication factor by 10 to 15%.

In several laboratory experiments we determined the stability of the solution containing uranium and the neutron absorbers. When the solution was slowly evaporated in a stream of air at room temperature, a precipitate did not begin to form until the solution was concentrated to about 370 g/liter U. The solution began to freeze at about 13°C. Analysis of the "ice" crystals and supernatant liquid showed that, within experimental error, the "solution" does not change composition upon freezing.

As a result of these calculations, the uranium concentration will be maintained at between 100 and 200 g/liter, the cadmium at least at 0.3 mole per mole of uranium, and the gadolinium at least 0.025 mole per mole of uranium.

Analyses of samples of the solution withdrawn at intervals during the past 13 months are presented in Table 1.3. The average uranium

Table 1.3. Analyses of Solution in TRUST Tank During First 13 Months' Storage

Date Sampled	Solution Volume (liters)	Uranium (kg)	HNO_3 (M)	Soluble Poison Content			
				Cadmium		Gadolinium	
				(kg)	(moles/mole uranium)	(kg)	(moles/mole uranium)
9-11-68	1110	0	0.11	164.2		21.4	
2-20-69	6970	1040	2.72	164.2	0.33	16.2	0.023
3-28-69	7100	1036	2.57	142.4	0.29	14.8	0.021
4-17-69	7240	1039	2.66	144.8	0.29	15.1	0.022
7-29-69	7300	1053	2.59	142.4	0.28	14.6	0.021
10-3-69	Added 14.2 kg Cd and 3.8 kg Gd to tank						
10-10-69	7280	1055	2.46	143.4	0.28	15.3	0.021
11-11-69	7030	1041	2.51	152.9	0.31	17.8	0.025
4-6-70	7085	1020	2.65	145.3	0.30	16.6	0.024

content is 1045 kg as compared to 1047 kg determined from analyses of the individual incoming shipments. Discrepancies in the soluble poison content are probably due to inadequate mixing of the solution before sampling; however, analytical error or deposition of the poisons is possible. Initial efforts to sparge the solution for a long period of time resulted in excessive radiation exposures from the off-gas piping and filter. This system was redesigned with a de-entrainment separator and small filter, so better mixing will be possible for future samples.

Fuel Preparation for the High-Temperature Lattice Test Reactor

J. R. Parrott F. J. Furman

Last year we reported[2] that we were preparing about 32 kg of pyrolytic-carbon-coated $(Th,^{233}U)O_2$ microspheres for use in reactor physics tests as part of a national effort in support of high-temperature gas-cooled reactors. At the time of the last report, about 17 kg of the required spheres had been formed, and coating operations had begun. This program has now been successfully completed and reported,[3] and the spheres have been shipped to Pacific Northwest Laboratory, where the planned reactor physics experiments are in progress.

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[2] J. W. Snider, F. L. Daley, J. R. Parrott, R. G. Shannon, F. J. Furman, Jr., and R. A. Bowman, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 3–10.

[3] J. R. Parrott, F. J. Furman, F. L. Daley, J. W. Snider, and J. D. Sease, Preparation by the Sol-Gel Process and Pyrocarbon Coating of 32 kg of 25% $^{233}UO_2$–75% ThO_2 Microspheres for the High Temperature Lattice Test Reactor, ORNL-4594, in preparation.

2. THORIUM-URANIUM RECYCLE FACILITY

J. M. Chandler

The safety analysis for the facility was published.[1] This report describes the plant and was submitted to the AEC-ORO preoperational review committee for use in their consideration of acceptance of the TURF Facility for use in performing a broad spectrum of research activities. Acceptance by the AEC was received in January 1969.

The TURF Facility Maintenance Manual was completed. This manual gives procedures for conducting the facility preventive maintenance program, procedures for conducting process equipment maintenance, and procedures for testing safety equipment such as hoists, slings, air filters, radiation monitoring and alarm equipment, etc. This is probably the most complete and up-to-date manual of its kind and exemplifies laboratory practice of quality assurance standards.

Cell G, which was used for the $^{233}UF_4$-^{7}LiF (MSRE) fuel preparation, became contaminated; it was cleaned and decontaminated after the ^{233}U product was removed from the cell. All excess LiF–27 mole % $^{233}UF_4$ was stored in Hole N of the Building 3019 storage facility. The cell was cleaned to prepare for installation of equipment for isolating isotopically pure ^{248}Cm after separating it from the ^{252}Cf precursor. The cell was cleaned in three phases and according to detailed written procedures. Successful completion of the work without spread of contamination outside the highly contaminated cell is an example of the effectiveness of written operation procedures for such work.

Cell G was smeared in January 1970 to measure the transferable radioactivity present on the internal surfaces. The smears ranged from 40 to 500 dis/min and averaged about 300 dis/min, which is in good agreement with earlier smear results. There were a few smears in the 1000-to-9999 dis/min range and only two higher at 12,600 and

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[1]J. W. Anderson, S. E. Bolt, and J. M. Chandler, Safety Analysis for the Thorium-Uranium Recycle Facility, ORNL-4278 (May 1969).

23,500 dis/min. The higher smears were on the edge of a window that had been relocated in the cell; this operation undoubtedly dislodged some contamination that was hidden in areas not reached when we cleaned the cell. At one time the cell G surfaces smeared as much as 10^6 dis/min. These low levels of contamination in cell G allowed direct rather than remote installation of equipment for ^{248}Cm production, saving at least $10,000. The cleanliness also precludes the contamination of the pure transuranium products to be prepared in the cell.

A 2-mg source of ^{252}Cf was used to examine the cell G neutron shielding ability because the 5.5-ft-thick reinforced concrete walls were designed primarily to shield from gamma radiation. No significant increase in neutron or gamma radiation levels was measured outside the cell when the ^{252}Cf source was inside the cell. However, we did locate two areas outside the cell that we may use as reference points when a larger mass of ^{252}Cf is present. In delivering the ^{252}Cf source to cell G from TRU and then shipping the source off site, we used our written operational procedures and found them adequate. The "Cannon-Ball" shielded carrier was used in these tests. We also recorded radiation levels inside the cell and recorded the amount of radiation detected at the stainless steel pan in the roof hatch for use as reference when it is necessary to remove the shield blocks from the hatch.

The first batch of ^{252}Cf was processed, and the initial ^{248}Cm product containing 320 μg was isolated in March 1970.

The efforts to place the in-cell CO_2 fire protection system in condition for acceptance test by the Factory Mutual Company continued. This is a rather extensive job, requiring modification to the CO_2 piping, to some structural parts in cell A, and to the ventilation control system of cells A and E. The fire protection system is unique in that gaseous rather than liquid CO_2 is supplied to the cell on fire. This type system places added burden on the cell ventilation flow and pressure control equipment.

The in-cell fire protection system was tested using a redesigned master carbon dioxide flow valve. This valve has a Teflon-to-metal seat, which is an interference fit of Teflon between two steel surfaces.

It provides the desired characteristic of tight shutoff of CO_2 gas after having served periodically as a quick-opening valve. We learned from several years' effort spent in testing valves designed for this CO_2 service that such service is very demanding on an automatic valve and is difficult to attain.

Once we had a reliable master CO_2 control valve we turned our attention and efforts to the testing and perfection of the remainder of the in-cell CO_2 fire protection system. The pilot control valve system piping was cleaned of debris, and filters were installed in the lines to protect closely fitting parts of the pilot control valves and the selector valves. We also modified the pilot control valves to prevent "floating," which results in failure to open the selector valves. This modification made reliable the delivery of CO_2 to the cells when a fire alarm sounds. We then changed the cell ventilation system to accommodate the rapid flow of CO_2 gas into the cells without over-pressurization of the cells and associated air handling system. These changes included the installation of an automatic valve in the ventilation duct between cells A and B and changes in the instrumentation of the ventilation systems of cells A, B, E, and F and of the atmospheric relief valve in the main off-gas line.

The above alterations to the cell CO_2 fire protection system were made after an unsuccessful attempt in September 1969 to get acceptance for preferred risk protection with a representative of Factory Mutual Insurance Company present for the testing. Recent tests of the cell fire protection system have been successful and we plan to present our data to Factory Mutual for their consideration of acceptance. Our data, along with on-site spot checks of the TURF CO_2 fire protection system, will be used as the basis for acceptance for preferred risk protection by Factory Mutual.

We maintained the TURF equipment in operational readiness in support of the heavily shielded cell bank designed for the remote maintenance and operation of the in-cell process equipment. To do this we altered or replaced some faulty electrical motors, revised some ventilation control instrumentation, and added some equipment to better

fit the expected needs. All changes were based on the results of tests made of the existing equipment pieces, individually or in functional groups. For example, the diesel-electric emergency power generator fuel system was replaced.

Cell B outlet filters were replaced to permit a test of a "MICRETAIN" filter of the same quality as, but less costly than, the filters originally installed. One MICRETAIN filter was installed in cell B adjacent to two Cambridge Company filters of the original type so performance could be compared under the same service conditions.

The filters that were removed from cell B after about 1 year service contained a total of 14.8 lb of dirt, about 5 lb per filter. There was no evidence of a decrease in the effectiveness of these filters, but there was a 10% increase in pressure drop across the dirty filters.

One area of the TURF Building 7930, the cell G pump room, was altered to provide work space and off-gas and waste handling equipment for a glove box installation there.

The Pyrex glass Raschig ring monitoring string in the waste tank C-6-T was removed for annual inspection. We saw no deterioration of the glass rings from one year's exposure to various acid and basic solutions and no evidence of breakage. However, redesign of the method for removal of the monitoring strings is necessary if they are to be removed safely after becoming highly contaminated. This was done and the new withdrawal system was installed. We will demonstrate its effectiveness when we next check safety of the rings.

Approval was received to wire emergency power to the 300 ft^3/min (STP) air compressor. This change will enable the TURF and TRU to supply each other with compressed air during an emergency.

3. SOL-GEL PROCESS DEVELOPMENT

W. D. Bond P. A. Haas

The sol-gel process development studies have been concerned primarily with the preparation of thoria, urania, and plutonia (and their binary mixtures), although many other oxide sols have also been prepared in laboratory studies. A primary current objective is to develop procedures and equipment useful for remotely operated fuel preparation in the Thorium-Uranium Recycle Facility (TURF).

Last year, we demonstrated on an engineering scale the sol-gel process for preparing ThO_2-UO_2 microspheres by preparing 120 kg of spheres while operating process equipment at 10 kg/day. Engineering development of the CUSP UO_2 sol process was begun, and approximately 230 kg of UO_2 sol was prepared. Further development work was carried out on gel sphere forming development and included the following topics: studies of variables by factorial experiments, recycle of 2-ethyl-1-hexanol (2EH), sphere preparation from CUSP UO_2 sols, development of fluidized-bed columns, preparation of small (< 200-μm-diam) spheres in nonfluidized columns, and preparation of test materials for recycle test elements (RTE's).

Demonstration of the Engineering-Scale Production of ThO_2-UO_2 Microspheres

P. A. Haas B. C. Finney

The present emphasis is on demonstration of the procedures and equipment to be used in the TURF. The reference material is 300- to 500-μm-diam ThO_2-UO_2 microspheres with a thorium-to-uranium atom ratio of 4.25, as required for one HTGR recycle fuel composition. The ThO_2-UO_3 sol was prepared by amine solvent extraction and was converted into oxide microspheres in equipment having a design capacity of 10 kg/day. The process flowsheets were demonstrated during periods of operation less than 8 hr. Continuous operation for more than 100 hr was undertaken

(1) to determine the reliability and behavior of both the processes and equipment for extended operating periods, (2) to adapt the equipment to remote operation, and (3) to provide ThO_2-UO_2 microspheres for fabrication and reprocessing studies. This demonstration is reported in detail[1] and is summarized below.

Preparation of ThO_2-UO_3 Sol by Amine Solvent Extraction

The engineering-scale amine solvent extraction equipment described previously[2] was operated continuously for 10 days to produce sol containing about 120 kg of ThO_2–19% UO_3 and to demonstrate the feasibility and consistency of operation of the amine solvent extraction process. The thorium-to-uranium atom ratio of 4.25 is representative of the Gulf General Atomic (PSC) reference recycle fuel; however, slightly depleted uranium was used in place of the ^{233}U.

The ThO_2-UO_3 sols were produced by extraction of the nitrate from $Th(NO_3)_4$-$UO_2(NO_3)_2$ [0.3 M in (Th + U), 1.37 M in NO_3^-] feed with 35% excess 0.75 M Amberlite LA-2 (a secondary amine) in n-parrafin. Three nitrate extraction stages and two amine regeneration stages – a water scrub followed by a carbonate scrub – were used. The water scrub was combined with the nitrate feed, and the carbonate scrub was routed to waste. We used the countercurrent flowsheet in which fresh amine enters the third nitrate extraction stage and the nitrate feed enters the first stage; however, the liquid flow in the six compartments of each extractor is cocurrent, with the aqueous and organic streams entering at the top and leaving at the bottom. The aqueous phase was digested at approximately 100°C for 30 min between the first and second extractors to promote crystallite formation and, concomitantly, to release additional nitrate for extraction. The dilute sol (forty-three 33.2-liter batches), which was about 0.315 M in (Th + U) and had 0.12 mole NO_3^- per gram-atom

[1]C. C. Haws, B. C. Finney, and W. D. Bond, Engineering-Scale Demonstration of the Sol-Gel Process: Preparation of 100 kg of ThO_2-UO_2 Microspheres at a Rate of 10 kg/day, ORNL-4544, in press.

[2]B. C. Finney and A. D. Ryon, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 22–30.

total metal, was concentrated in the forced-circulation vertical-tube evaporator[2] to 1.64 M (Th + U) and then used to form 300- to 500-μm-diam microspheres.

Analyses of periodic samples showed very little fluctuation in the flowing streams during the run, and the equipment operated very satisfactorily with no interruptions during the entire run. The overall material balances (see Table 3.1) for (Th + U) were 100.2 and 100.4% for the solvent extraction equipment and the evaporator, respectively. Overall heavy metal losses were 0.04% to the carbonate waste stream and 1 to 5 ppm to the condensate during evaporation of the sol; the sol product entrained approximately 0.02 vol % of the organic.

Table 3.1. Overall Material Balances for Ten-Day Continuous Operation of Amine Solvent Extraction Equipment Producing Approximately 120 kg of ThO_2–19% UO_3 Sol

Sol Preparation by Solvent Extraction[a]	
Entering system:	
Dilute feed	465.3
Leaving system:	
5 liters leaking out pump seal	1.90
50 liters remaining in feed tank at conclusion of run	18.15
Sol product, forty-three 33.2-liter batches	443.46
4.6 liters in sol product drum at conclusion of run	1.43
2.15 liters of samples	0.70
1.18 liters of sample purges	0.32
Carbonate scrub (waste)	0.20
TOTAL	466.2
Overall material balance	100.2%
Sol Concentration by Forced-Circulation Evaporation[a]	
Entering system:	
Dilute sol feed, forty-three 33.2-liter batches	443.46
Leaving system:	
Concentrated sol product, forty-three approximately 6.4-liter batches	445.2
Overall material balance	100.4%

[a]All values except material balances are given in g-mole (Th + U).

Operation and Results in the Microsphere Preparation Pilot Plant

An extended operating test of the microsphere preparation pilot plant was successfully completed. The prime objective was to demonstrate continuous operation of the microsphere forming column. We expected to be concerned principally with problems related to long-term surfactant control and buildup of surfactant degradation products in the column circuit. Particle sphericity, cluster formation, and sticking to walls of the column were known to be affected by these two factors. Drying and calcining operations were to be realistically conducted in conjunction with the column study; however, being batch operations they could be conveniently studied separately, if necessary.

For operation to be considered satisfactory, microspheres resulting from the column and subsequent operations had to meet specifications established before the first campaign started. These were:

1. particle size, 350 ± 100 μm;
2. thorium-to-uranium ratio, 4.25;
3. permissible contaminant levels, 10 ppm B equivalent, < 600 ppm Fe;
4. roundness, ≥ 98% with ratio of extreme diameters ≤ 1.10;
5. oxygen-to-uranium ratio, < 2.03;
6. gas release, 0.3 cm^3/g to 1200°C;
7. particle density, > 95% of theoretical;
8. carbon content, < 500 ppm.

No previous data on other particle properties are available, so no specification can be given at this time.

A ten-day run was planned at a nominal 10 kg/day rate, but recurring temperature excursions in the dryers forced termination of the test. Thus, the run was broken into two periods of approximately five days each, referred to herein as the first and second campaigns.

The First Campaign. — The operation of the column was gratifyingly successful during the first campaign. We processed 73 kg of oxide into beads during the period. Surfactant was added at the start of the operation to 0.1 vol % for both Span 80 and Ethomeen S/15. Clustering to a minor extent was observed early in the run. Span 80 was added periodically

over the first 36 hr of operation to prevent clustering. A total of 0.5 vol % was added up to this point. Clustering was then effectively eliminated throughout the rest of the campaign by regular additions at the rate of 25 cm^3/hr. The Ethomeen S/15 concentration was raised to 0.15 vol % after 6 hr of operation. At campaign's end (113 hr of operation) the Span 80 additions totaled 1.5 vol % and the Ethomeen S/15 additions reached 0.25 vol %. No other problems were encountered, and the column was under satisfactory control throughout the entire operating period. Clustering was never severe enough to be a concern. Visual examination showed that the beads leaving the column were of satisfactory quality throughout the campaign.

The dryers, which had been adequate for thoria microsphere production in previous work, were simply inoperable with the 20-kg batches of mixed oxide microspheres. Temperature excursions repeatedly ruined the product. Losses ranged from 100% in the first batch to 50% in the last batch. Excursions had occurred in 5-kg batches of mixed oxide beads prepared in these dryers in earlier scouting runs; however, bead breakage never exceeded 10%. The larger batch size (20 kg) presented a problem of different magnitude. These larger batches liberated more heat, and the increased amount of heat was more difficult to transfer to the dryer wall and remove because of the insulating effect of the microspheres themselves. Temperatures would jump from the 100-to-150°C range to 300 to 350°C in 3 to 4 min. Such a rapid temperature rise simply pulverized the product.

It was obvious from a study of the design of the dryers that temperature indication and control were inadequate to cope with the excursion problem. Control thermocouples were located adjacent to the electrical heating element, outside the dryer shell. These control thermocouple readings were useless because they represented the temperature of the outer dryer shell surface, which had to be held at 150°C to get the beads up to the desired 105 to 120°C. Other thermocouples were welded to the shell of the dryer spaced halfway between heating elements. Reading at these points lagged too much to be of much help, although they gave indication of excursions. Obviously heat distribution was

poor. Hot spots were occurring directly under the heaters, and these locations were the initiating points of the excursions. Areas only a few inches away remained relatively cold. This condition was the result of the dryer shell being too thin (1/16 in.).

Another severe problem occurred in handling the dryer product after an excursion. The excursion left the beads with an active surface and in a partially reduced state. They oxidized when exposed to air, and the heat of this reaction caused them to glow red while they were being loaded into the calciner crucibles. This reaction is not observed in beads that have not undergone a temperature excursion. Enclosures blanketed with inert gas would have been required for handling the reduced oxide spheres with safety. Such equipment could not be immediately provided.

We concluded that the thermocouples on the old dryers were improperly located and too few and that temperature distribution had to be markedly improved before 20-kg quantities of beads could be successfully dried within the required time. A complete redesign of the dryer must therefore be undertaken.

A 10-kg quantity of good microspheres was screened from the last dryer batch and fired in crucibles in a muffle furnace. The fired microspheres were then evaluated with the following results:

1. 95% of the particles were spherical;
2. the mean particle size was 342 μm (σ = 25);
3. in a frangibility test less than 1% of the particles were chipped or broken;
4. the oxygen-to-uranium ratio ranged from 2.03 for beads taken from the top layer of the crucibles to 2.07 for beads from the bottom. These results were not satisfactory, indicating the difficulty of reducing the uranium in deep beds of microspheres. A better gas-solid contacting arrangement during calcination was needed. Thus the microspheres that survived the drying were of good quality, but the temperature excursion problem overshadowed the whole operation.

Revisions to the Equipment. — An assessment of the results of the first campaign led to three changes before the start of the second

campaign. (1) A dryer with considerably improved heat transfer characteristics and instrumentation was installed. (2) A calciner based upon the concept ultimately planned for the Thorium-Uranium Recycle Facility was provided. This calciner would provide much better gas-solid contact for uranium reduction. (3) Equipment permitting continuous 2EH cleanup by purging surfactant degradation and other waste products from the column circuit was installed.

Improved Dryer. — The features of the new dryer design are described below. Similarities to and differences from the old design are noted.

1. The new dryer (Fig. 3.1) was built of 6-in. sched 80 pipe, as compared with sched 10 pipe in the earlier model. The thickness of the conical bottom was increased from 1/16 to 3/8 in. These increases in thickness were made to improve heat distribution peripherally and longitudinally.

2. Heat-conducting, internal fins were the same in both models.

3. A 3/8-in. tube was continuously welded to the outer surface of the dryer shell in both models. Coolants (air and water) were connected to this coil. With this feature we are able to quench an excursion within the dryer.

4. Tubular electrical heaters were wound in a helical pattern around the outside of the coolant tube. Metal-to-metal contact between the heaters and the shell was thus avoided since the heaters had only point contact with the outer wall of the cooling coil. The resulting poor heat transfer from heater to shell prevented hot spots and permitted heat absorbed by the shell to be transmitted uniformly. In the older models, flat heating elements were tack welded outside the shell at the base of each heating fin. This localized heat source and direct contact between heaters and shell led to the hot spots at the base of the fins responsible for poor dryer operation in the first campaign.

5. In the new dryer, four additional tubular heaters were installed in wells extending down from the cover plate (see Fig. 3.1). These wells are located in each of the areas bounded by the inner dryer wall and the heat conducting fins. The wells extend to within 0.5 in. of the bottom of the dryer. Heat can be supplied from them to the very center of these large bed volumes, previously remote from any heat source.

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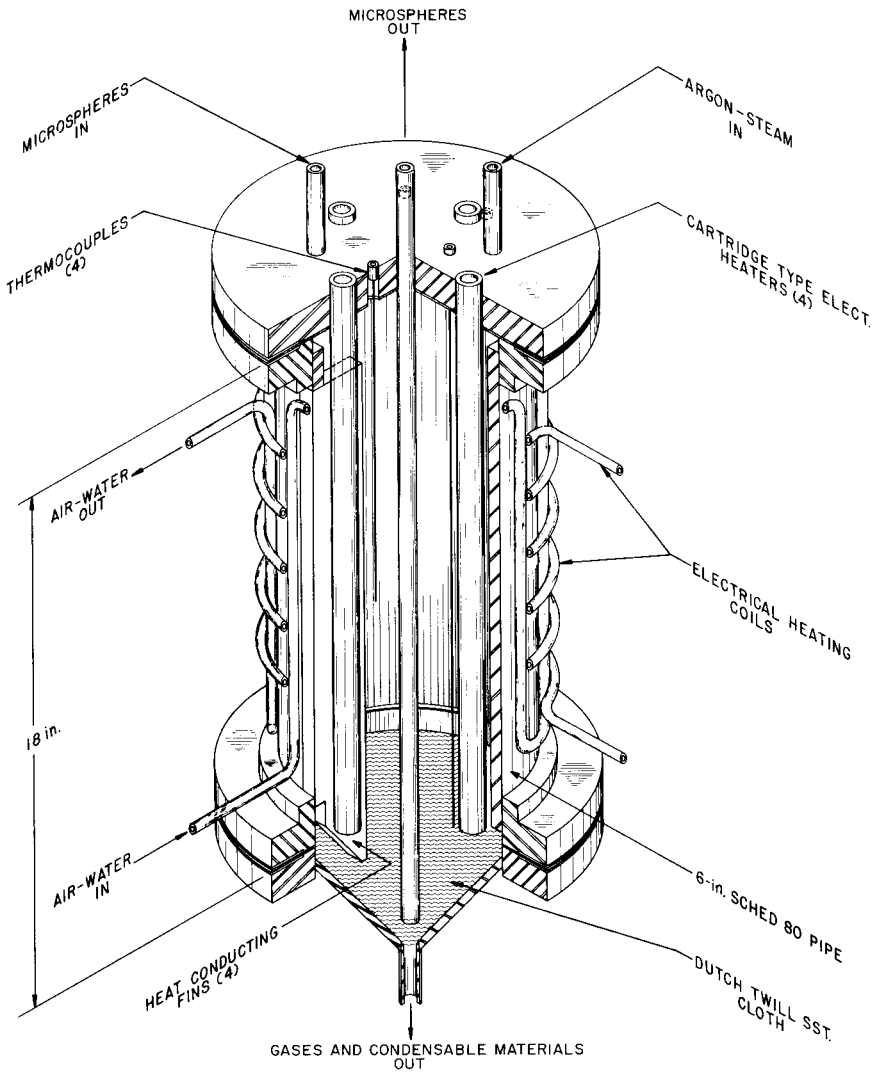

Fig. 3.1. Internal Arrangement of the Improved Microsphere Dryer Used in the Second Campaign.

6. Thermocouples were welded directly to the dryer shell and one of the tubular heater wells to improve response. Bed temperatures were also obtained from thermocouples located at the center of the bed, on the inner wall of the dryer, and in the corner between one of the heating fins and the inner wall of the dryer.

We decided to build only one new dryer and to provide an off-line settling tank to collect the microspheres while the first batch was

being dried. At the completion of the first drying cycle, the beads in the settling tank could be rapidly transferred by vacuum into the dryer and the cycle repeated. Uninterrupted operation could thus be simulated by continuing to collect beads in the settling tank. This scheme was successful and should be considered for remote operation to avoid a second, expensive dryer installation.

2EH Cleanup System. — A constant purge system was arranged for pumping fresh 2EH into the column circuit. An overflow weir allowed excess 2EH to flow out of the system at a rate equal to the input. The 2EH entering the system contained the necessary surfactants in concentration equal to that already present in the column circuit. The waste leaving the system contained surfactants and accumulated waste products. A purge rate of 10 liters/hr was selected since this rate would permit impurities to accumulate to 95% of their equilibrium value in three days. This was an adequate and practical rate since we had already demonstrated a five-day operation in the first campaign with no removal of surfactants or degradation products. Space and handling problems prevented continuous use of the equipment, but it was operated enough to show conclusively that it would work.

Sphere Calciner. — A calciner was obtained by revising a furnace already on hand. A high-purity alumina flask was bought and built into this furnace as shown in Fig. 3.2. This apparatus is not considered to be truly prototypical of what will be installed in TURF but is useful in testing the concept.

The calciner operational concept and design assumptions were that (1) dried microspheres would be loaded by gravity from a storage vessel into the alumina flask permanently located inside a furnace; (2) air to burn off residual organics during heating to 1150°C and Ar—4% H_2 for reducing the U_3O_8 to UO_2 during holding at 1150°C for 4 hr would be introduced through a tube extending to the bottom of the bed of beads; and (3) at the completion of reduction the beads would be cooled under argon and pneumatically transferred to a storage container. Interparticle sintering, even in a bed of this depth, was not expected to be severe enough to impede the vacuum transfer. Complete reduction and

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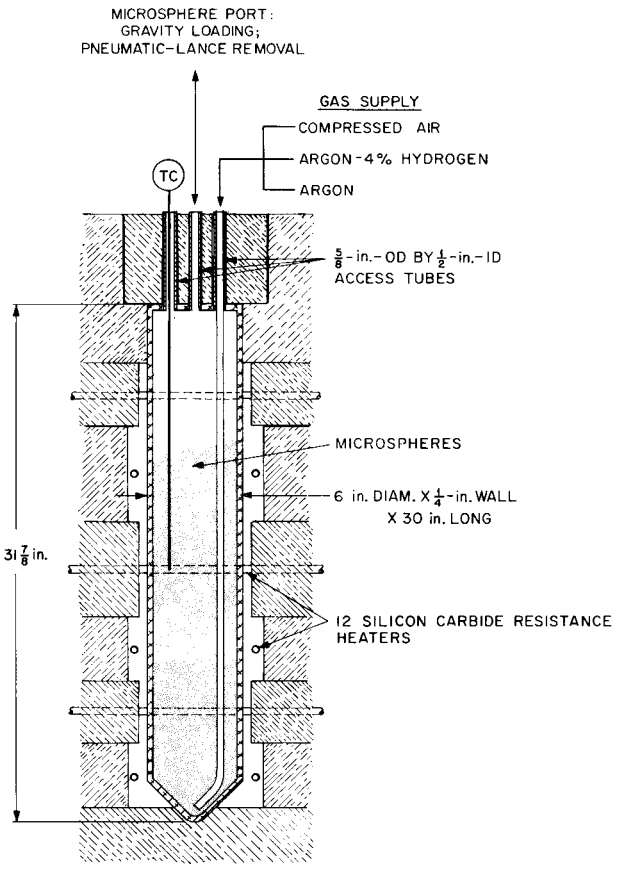

Fig. 3.2. Calciner Tested in Extended Operation with Mixed Oxide Microspheres.

carbon elimination (per specifications) would be obtained as a result of gas entering at the bottom of the bed of beads and rising in intimate contact with the beads.

Operations During the Second Campaign. — This campaign was without significant process problems. Operating control of the column and microsphere quality were good.

Three interruptions to continuous column operation occurred during the period. None of these was related to any fault in the sol-gel process. The first was a control valve failure, the second was a complete power failure in the building, and the third was a scheduled shutdown for changing from the specification sol being fed to a non-specification sol used to fill in the remainder of the planned five-day operation.

The control of surfactant and waste product concentrations by continuous purging of the column circuit was completely successful. Routine manual additions of Span 80 (equivalent to 25 cm^3/hr) also gave satisfactory control, as we switched from one method to the other during the test. Column control was excellent, particularly during the periods of purging.

Dryer operation was also satisfactory for the second campaign. Two batches were processed. The first batch went smoothly, but a heating element failed at the end of the second batch, and we were unable to give the batch a 4-hr final heating at 210°C as we had the first batch. The effect of this upon product yield will be discussed later. Calciner operation went exactly as programmed, and the microspheres were removed pneumatically with no evidence of bead-to-bead sintering. Both dryer and calciner worked well enough to consider their performance proof that each now represents a demonstrated concept.

Chemical Evaluation of the Product. — Chemical analyses are given in Table 3.2. Tabulated values easily meet the proposed specifications.

Table 3.2. Analytical Evaluation of the Microsphere Product

Calciner Batch	Oxygen-to-Uranium Ratio	Surface Area (m^2/g)	Mercury Density at 15,000 psi (g/cm^3)	Carbon (ppm)	Gas Release to 1200°C (cm^3/g)
1	2.004	0.017	10.17	40	0.026
2	2.010	0.005	10.19	40	0.009
3	2.011	0.122	10.11	30	0.030
4	2.015	0.009	10.22	40	0.019

The oxygen-to-uranium ratio of the product is much better than the specified maximum of 2.03. The carbon content is also an order of magnitude less than that specified. The new calciner gave excellent gas-solid contact; hence, the good results.

The calculated surface area for 358-μm-diam microspheres is 0.00165 m^2/g. The very high value for calciner batch 3 was rechecked

and confirmed. No other analytical or physical tests show any difference between this and the other products, so we offer no explanation for this high value. By Vegard's law the theoretical density of the microspheres is 10.18 g/cm^3; thus, the product is essentially of theoretical density. The gas release values are no greater than one-tenth that specified.

The specification for contaminants in the microspheres was not met, but we are not concerned about this problem. The alumina gas entry tube and the alumina thermocouple sheath originally provided with the calciner flask were not adequate; thus stainless steel parts were substituted to avoid undue delay in the work. The contaminants were corrosion products of stainless steel. Hence their prevention by use of alumina parts would allow us to meet the specification.

The maximum eccentricity of the microspheres was determined by measuring the largest diameter shown by a particular microsphere and then the smallest diameter of the same microsphere. The diameter ratios thus obtained are summarized in Table 3.3 for 200 microspheres. The microspheres are very nearly spherical, with the maximum eccentricity for any particle being about 9 μm. Specifications will be upgraded to reflect the higher quality product obtainable.

Table 3.3. Summary of Microsphere Sphericity or Roundness Ratio[a]

Calciner Batch	Ratio of Greatest Diameter to Smallest	
	Average	Maximum
1	1.0076	1.0236
2	1.0070	1.0133
3	1.0067	1.0251
4	1.0067	1.0257

[a]All batches contained some spherical particles (ratio 1.0000).

The physical properties of the product-grade microspheres are shown in Table 3.4. Of the microspheres charged to the calciner, 86% met all

Table 3.4. Results of Calciner Operation and Physical Data on Calciner Product

Calciner Batch	Corresponding Dryer Batch	Weight of Dried Beads Charged to Calciner (kg)	Weight of Calcined Product (kg)	Physical Evaluation of the Calcined Microspheres			
				Weight of Round Particles in Product (kg)	Round Particles in Product (%)	Particle Size (μm)	Standard Deviation (μm)
1	1	10.0	9.578	8.678	90.6	370	19
2	1	10.0	9.473	9.198	97.1	356	23
3	2	10.0	9.166	7.250	79.1	354	38
4	2	11.053[a]	10.391	8.063	77.6	351	29
		TOTALS	38.608	33.189	AVERAGE 86.0		

[a]Charged with 9565 g from dryer batch 2 plus 1488 g of beads from miscellaneous run samples.

specifications for fuel element fabrication. The overall process yield (from feed tank to fuel element) was 84%. This somewhat low yield reflects an equipment malfunction.

Note the sharp drop in product yield between the two dryer batches. Because of a heating element failure at the end of the second dryer batch we could not give the second dryer batch the same heating cycle as we did the first batch. Instead, we decided to try to complete the cycle in the calciner. Temperature control of the calciner is poor at the lower (210°C) end of the temperature range and the product was damaged, as shown by results on samples taken before and after processing the last two batches through the calciner. Results show that the second dryer batch did indeed yield approximately the same percentage of spherical product as did the first; hence, with dryer repair and a proper heating cycle we could actually expect a significant improvement in yield. A satisfactory 99.5% material balance was obtained well within our expected margin of error.

We feel that the following conclusions are justified by the described test.

1. The microsphere forming column and its accessories are now at a state of development permitting continuous operation. Additional work, particularly in on-line instrumentation, is needed to allow final remote application of the equipment.

2. The dryer method, as described, is operable at a scale of 10 kg/day. Some additional work is needed to bring the dryer to the same state of development as the column.

3. The calciner is proved, but it probably needs more work than the dryer to provide a basis for fabricating equipment for use in TURF.

4. The product prepared in the above operations meets the specifications set with the sole exception of contaminants.

5. Process yields of 84% are low but should improve markedly with minor effort. Material balance data show no significant process loss.

CUSP Solvent Extraction Preparation of UO_2 Sol

J. P. McBride B. C. Finney W. L. Pattison
K. H. McCorkle J. R. Flanary

A process called CUSP[3] (Concentrated Urania Sol Preparation) for the preparation of concentrated ($\geq$ 1 M) urania sols directly by solvent extraction has been developed in the laboratory and is being developed in engineering equipment at scales of 1 and 4 kg UO_2 per batch. In the process, nitrate ion is extracted continuously at a controlled rate from a U(IV) nitrate-formate solution with an organic solution of Amberlite LA-2 (a high-molecular-weight secondary amine). Following a prescribed conductivity-temperature-time path produces a highly crystalline, stable, 1 M urania sol with a high U(IV) content. The process is being used in engineering-scale equipment, and sols containing more than 230 kg UO_2 have been prepared.

Basic to the development of the process was the discovery that nitrate must be extracted at the crystallization temperature to promote crystallization of the produced sol. Once crystallization has been initiated, it proceeds rapidly, releasing additional extractable nitric acid. The rate of nitrate extraction is increased at this point to minimize U(IV) oxidation. By extracting the nitrate at a controlled rate (monitored by measuring the conductivity of the aqueous phase) and controlling the temperature of extraction as dictated by the conductivity readings, we can reproducibly prepare concentrated, stable, highly crystalline sols of high U(IV) content.

Development of the process was greatly aided by the use of x-ray diffraction techniques and the electron microscope. We could relate the height of the x-ray diffraction peak to the concentration of crystalline solids in product sols and thus determine the fraction of crystalline material in the sol. Electron micrographs showed that, during

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[3] J. P. McBride, K. H. McCorkle, W. L. Pattison, and B. C. Finney, "The CUSP Process for Preparation of Concentrated, Crystalline Urania Sols by Solvent Extraction," to be published in Nuclear Applications & Technology.

the extraction process, rather large, noncrystalline agglomerates (250 to 350 Å in diameter) are formed first. As extraction and heating continue, crystallization occurs within the agglomerates, resulting in uniformly sized aggregates of uranium dioxide crystals.

Laboratory Development

In the laboratory development of the CUSP process, 1 to 1.3 M U(IV) solutions with NO_3^-/U and $HCOO^-/U$ mole ratios of 2.0 and 0.5, respectively, were prepared by reducing stirred uranyl nitrate-formate solutions with hydrogen in the presence of a PtO_2 catalyst.[4] Nitrate was extracted continuously from the U(IV) solution with a 0.25 M solution of Amberlite LA-2 (n-lauryltrialkylmethylamine) in diethylbenzene—25% n-paraffin. The amine was contacted with the U(IV) solution, continuously regenerated by contacting with a Na_2CO_3-NaOH solution, and recycled through the uranium solution. An initial nitrate extraction was carried out at 35°C until the conductivity of the U(IV) solution indicated a free acid concentration just high enough to prevent gelling (point 1, Fig. 3.3). At this point the solution was heated to 58 to 63°C (the temperature range in which rapid crystallization occurs), while the nitrate extraction was continued at a rate that maintained the solution conductivity (free nitric acid concentration) just above the "gel line." At the crystallization temperature, nitrate extraction was continued or accelerated to promote crystallization (point 2, Fig. 3.3). Crystallization of the U(IV) was indicated by a change from green to black, by off-gassing of the solution, and by a conductivity excursion. Nitrate extraction during crystallization was regulated to minimize the conductivity excursion and to prevent excessive oxidation. When crystallization was complete, nitrate extraction was continued at about 62°C until a predetermined conductivity was reached (point 3, Fig. 3.3), whereupon the solution was cooled to room temperature. Here, the conductivity was adjusted by further extraction of nitrate to yield final conductivities of about

[4]Adams catalyst obtained from Englehard Industries Division, Englehard Minerals and Chemicals Corp., Newark, N.J.

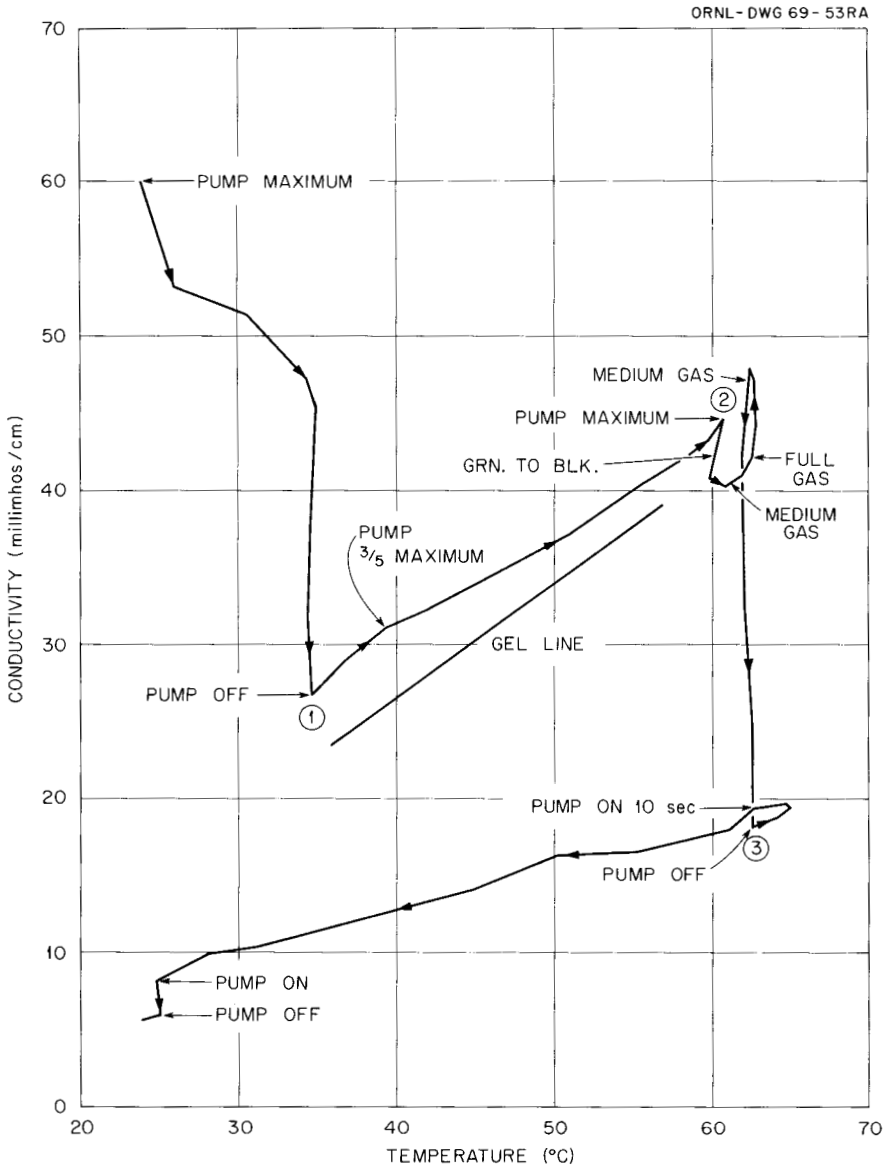

Fig. 3.3. CUSP Operating Curve.

6000 μmhos/cm for 1.3 M sols and 4000 μmhos/cm for 1.0 M sols. Such conductivities (or corresponding free nitric acid concentrations) resulted in a NO_3^-/U mole ratio of 0.11 ± 0.02 in the sols. The optimum time for the initial nitrate extraction was 1.5 hr, while that for the extraction at the crystallization temperature was 1 to 1.5 hr.

The product sols, in general, contained 85 to 90% U(IV) and a large fraction of crystalline solids (75 to 100%) with an average crystallite size of 39 ± 1 Å. The sols were very stable, with shelf lives of several months, and could be concentrated readily to produce 2.5 to 3 M sols.

Engineering Development and Sol Production

Existing equipment for the continuous production of dilute urania and dilute ThO_2-UO_3 sols by a multistage extraction-digestion process[5] was adapted for the engineering-scale demonstration of the CUSP process. The major changes in the equipment were confined to one of the three extraction stages of the original system. The aqueous surge tank, a pump, conductivity instrumentation, and piping to recycle the aqueous to the extraction column were the principal new items added (see Fig. 3.4). Operating time for the extraction equipment is about 5 hr per 15-liter batch (4 kg UO_2) of 1 M UO_2 sol.

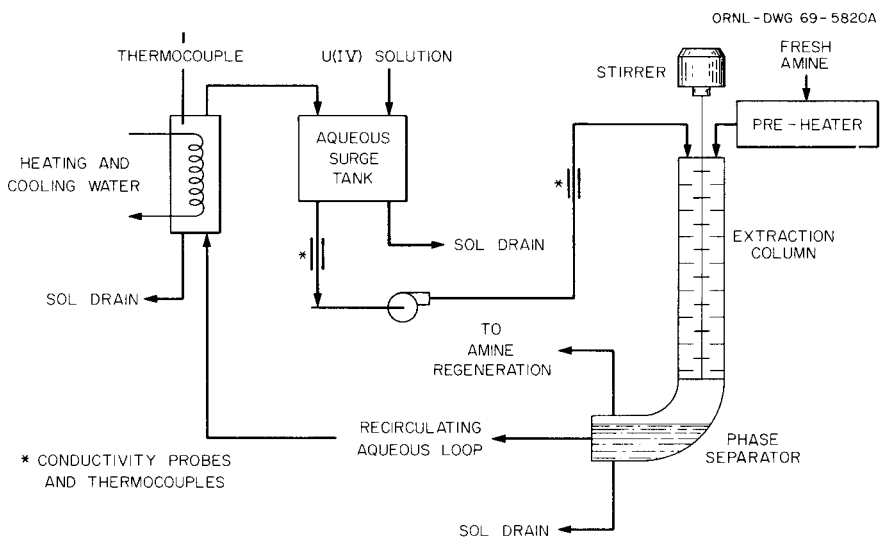

Fig. 3.4. Diagram of Modified Extraction Stage of Engineering-Scale Equipment for Concentrated Urania Sol Preparation (CUSP).

The equipment and chemical flowsheets for the engineering-scale demonstration of the CUSP process and sol production runs are presented in Figs. 3.5 through 3.7. The equipment consists primarily of the slurry reductor, an aqueous nitrate extraction and circulation loop, which is shown in schematic form in Fig. 3.4, three mixer-settler

[5]R. G. Wymer, "Laboratory and Engineering Studies of Sol-Gel Processes at Oak Ridge National Laboratory," pp. 43–45 in Sol-Gel Processes for Ceramic Nuclear Fuels (Proceedings of a Panel, Vienna, 6–10 May 1968), International Atomic Energy Agency, Vienna, 1968; also ORNL-TM-2205 (May 1968).

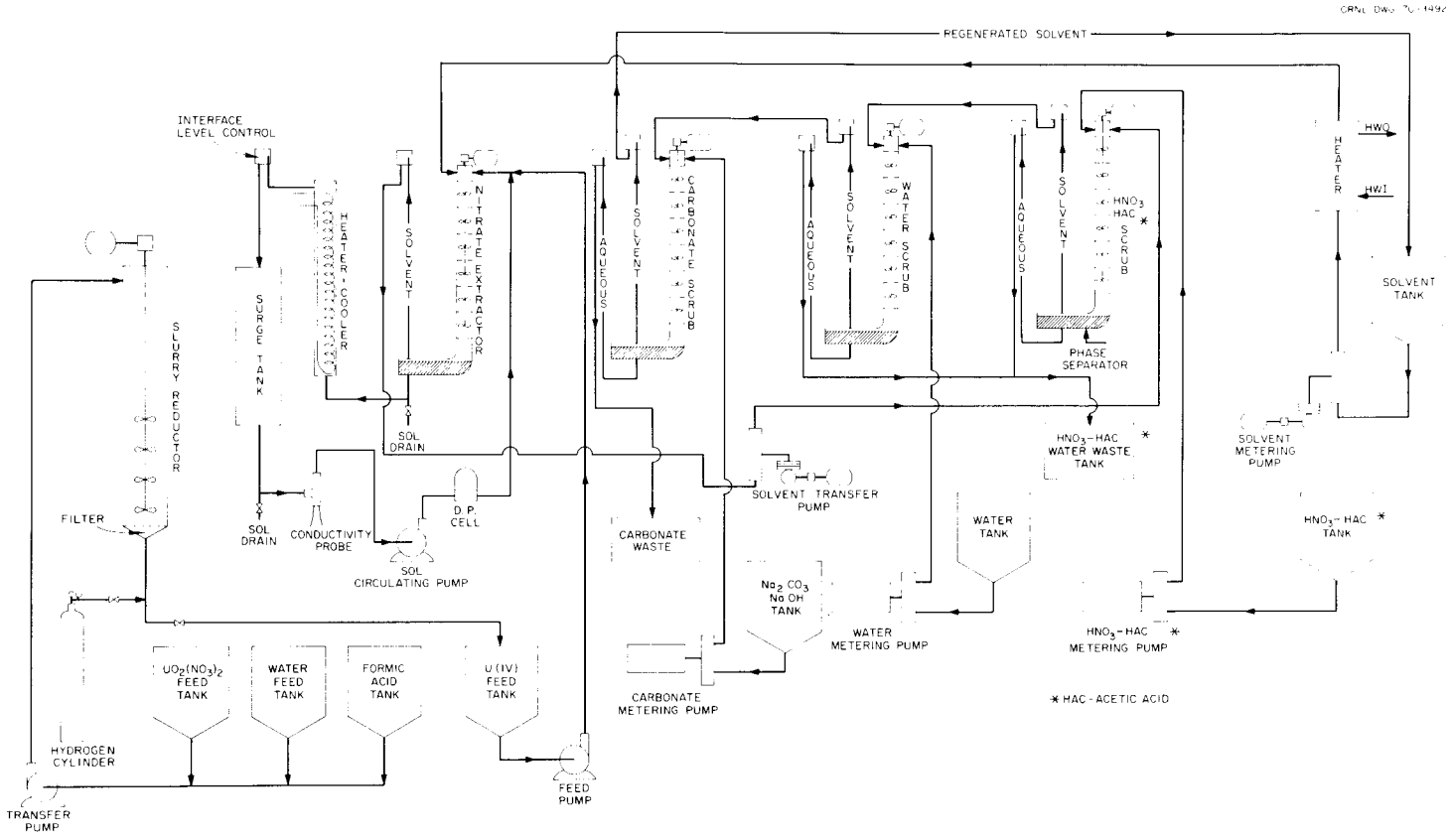

Fig. 3.5. Engineering Equipment Flowsheet for the Preparation of UO_2 Sol by the CUSP Process.

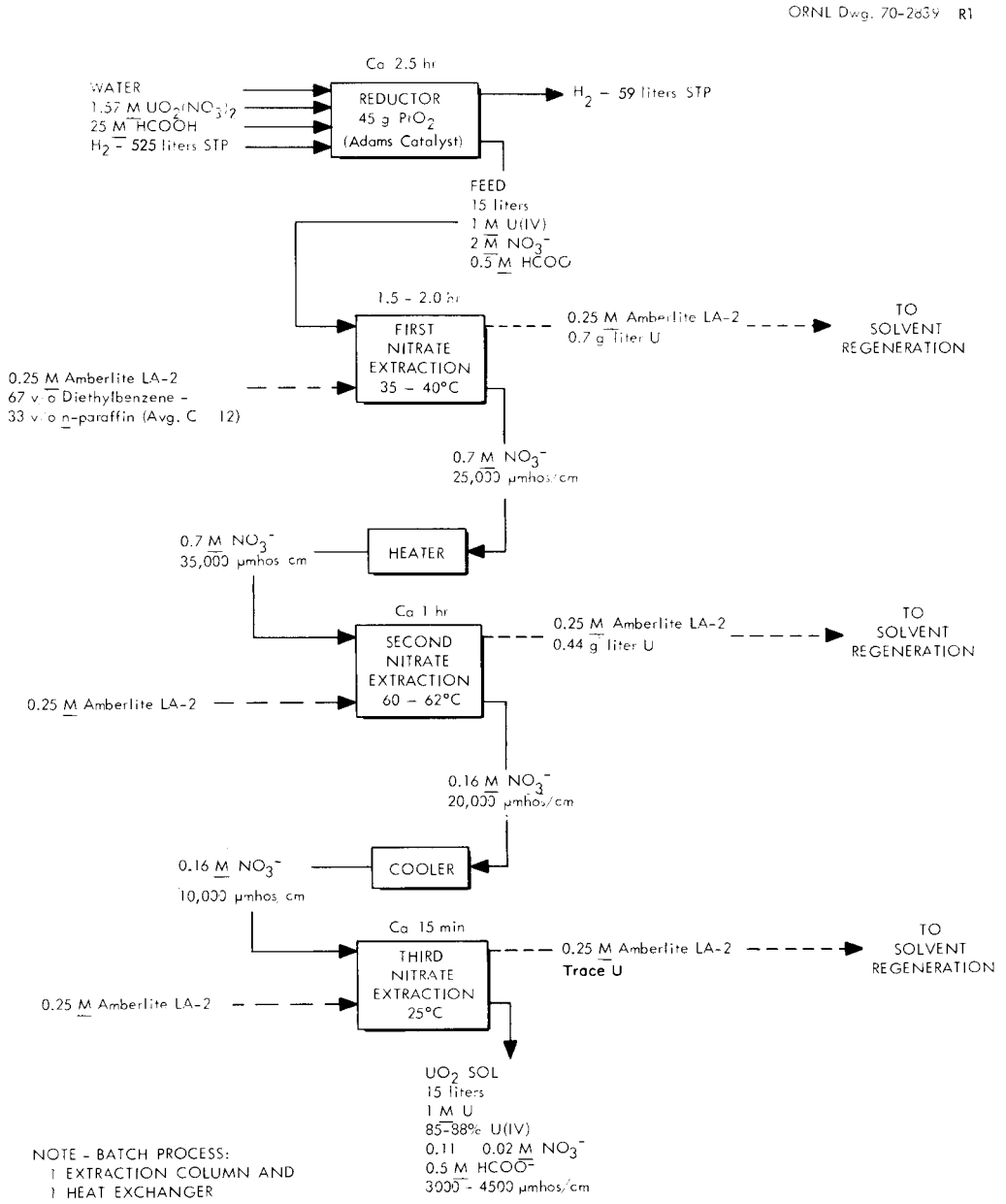

Fig. 3.6. Chemical Flowsheet for Engineering Demonstration of UO_2 Sol Preparation by the CUSP Process.

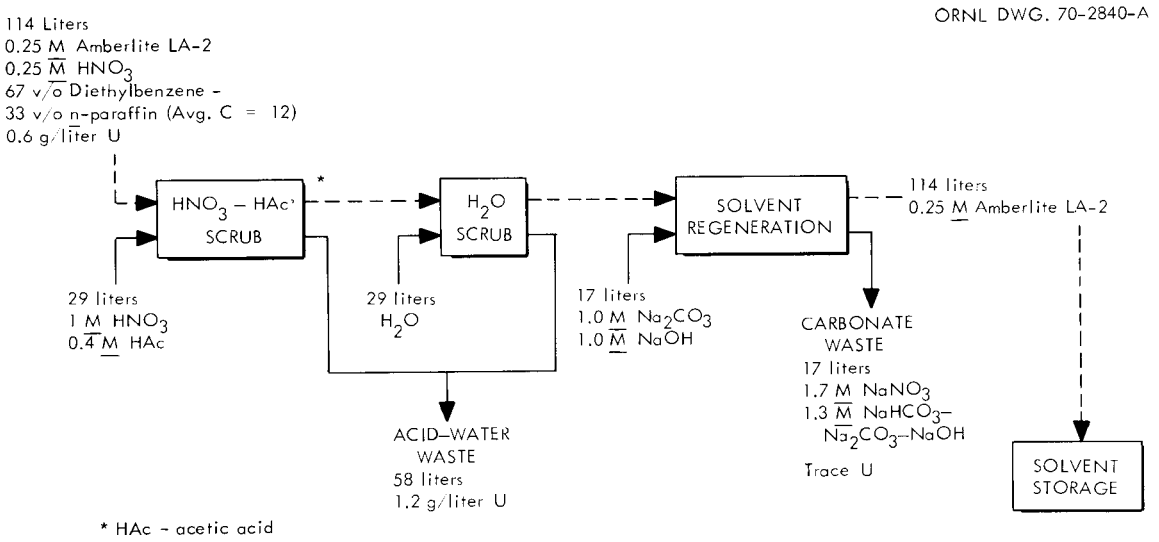

Fig. 3.7. Chemical Flowsheet for Engineering Demonstration of Regeneration in the CUSP Process.

extraction contactors for solvent cleanup and regeneration, and appropriate tankage and pumps. Figure 3.6 shows typical concentrations, times, temperatures, and conductivities for the preparation of 15 liters of 1 M UO_2 sol, and Fig. 3.7 is the chemical flowsheet for the organic solvent cleanup and regeneration.

Using the reduction procedure and the conductivity-temperature path and approximate time schedule developed in the laboratory, five developmental runs were made to ensure that the equipment and the operating procedures would permit reasonably routine operation. When the conductivity probes were properly located (after run 1) in the extraction system, control of the extraction step by measurement of the conductivity was straightforward and reproducible.

Following the developmental runs, urania sol containing more than 200 kg was prepared in the engineering equipment in 4-kg-UO_2 batches. We made 26 of the 50 runs to demonstrate sol production. The others were made to supply specific needs and to investigate process variables or equipment performance. The results showed that the CUSP process was relatively easy to control in the engineering-scale equipment and consistently produced 1 M sols with shelf lives of three months or longer under argon.

Chemical data for some of the sols made in demonstration production runs are summarized in Table 3.5. After the conductivity probes used in the first demonstration run were relocated, we produced fully crystalline sols that could be readily concentrated to fluid 3 M sols (runs 2, 3, and 4). In runs 5 and 6, ammonia produced during the feed preparation step resulted in inferior products (see below). After run 4, x-ray equipment was not available to determine crystallinity.

The production runs were made during a period of several weeks in which processing was carried out two shifts per day and five days per week. A run producing 4 kg of UO_2 sol was made each 8-hr shift. The 1 M U(IV) feed solution with NO_3^-/U and $HCOO^-$/U mole ratios of 2 and 0.5, respectively, was prepared during the preceding shift by reduction with hydrogen at atmospheric pressure using a PtO_2 catalyst. Reduction times varied from 2.0 to 3.9 hr with an average of 2.8 hr. The initial operating procedure for the production runs was to leave the depleted organic solvent and 1.5 to 2 liters of sol in the solvent extraction equipment between runs to maintain interfaces. The third and succeeding batches prepared with this procedure (through run 18) showed distinct color differences, larger and less uniform micelles, and very poor performance in the formation of gel microspheres. Completely draining the solvent extraction system between batches and flushing the equipment with two water washes eliminated the differences between sols.

Numerous analyses were made during the production runs. A summary of the results of these analyses is as follows. Uranium concentration in the sols consistently exceeded that in the feed solutions by less than 1%. The U(IV) content varied from 85 to 90% (with two exceptions, 82 and 84%), with an average of 87%. Sols prepared from fresh feeds contained 85% U(IV) and had smaller average micelle sizes (260 Å) than those prepared from feeds that had aged overnight [88% U(IV), average micelle size 330 Å]. This limited experience indicates that aging the feed about a day before sol preparation increases micelle size.

There was no apparent correlation between the conductivities and pH's of the sols. The conductivities varied from 4000 to 6000 μmhos/cm; the pH's varied from 2.1 to 2.9, with most of the values between 2.2 and 2.6. The conductivity increased 2 to 3%/day for the first ten days. For

Table 3.5. Properties of 1 M CUSP UO_2 Sols Prepared in Engineering-Scale Process Development

Run	U(IV) Content (% of U)	Mole Ratio			Conductivity at 25°C (μmhos/cm)	Aging Time to Gelation (months)
		NO_3^-/U	$HCOO^-/U$	NH_4^+/U [a]		
					$\times 10^3$	
1	82	0.14	0.41		6.60	> 1
2	86	0.09	0.47	0.0017	3.50	> 9
3	90	0.11	0.50		2.25	> 9
4	86	0.14			4.25	> 9
5	83	0.08	0.47	0.020	3.75	2
6		0.08	0.50	0.029	5.00[b]	
7	93	0.12	0.45	0.0017	3.02	> 9
8	85	0.11	0.32	0.0019	3.75	2
9	87	0.09	0.35	0.0015	3.10	4
10	86	0.10	0.41	0.0017	3.10	3
23	88	0.11	0.49	0.0008	3.99	> 5
24	88	0.11	0.45	0.0012	4.30	> 4
31	88	0.09	0.46	0.0012	4.10	> 8
38	84	0.10	0.45	0.0012	5.90	5
43	88	0.11	0.46	0.0012		6
44	88	0.08	0.48	0.0008		> 6
45	86	0.11	0.50	0.0009	3.56	> 6
46	86	0.10	0.52	0.0017	3.89	> 6
47	86	0.10	0.37	0.0008	3.31	6
48	84	0.11	0.43	0.0017		3
49	84	0.11	0.43	0.0016	3.75	3
52	86	0.13			4.24	4
53	84	0.11			3.65	4
54	83	0.10	0.44	0.0012	3.94	> 3

[a] The NH_4^+/U mole ratio was determined for the uranous nitrate feed.

[b] Gelled during final NO_3^- extraction because of high NH_4^+ content of feed solution.

an additional two months of aging, the increase in conductivity was 0.4 to 0.8%/day. Ionic contents determined in the sols are summarized in Table 3.6.

Table 3.6. Ionic Contents in CUSP Sols

Mole Ratio	Value Range	Average
NO_3^-/U [a]	0.08–0.12	0.10
$HCOO^-/U$	0.40–0.50	0.47
NH_4^+/U	0.0004–0.0016	0.0011
Na^+/U	0.0006–0.0030	0.0013

[a]Nitrate analyses are accurate to only ±20% at the 95% confidence level.

X-ray diffraction data were not available to determine the degree of crystallinity of most of the sols, but the long shelf lives and relatively small changes in conductivity on aging indicate a highly crystalline sol. Electron micrographs, such as Fig. 3.8, showed uniform, spherical micelles with average sizes varying between 250 and 300 Å and composed of many crystallites. X-ray diffraction line broadening indicates an average crystallite size of 40 Å. X-ray diffractometry showed this sol to be made of completely crystalline solids.

Preparation of U(IV) Feed Solutions

The U(IV) feed solutions are prepared with the batch slurry reductor shown in Fig. 3.9. The reductor as shown and previously described[6] was modified by adding three impellers at 10-in. intervals from the bottom. Inadequate agitation in a single run made with only one impeller resulted in localized overreduction and an excessive NH_4^+ concentration (0.03 M)

[6]R. G. Wymer, "Laboratory and Engineering Studies of Sol-Gel Processes at Oak Ridge National Laboratory," pp. 43–45 in Sol-Gel Processes for Ceramic Nuclear Fuels (Proceedings of a Panel, Vienna, 6–10 May 1968), International Atomic Energy Agency, Vienna, 1968; also ORNL-TM-2205 (May 1968).

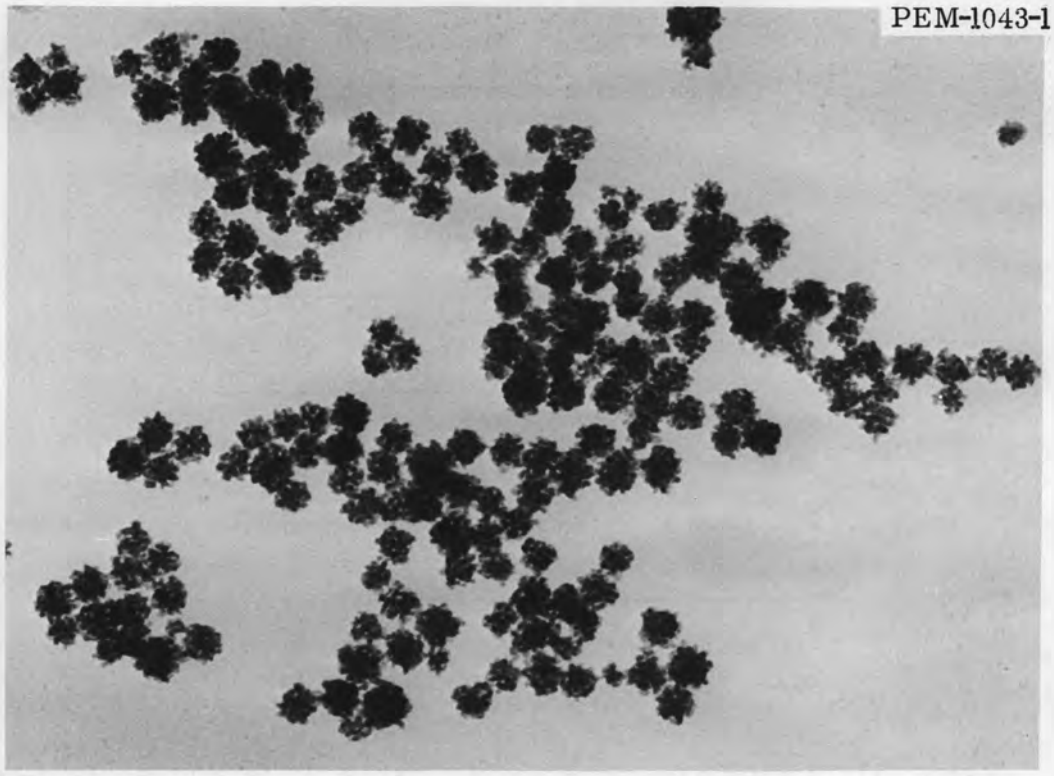

Fig. 3.8. Solids from a CUSP UO_2 Sol. The material is fully crystalline with primary crystallites 40 Å in diameter.

in the solution. We have prepared 8-, 13-, and 15-liter batches of feed solution in 2 to 4 hr by simply bubbling hydrogen at atmospheric pressure through a 1 M UO_2^{2+}, 2 M NO_3^-, and 0.5 M HCOOH solution using a finely divided PtO_2 catalyst (Adams catalyst). The reduction was monitored by measuring the redox potential of the solution, using a platinum electrode against a reference glass electrode system. The end point is readily detected as a sharp break in emf, which occurs between 96 and 100% U(IV). The absence of the U(VI) can be verified by precipitating U(IV) from a sample of the feed solution with oxalic acid and then adding potassium ferrocyanide to the supernate; a brick-red color indicates the presence of U(VI).

Use of a slurry catalyst and of batch reduction with good agitation was dictated by the necessity of stopping the reduction when the uranium was completely reduced. Overreduction, caused by continuing the hydrogen flow after uranium reduction is complete, produces ammonia and makes the feed unsuitable for good sol preparation. The finely divided Adams

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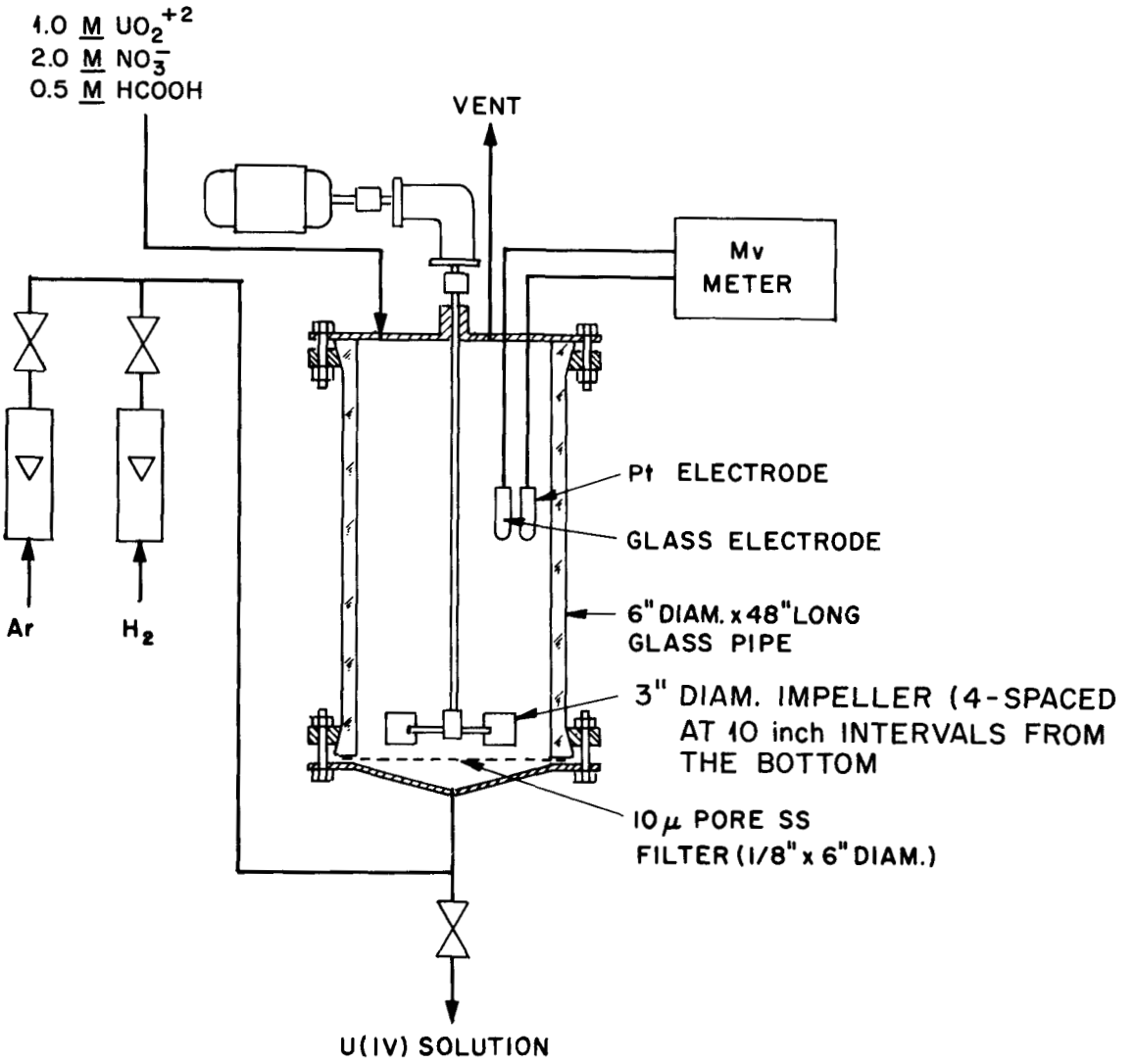

Fig. 3.9. Batch Slurry Uranium Reductor.

catalyst was selected because in an aqueous system the reduced catalyst flocculates in the presence of hydrogen, permitting easy removal by filtration.

The general practice has been to use the 1 M U(IV) nitrate-formate feed solution ($NO_3^-/U = 2$; $HCOOH/U = 0.5$) to prepare a UO_2 sol the day after the feed was prepared. Four CUSP UO_2 sol preparation runs were made using feed solutions that had been aged for 21, 46, 70, and 94 hr. Chemical tests on the feed indicated no self-oxidation of the feeds as

a result of aging under argon. In all cases, a high-quality, crystalline UO_2 sol with 87 ± 1% U(IV) was prepared.

Amine Solvent Cleanup and Regeneration

When only a water-carbonate solvent cleanup and regeneration system is used in preparing UO_2 sol by the CUSP process, amine is lost from the extractant during each run, so the solvent becomes discolored (with UO_2) during the production runs. The amine concentration decreased from 0.21 to 0.11 M during the 26 runs. This was reflected in an increase of total run time from an initial 4 hr to a final 6.4 hr. There is no evidence that the use of the discolored extractant has a deleterious effect on the sol products, but interfacial levels are obscured, and black crud accumulates at the organic-aqueous interface in the regeneration contactors. Five runs tested the use of a $NaNO_2$ scrub for cleaning the extractant. A scrub consisting of 0.2 M $NaNO_2$–0.5 M HNO_3 at an extractant-to-scrub flow ratio of 10 did clean the solvent by oxidizing the entrained U(IV) to U(VI) and extracting it into the aqueous phase. The $NaNO_2$ and HNO_3 were mixed just before use. However, loss of amine was intolerable, increasing to 14 to 24% per run, whether the scrub contactor operated at 35 to 40°C or 55 to 60°C. We concluded that the $NaNO_2$-HNO_3 cleanup of the solvent was undesirable because of operating inconvenience occasioned by the rapid loss of amine.

A revised scrub system in which an acetic acid–nitric acid scrub and a water scrub precede the carbonate caustic regeneration appears to be satisfactory. The results of five laboratory experiments lead to the following conclusions. (1) The acetic acid reacts rapidly with the uranium. (2) The acetic acid does not need to be added directly to the organic phase. It can be premixed with the dilute acid scrub if the nitric acid concentration is at least 1 M. (3) Except when the nitric acid concentration was too low, the fraction of the uranium stripped was uniform at close to 96%. This suggests equilibrium, with a stripping coefficient of around 70, which is a reasonable value.

Nitrate Extraction Development

We are developing improved equipment for preparing UO_2 sol by the CUSP process. This equipment (see Fig. 3.10) consists of a nitrate extraction contactor, solvent reservoir, aqueous phase surge tank, heat exchanger, circulating pump, differential pressure cell, and conductivity cell. Similar equipment will be added to the existing Solex facility[7] in Building 3019 to prepare mixed sols containing UO_2–20% PuO_2. The equipment has an aqueous phase capacity of 4 liters, which is equivalent to 1 kg of UO_2 for a 1 M uranium sol.

[7]J. W. Snider, The Design of Engineering-Scale Solex Equipment, ORNL-4256 (April 1969).

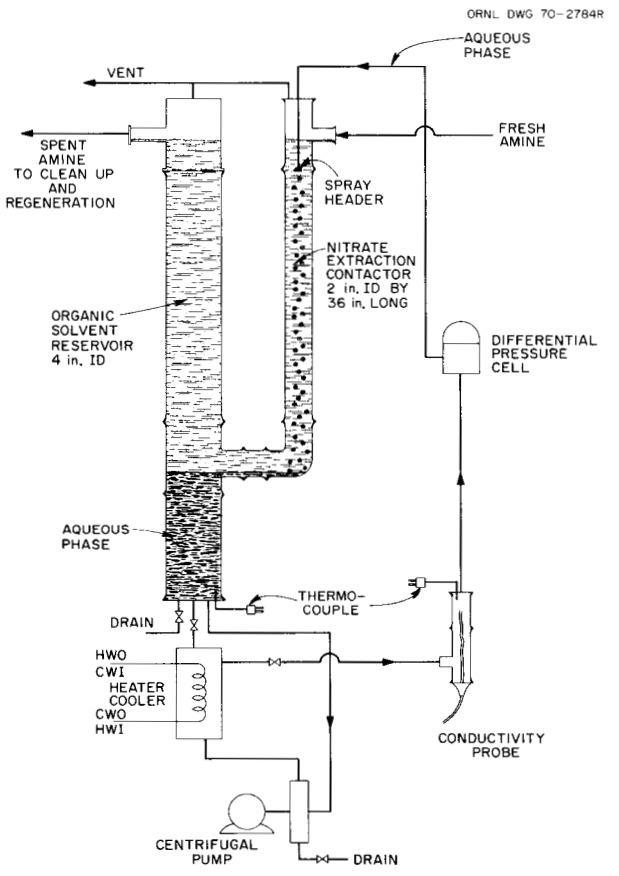

Fig. 3.10. Spray Column Contactor for UO_2 Sol Preparation.

Three nitrate extractor-contactors were tested: a column packed with ceramic berl saddles, a free-fall column using a perforated plate, and a spray header to disperse the aqueous in the organic solvent. The mode of operation was organic continuous with cocurrent downflow. With the packed column and perforated plate, vapor locking caused by the gas release during crystallization led to hydraulic difficulties. The spray column (Fig. 3.10) operated very satisfactorily with no difficulties. The gas released during crystallization is vented off through the annulus between the spray header and the column wall.

Sol properties for four spray column runs (SCHB 9–12) are summarized in Table 3.7. The sols as prepared were of very good quality, containing 85 to 90% U(IV) and still very fluid after more than 3.5 months.

Table 3.7. Properties of CUSP UO_2 Sols Prepared in a Free-Fall Spray Column

Run	Uranium (g/liter)	U(IV) Content (%)	NO_3^-/U Mole Ratio	Conductivity at 25°C (μmhos/cm)	Aging Time to Gelation (months)
SCHB-9	239.8	86	0.12	4275	> 3.75
-10	238.3	88	0.11	3329	> 3.75
-11	240.3	85	0.106	4184	> 3.5
-12	239.3	90	0.07	2668	> 3.5

Gel Sphere Forming Development

P. A. Haas C. C. Haws
W. D. Bond A. B. Meservey
K. J. Notz A. P. Luiña
J. W. Snider

When a specified sol feed is used to form gel spheres, the composition of the organic fluidizing medium is the principal operating variable. The successful continuous operation of a sphere-forming column requires that the alcohol composition be controlled within satisfactory ranges.

This is still largely empirical and requires demonstration operation in three stages:[8]

1. satisfactory initial conditions,
2. control of surfactant depletion, and
3. control of excessive accumulations of surfactants, degradation products, or impurities.

For the CUSP process for preparing UO_2 sols (see previous section), tests to develop and demonstrate the stages listed above were continued. The results to date show more problems for sphere formation from CUSP sols than for the ThO_2 or ThO_2-UO_3 sols. Quantitative measurements are difficult, and the interactions between variables are complex. This can be illustrated by generalized diagrams to show the four most common operating problems as functions of the Span 80 vs Ethomeen S/15 concentration [Fig. 3.11(a) through (d)]. The curves shown give the most commonly observed trends. However, the sol characteristics, the 2EH pH, and other variables result in large changes in numerical values or in changes of the curve shape. Therefore, numerical values of the surfactant concentrations are not given in Fig. 3.11. When these diagrams are superimposed, they may allow a large region of good operation as for Fig. 3.11(e) or a small region with many different combinations of poor operation as for Fig. 3.11(f). Most of the sphere preparation study for CUSP UO_2 sols has been on the determination and control of organic compositions to maintain good operation.

Study of Variables by Factorial Experiments

A factorial experiment on three variables in microsphere forming columns of 2EH has been described.[9–11] The sols used contained 3 moles ThO_2 per mole UO_3 and were prepared by amine extraction. The variables

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[8]P. A. Haas, Sol-Gel Preparation of Spheres: Design and Operation of Fluidized Bed Columns, ORNL-4398 (September 1969).

[9]K. J. Notz and A. B. Meservey, Microsphere Forming Conditions for ThO_2-UO_3 Sols: A Factorial Experiment, ORNL-TM-2516 (August 1969).

[10]W. D. Bond, A. B. Meservey, and K. J. Notz, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 59–62.

[11]Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, pp. 193–99.

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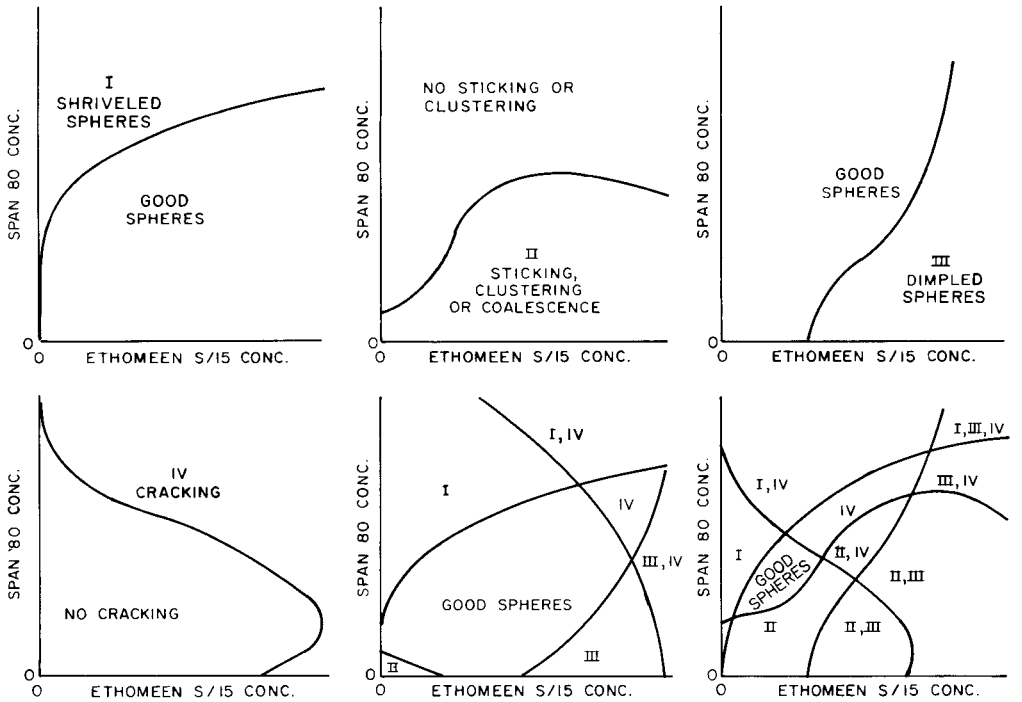

Fig. 3.11. General Effects of Surfactant Concentrations on Sphere Formation. (a) Raisin distortion. (b) Sticking, clustering, and coalescence. (c) Dimple distortion. (d) Cracking. (e) Combined effects for easy-to-form sol, such as ThO_2. (f) Combined effects for difficult-to-form sol, such as UO_2.

were the concentration in the 2EH of water, acid, and the surfactant Ethomeen S/15. In continuation of this work, a second factorial experiment has been completed[12] with the addition of a fourth variable, the concentration of the additional surfactant Span 80. This surfactant is always used along with Ethomeen to control clustering and coalescence of droplets during fluidization when ThO_2-UO_3 spheres are formed in continuously operated columns.

In this second study, sols of steam-denitrated thoria and of UO_2 were used in addition to ThO_2-UO_3 sols. Since the three sol types were

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[12]A. B. Meservey and K. J. Notz, Microsphere Forming Conditions: Further Factorial Experiments on ThO_2-UO_3, ThO_2 and UO_2 Sols, ORNL-TM-2957, in preparation.

of different colors (white, black, and red), all three were frequently formed in the same experimental 2EH column at the same time and examined when dry in the same microscope field. This technique ensured identical forming conditions and emphasized differences among sols when the microspheres were examined side by side.

We used 2EH with the same Ethomeen and HNO_3 contents in the second study as in the first — Ethomeen S/15 at 0.05 and 0.5 vol %, and HNO_3 at 0.001 and 0.01 M — and slightly higher water levels: 0.5 and 1.7 vol %. Three Span 80 levels were studied in each of the eight 2EH batches, at 0, 0.05, and 0.5 vol %, making 24 separate combination levels. Differences between columns, such as were occasionally noted in the first study, were avoided by using only one forming column.

The results of this study will be summarized only briefly since a topical report has been prepared.[12] The effects of Span 80 additions were complex, and its addition was largely detrimental to the ThO_2-UO_3 sols in many of our solvent compositions. We tested three different ThO_2-UO_3 sols in the factorial experiment: sol A, prepared by the standard cocurrent amine extraction flowsheet; sol D, same as A except that crystallinity was increased by digestion; and sol G, prepared by the standard countercurrent amine extraction flowsheet. Sol G was considerably less sensitive to solvent composition than were the others because of its lower nitrate-to-metal ratio. The countercurrent flowsheet conditions have since been selected as our standard for sol preparation.[13]

In the previous factorial experiment,[9] the best yields were obtained at 0.05% Ethomeen, 0.001 M HNO_3, and 1.6% H_2O. When Span was added to this formula, wrinkled pits appeared in the spheres, and the problem became more severe with increasing Span 80 concentration (Fig. 3.12). Examination of all of our results showed that use of Span 80 requires a proper balance among the Span 80, Ethomeen S/15, H_2O, and HNO_3 concentrations. For example, very good results with Span 80 addition were

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[13]C. C. Haws, B. C. Finney, and W. D. Bond, Engineering-Scale Demonstration of the Sol-Gel Process: Preparation of 100 kg of ThO_2-UO_2 Microspheres at a Rate of 10 kg/day, ORNL-4544, in preparation.

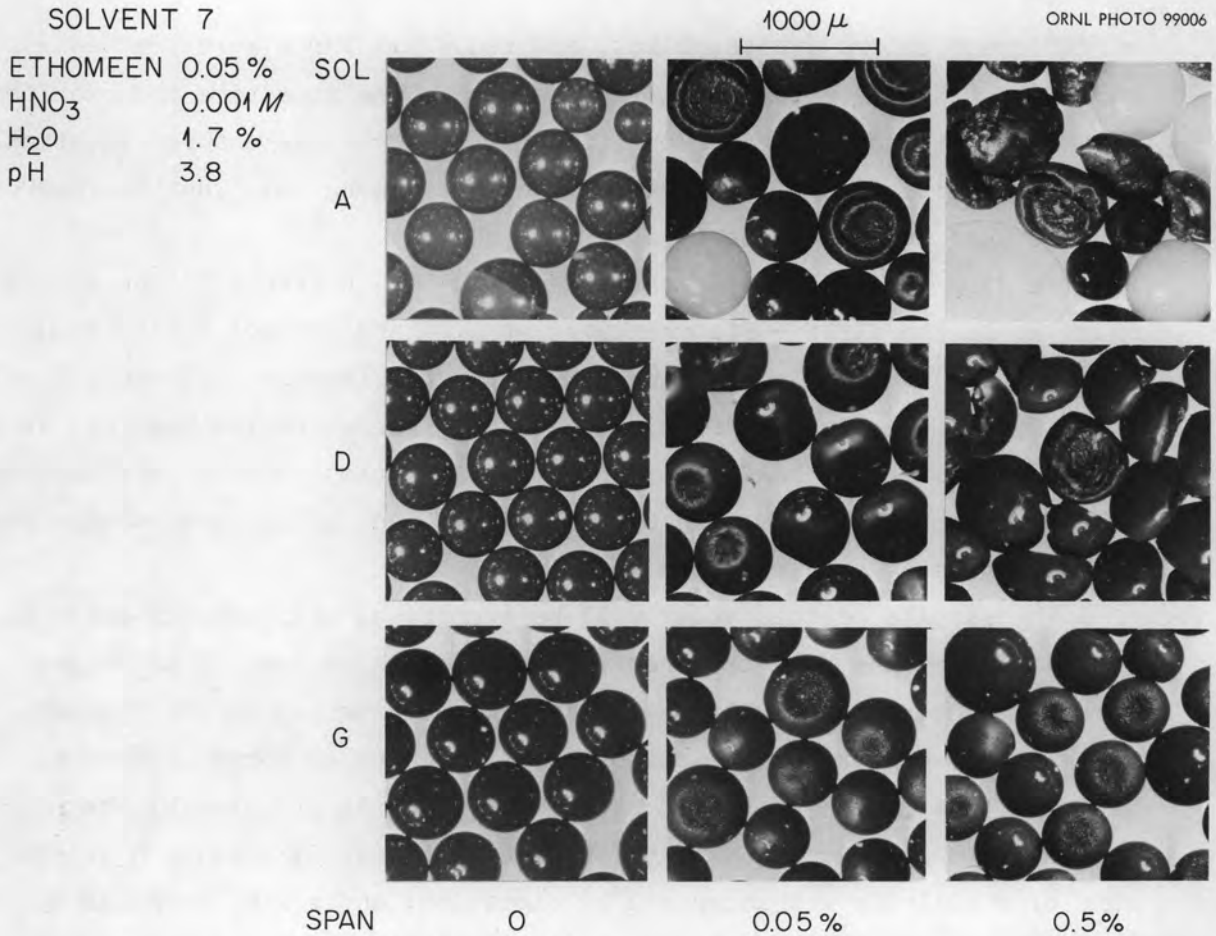

Fig. 3.12. Effect of Span 80 on Wrinkle and Pit Formation at Low Ethomeen S/15 Concentration.

obtained at 0.5% Ethomeen S/15, 1.7% H_2O, and 0.001 M HNO_3 for sol G (Fig. 3.13). When Span and Ethomeen were both present at 0.5% with 0.001 M HNO_3, water concentration had little, if any, effect.

Studies of 2EH Recycle Methods

Previously we showed that pH, surfactant concentration, and water content of 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. A portion of the used solvent is heated at 150 to 160°C to remove most of the water, and this relatively dry 2EH is mixed with the remaining

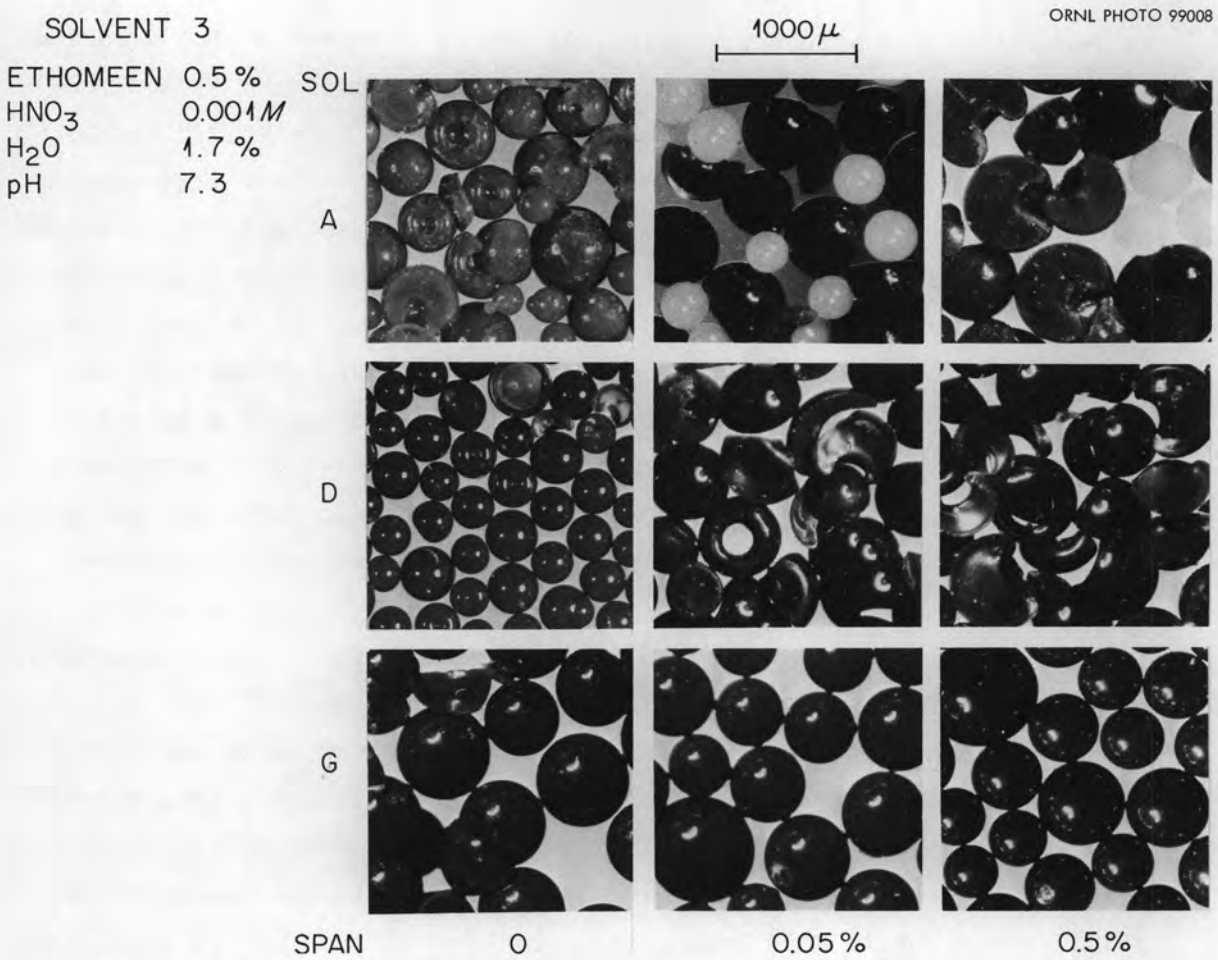

Fig. 3.13. Effect of Span 80 on Wrinkle and Pit Formation at High Ethomeen S/15 Concentration.

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 distillation, and formic acid interferes with long-term column operation with urania sols by promoting clustering. Therefore, the use of caustic scrub solutions and of ion exchange resins for removing these acids from 2EH is being investigated. We are also studying a total 2EH purification method in which it 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.

Laboratory studies have shown that reactions of nitric acid with 2EH and surfactants during distillation could essentially be eliminated

by removal of the acid before distillation by contacting with alkaline solutions or ion exchange resin. The acid content of the alcohol could then be maintained at the desired level by adding nitric acid to the alcohol after the removal of water by distillation. We tested caustic scrubbing as a means of controlling the pH and surfactant concentration of the engineering-development sphere-forming column during continuous operation. Scrubbing with alkaline solutions[14] was not satisfactory because of emulsification and entrainment problems. Emulsification problems were lessened but not eliminated by scrubbing in a packed column with the organic phase continuous. A liquid-liquid membrane separator (Selas Corporation) was used in conjunction with the packed column but became plugged after about 6 hr. We are, therefore, now investigating anion exchange resins for removing the nitric and formic acids. No phase separations are required in the ion exchange approach, and the emulsion and entrainment problems are avoided.

Use of Anion Exchange Resins. — Laboratory studies showed that a weak-base resin (Amberlite IRA-93) is almost as effective as a strong-base resin (Amberlite IRA-900) for the removal of both nitric and formic acids. The nitric acid is removed in preference to the weaker formic acid, so the formic acid breaks through first as a column becomes loaded by a mixture of both acids. With the macroreticular (highly porous) weak-base resin, even formic acid was taken out fairly rapidly; 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. Although a strong-base resin should be more effective than the weak-base type for removing weak acids such as formic, regeneration is more difficult, particularly from the nitrate form. Therefore, both chemical types were tested. Only macroreticular resins were tested initially. The surfactants (Span 80 and Ethomeen S/15) do not appear to interfere with acid removal. Losses of surfactants to the resin have not been determined.

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[14] Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, pp. 197–99.

We have installed a resin column in the circuit of our engineering-development sphere-forming equipment, are testing anion exchange resins for the removal of nitric and formic acids, and are determining the degree of removal of nitric and formic acid that is required for satisfactory sphere forming.

Use of Distillation. — Recovery of 2EH from surfactants requires fewer distillation stages when water is present. Also the surfactants decompose considerably less than in our previous study,[14] where water was not present. We have carried out laboratory studies on the recovery of 2EH by distillation of two phases at 100°C and of a single phase at 150 and 180°C. We determined the maximum initial rates of distillation that could be attained with our laboratory equipment at several temperatures for 2EH free of surfactants. Also, we determined the volume of water required per volume of 2EH purified. The results are shown for the two-phase distillation at 99 to 100°C in Table 3.8 and for single-phase distillation at 150 and 180°C in Table 3.9.

Table 3.8. Two-Phase Distillation of Used 2EH and Water at 100°C

Conditions: The 2EH feed contained surfactants and had been used in microsphere-forming columns. An electrically heated (600 W max), 5-liter stillpot was used.

Rate of Distillate Collection (ml/min)	2EH in Distillate (vol %)	Rate of 2EH Recovery (ml/min)
3.55	28	0.99
3.55	20	0.71
3.60	20	0.72
3.40	24	0.82
4.80	21	1.00
8.30	19	1.58
12.6	16	2.02

Table 3.9. Single-Phase Distillation of Used 2EH and Water Solutions

Conditions: The 2EH feed contained surfactants and had been used in microsphere-forming columns. An electrically heated, 1-liter stillpot was used.

Temperature (°C)	Rate of Distillate Collection (ml/min)	2EH in Two-Phase Distillate (vol %)	Rate of 2EH Recovery (ml/min)
150[a]	8.0	68	5.4
	8.0	73	5.8
	11.0	79	8.7
	12.0	77	9.2
	12.5	76	9.5
155[a]	15	78	11.7
180[b]	15	~ 100	15.0
	27.5	~ 100	27.5
	45.0	~ 100	45.0

[a]Used 2EH and about one-fourth volume of water were metered into the distillation pot.

[b]Used 2EH that had been saturated with water at room temperature (2.5% H_2O) was metered into the distillation pot.

The distillations at 100 and 150°C were carried out by metering the used 2EH and water into a distilling pot, collecting the condensate, and then separating the 2EH and water phases in the condensate. The 180°C distillation was carried out in the same manner except that the distillate was redistilled at 180°C. All of the 2EH recovered was free of surfactant (< 0.005 vol %). The rate of distillation was varied by varying the applied voltage to the electrical heaters. The rates attained at 100°C cannot be directly compared to those obtained at 150 and 180°C. A 5-liter round-bottom flask heated by a 600-W heater was used in the 100°C distillation, whereas a 1-liter round-bottom flask heated by a 380-W heater was used at the other temperatures.

Simple prorating of the volume-power ratio of the 5-liter flask to the 1-liter flask indicates that rates of 2EH recovery in the 100°C distillation would have been about 0.55 times as great had the experiment been performed in the same equipment.

Sphere Preparation Development for CUSP UO_2 Sols

We established[15] 0.4 vol % Span 80 and 0.05 vol % Ethomeen S/15 together as satisfactory concentrations for the first hour for microsphere preparation from CUSP UO_2 sol. The development and demonstration of longer periods of operation were started using the UO_2 sols from the development runs in CUSP engineering equipment.

Operation with virgin 2EH was first satisfactory but became unsatisfactory after short periods with excessive clustering and sticking. This happened when the volume of sol fed equaled about 3% of the system alcohol volume. The problem did not appear to be due to loss of surfactants, as surfactant additions resulted in only small, temporary improvements, and several additions caused particle distortions typical of those from excessive surfactant concentrations. Several different experimental results indicate that the sticking and clustering are due to accumulations of formate (extracted from the UO_2 sol) in the 2EH. Scrubbing the 2EH with aqueous solutions of NaOH, Na_2CO_3, or NH_4OH alleviated the sticking and clustering, while addition of extra formate caused clustering.[15] Analyses of the 2EH showed buildup of formate equivalent to about 30% of the formate in 1 M CUSP sol or 15% of the formate in 2 M CUSP sol. The difference may be due to the shorter gelation time for the more concentrated sol. The initial period of good sphere formation was extended by either caustic scrubbing of the 2EH or additions of HNO_3 to maintain low pH values in the 2EH. Without use of caustic scrub or addition of HNO_3, the pH of the 2EH rises rapidly during operation of the still that removes water during or after formation of sol into spheres. Although the CUSP sols have pH's of 2.1 to 2.9, feeding

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[15] P. A. Haas, S. D. Clinton, and C. C. Haws, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 45–53.

them into 2EH of pH 3 while the still is in operation rapidly increases the pH of the 2EH to over 5. Additions of HNO_3 to maintain the pH at about 2 prevents the sticking and clustering, possibly by oxidation of the formic acid in the still at 150°C.

The treatments listed for extending the operation without clustering or sticking all have resulted in other difficulties. For caustic scrubbing of the 2EH, the solution is entrained in the 2EH. The surfactants in the 2EH result in entrainment of very small drops of aqueous scrub solutions, even for relatively gentle mixing in a spray column. Water scrubs tend to emulsify with the 2EH solution and are not very effective for removing the entrained solution drops. The NaOH solution drops were dehydrated in the still at 150°C and were carried into the sphere-forming column as gelatinous, colloidal particles in the 2EH. The entrained Na_2CO_3 solution drops resulted in repeated plugging of the first heat exchanger in the still. Most of the NH_4OH is stripped out in the still, but enough dissolved NH_4OH is carried out into the sphere-forming column to visibly affect the gel spheres. The addition of HNO_3 to keep all the 2EH at pH 2 results in very rapid degradation of surfactants in the still.

A membrane-type liquid-liquid separator, purchased from the Selas Corporation, was tested for preventing entrainment of caustic solution in 2EH. The Selas separator appeared to prevent the entrainment, but the coalescing membrane plugged after 6 hr of use. The aqueous interface was maintained above this membrane for a second test (the interface was near the bottom for the first test). This change slowed down, but did not stop, the increase in pressure drop (indicating plugging) during operation. Even after the entrainment was reduced by use of a packed scrub column with the organic phase continuous, the Selas separator plugged. We do not plan any further tests of the separator for this application.

The contactor initially used for scrubbing the 2EH with 0.5 M NaOH consisted of two aqueous-continuous spray columns. This was changed to one 4-ft length packed with 1/2-in. ceramic berl saddles with the organic phase continuous. This packed column scrubber generally gave

much less entrainment of caustic solution than the spray columns and operated acceptably for the short periods (less than 6 hr) tested. Caustic droplets out of the scrubber were entrained much less than for the scrub contactors that had been previously tested, but some entrainment was still visible. The long-term acceptability of this entrainment and the effectiveness of the scrubbing would have to be demonstrated by long periods of operation before we could accept the packed column scrubber as a proven method. The scrubbing efficiency was measured by feeding 6 g/hr of HCOOH and 0.12 mole/hr of HNO_3 dissolved in 2EH. This provided known inputs of acids rather than the variable amounts extracted from sol drops. Analyses of the 2EH samples showed about 40 mg/liter $HCOO^-$ at the start and after 6 hr of scrub at the end without HCOOH feed. If this 40 mg/liter is subtracted from all analyses (this assumes it is an unextractable, constant material that shows up in the formate analyses), the buildup of $HCOO^-$ during HCOOH addition and the decreasing concentration during no addition both agree with 70% removal during flowing through the scrubber and still. Analyses of the two NaOH scrub solutions only show about 50% of the HCOOH that had been added to the system. The 70% scrubbing efficiency would allow about 0.002 M $HCOO^-$ in the 2EH at steady state based on (still or scrubber)-to-sol volume flow ratios of about 150. This appears just barely adequate.

Development of Fluidized-Bed Columns

A report was published to summarize information for designing and operating fluidized-bed columns for gel sphere preparation.[16] In this report,

> "... emphasis is on variables other than the sol characteristics. Among the problems considered are: premature discharge of incompletely gelled particles from the sphere-forming column, formation of nonspherical gel particles, and capacity limitations of the equipment. The correct configuration for the column and the use of a tangential fluid inlet to create a swirling motion of the

[16] P. A. Haas, Sol-Gel Preparation of Spheres: Design and Operation of Fluidized Bed Columns, ORNL-4398 (September 1969).

liquid are important factors in ensuring good fluidization. Successful continuous operation requires control of the composition of the fluidizing mixture by the addition of surfactants and the operation of a still to remove water. Capacities under normal conditions, in terms of grams of oxide spheres per hour, are estimated to be from 100 g/hr for dilute sols, using a 1-in.-ID (minimum) column, to 9000 g/hr for concentrated sols, using a 3-in.-ID (minimum) column. The dispersion of sol into uniform drops is also important to continuous and efficient operation; four useful dispersion techniques are described. The composition and size of the product spheres must be specified before equipment and procedures can be optimized."

The settling velocity and molarity of a sol drop as functions of time determine some fluidized-bed column requirements. These variables are calculated by use of a computer program (see below). Starting with a 1 M sol, the settling velocity of the drop has a minimum at about 1.5 M and varies little from 1 to 4 M (Fig. 3.14). The settling velocity at gelation (about 14 M) is only about 40% greater than the minimum. Thus the continuous removal of gelled spheres is possible only if the fluidization is carefully controlled and uniform and if there are very few oversize drops that would drop out ungelled. About 80% of the water extracted and 70% of the time required for gelation are for the 1 to 4 M range with a nearly constant settling velocity (Fig. 3.14). The sol drop has a much smaller volume and only spends 30% of the gelation time in the 4 to 14 M range, where the settling velocity is increasing. Thus a fluidized-bed column should be designed to provide a large bed volume for holdup of the 1 to 4 M sol drops compared to the volume for 4 to 14 M. This is the reason for the recommendation of a cylindrical section on top of a tapered section in the design report.[16]

Preparation of Spheres Smaller than 200 μm in Diameter in Nonfluidized Columns

This section describes the development of processes and equipment for preparing gel spheres without fluidization. The requirements with respect to control of the 2EH and sol flow rates, the surfactant concentrations, and the uniformity of sol drops are much less restrictive in the absence of fluidization; however, the maximum sphere diameter that can be produced is typically 200 μm or less for simple, nonfluidized

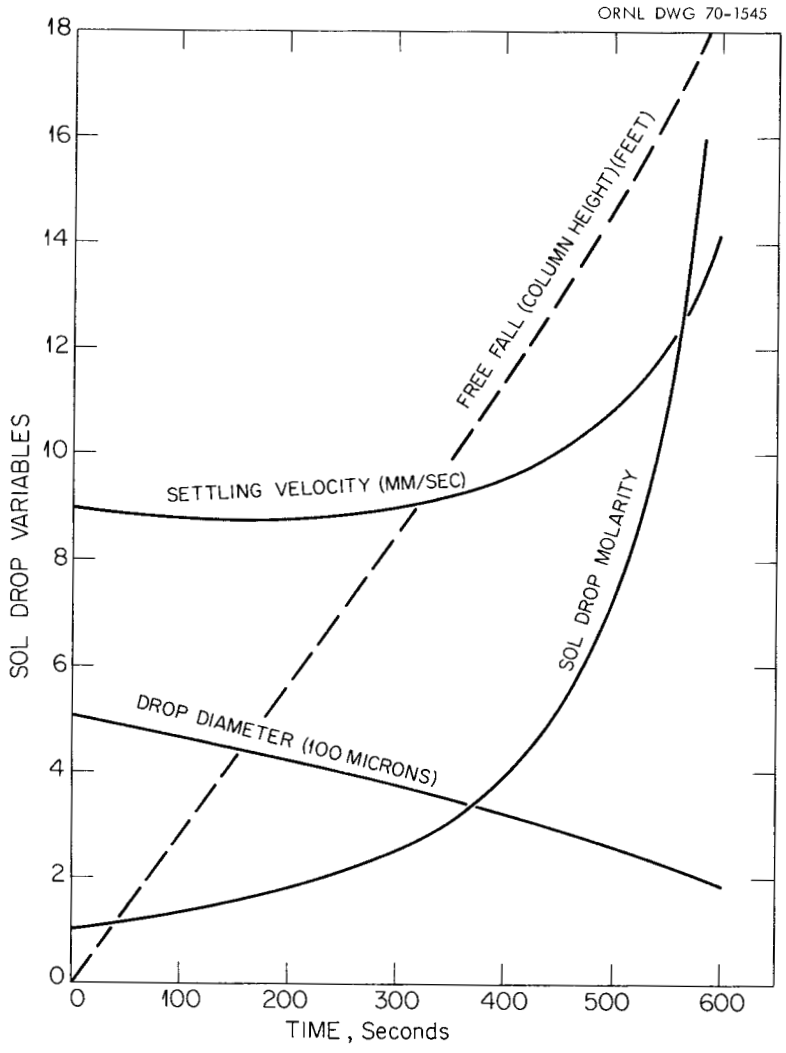

Fig. 3.14. Typical Variation of Sol Drop Variables with Time, From Mass Transfer Calculations.

systems. Materials prepared in our equipment were used for development studies at ORNL and elsewhere. These materials included about 50 kg of ThO_2 spheres, 10 kg of UO_2 spheres, 10 kg of UO_2-C spheres, and smaller amounts of spheres of other compositions. Both the ThO_2 and UO_2 spheres densified to greater than 9.9 g/cm^3 on firing to 1150°C.

A new system used for the nonfluidized preparation of gel spheres is shown in Fig. 3.15. The disperser forms sol drops in the top of a 4-in.-ID glass column. Water is extracted to form gel spheres as the sol drops and the organic liquid flow cocurrently down the 10-ft length

ORNL DWG 69-10336

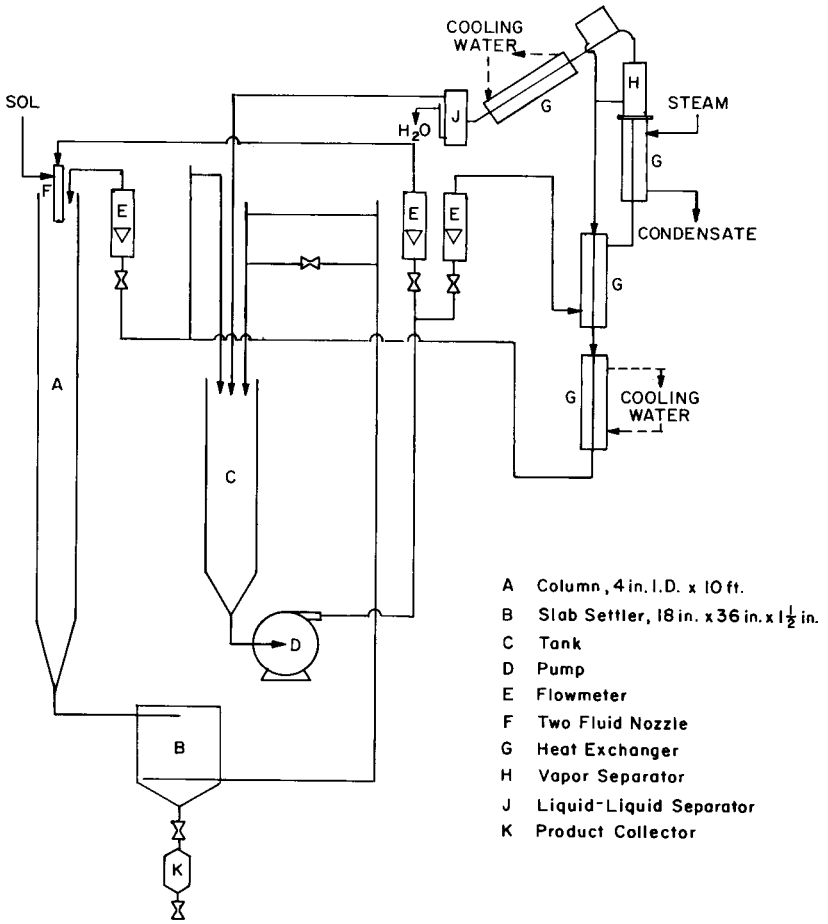

Fig. 3.15. Cocurrent Column System for Preparation of Gel Spheres Without Fluidization.

of column. The organic liquid is usually 2EH or isoamyl alcohol (iAA). The sol drops or gel spheres settle through the alcohol and have a shorter average residence time than the alcohol. Water is removed from the alcohol in a single-stage distillation, and the dry alcohol is returned to the column. The gel spheres are separated in an inclined slab settler and collected in a combination product receiver and gel sphere dryer. This receiver is valved off from the system, and the gel spheres are dried in batches.

The sol drops introduced into a nonfluidized column must be small enough to gel before they settle to the bottom. This is the principal limitation on nonfluidized preparation of spheres. The column heights

required depend on the mass transfer and settling velocity. The mass transfer as a function of sol drop and organic liquid variables was investigated and correlated by Clinton.[17] The settling behavior of drops or spheres is easily calculated with Stokes' settling velocity equation for laminar conditions and a drag coefficient for larger Reynolds numbers. The sol drop size and density both vary with time. Thus the mass transfer and settling velocity both vary with time, and analytical solutions are not possible. However, the mass transfer and settling velocity correlations are easily combined using a computer program[18] to give time and free-fall distance as a function of sol drop variables and organic variables. The computer program can be used to calculate the drop diameter, drop concentration, and free-fall distance as functions of time (Fig. 3.14).

The free-fall distance required to reach about 14 M (about 17 ft for Fig. 3.14) is the column height required for gelation without fluidization. These heights are plotted against the initial sol drop diameter in Fig. 3.16 for specified initial drop diameter and organic variables. The gelation times and fired diameters are also shown. The gelation time decreases as the sol molarity increases since both the rate of mass transfer increases and the amount of water to be removed decreases. But the column height required has a maximum at about 3.5 M. Below 3.5 M initial concentration, the column height required is less because of the lower settling velocity. Above 3.5 M initial concentration, less column height is required because the shorter gelation time has more effect than the higher settling velocity. Our initial sol concentrations are usually between 1 and 3 M. Thus, for a specified initial drop diameter the column height required for nonfluidized gelation is relatively independent of the initial sol molarity.

The free-fall distances or column heights of Fig. 3.17 are for 2 M initial sol, but initial sol molarities from 1.2 to 7 M would give heights

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[17]S. D. Clinton, Mass Transfer of Water from Single Thoria Sol Droplets Fluidized in 2-Ethyl-1-Hexanol, ORNL-TM-2163 (June 1968); M.S. Thesis, University of Tennessee, Knoxville (1968).

[18]D. A. Schneider and N. I. Salas, "Gelation of Small Diameter Thoria Sol Microspheres in Non-Flowing Alcohols," MIT Practice School study.

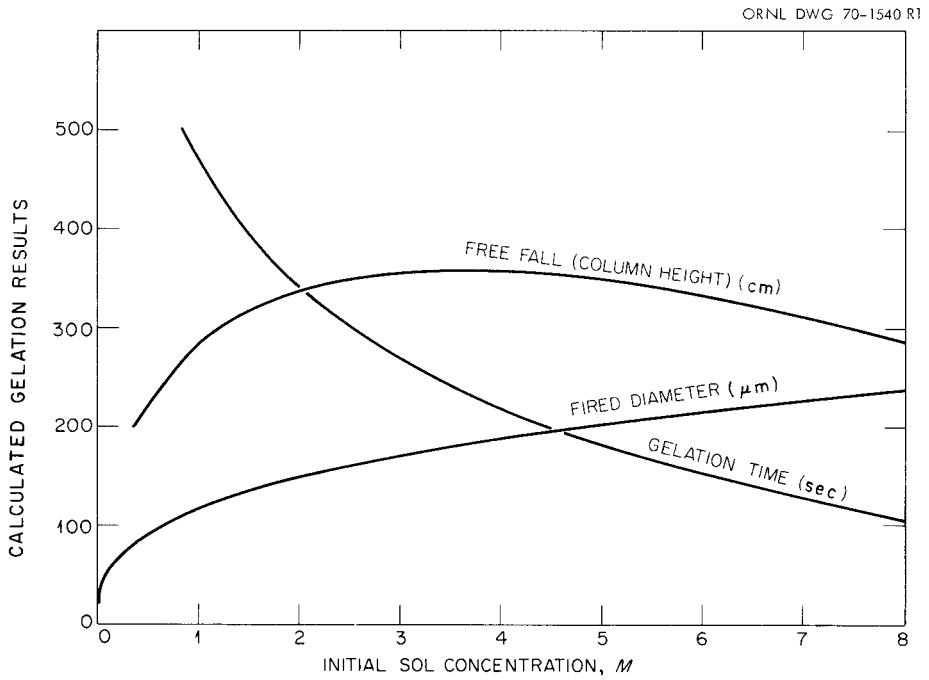

Fig. 3.16. Calculated Gelation Results Related to Initial Sol Molarity.

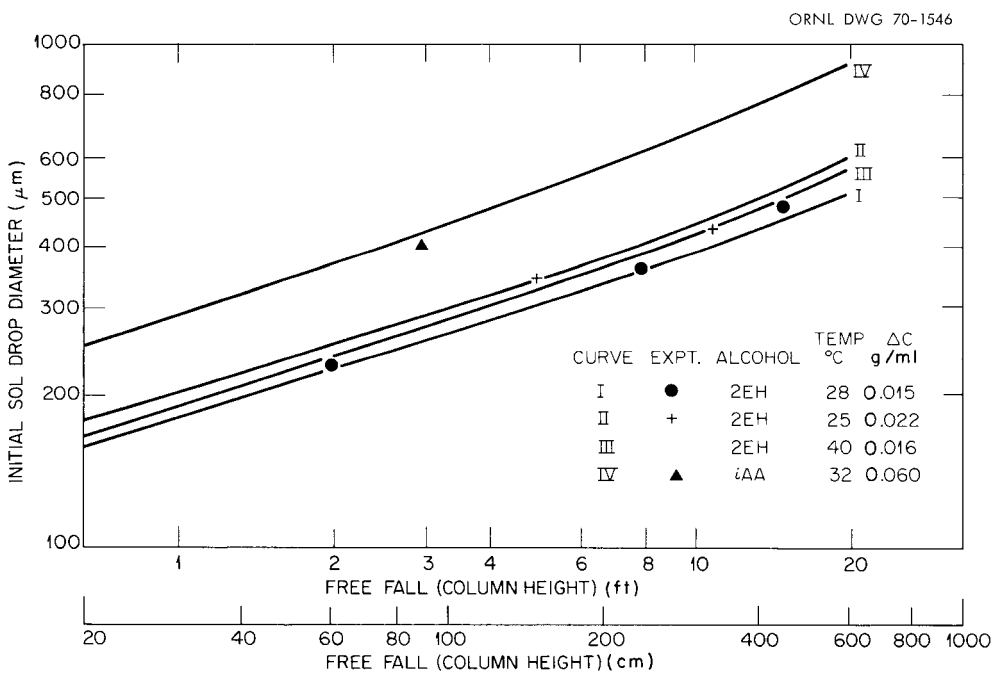

Fig. 3.17. Initial Sol Drop Diameter Plotted Against Column Height Required for Gelation.

within ±10% of these values. The curve I conditions correspond to previously reported[19] experimental values for 2EH. The curve II conditions were checked experimentally in 5- and 11-ft columns.[18] The curve IV conditions correspond to experimental conditions for isoamyl alcohol.

These results along with other experimental tests show that 300-μm-diam sol drops are easily gelled in nonfluidized columns, while 500- or 600-μm-diam drops are difficult. For 2EH, the difficulty is that large column heights are required, increasing from 4 to 6 ft for 300 μm to 20 to 30 ft for 600 μm. For iAA, the difficulty is that sol drops that are initially larger than 300 μm are almost certain to distort or crack as a result of the low interfacial tension and the high rate of mass transfer. The corresponding fired product sizes, assuming theoretically dense spheres, are given in Table 3.10.

Table 3.10. Sol Diameters from Free-Fall Columns

Initial Diameter (μm)	Fired Diameter, μm, from Various Initial Sol Molarities		
	1 M	2 M	3 M
300	90	110	125
500	145	185	210
600	175	220	250

Preparation of Test Material for Recycle Test Elements

J. R. Parrott F. L. Daley
C. C. Haws P. A. Haas
W. T. McDuffee R. J. Shannon
F. G. Kitts

Experimental fuel elements called Recycle Test Elements (RTE's) have been fabricated for irradiation in the first Peach Bottom Reactor. The

[19] P. A. Haas, S. D. Clinton, and C. C. Haws, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 45–53.

RTE's are an important part of the National HTGR Recycle Program. They will provide prototype 1100 MW(electrical) HTGR fuel in sufficient quantities for use in hot cell studies of head-end reprocessing operations and of prototype equipment to be used in the Thorium-Uranium Recycle Facility (TURF).

The Chemical Technology Division was to prepare oxide kernels for use in fabricating the RTE's and deliver to the Metals and Ceramics Division for coating with pyrolytic carbon. The requirements are given in Table 3.11. The preparation of some of these kernels is described below. The ThO_2 microspheres were selected from the product from the thorium engineering scale development run reported previously.[20]

Table 3.11. Microspheres Needed for Recycle Test Elements

Material	Quantity (g)	Size (μm)	Density
ThO_2	1300	400 ± 100	> 9.50 g/cm^3
ThO_2-$^{235}UO_2$ (Th/U = 4.2)	1000	350 ± 100	> 95% of theoretical
ThO_2-$^{235}UO_2$ (Th/U = 2.0)	2700	350 ± 100	> 95% of theoretical
$^{235}UO_2$	300	100 ± 30	> 10.20 g/cm^3

The ThO_2-$^{235}UO_2$ material was prepared in the engineering-scale sol-gel facility that had been operated previously to prepare 32 kg of ThO_2–0.25% $^{233}UO_2$ for tests in the High Temperature Lattice Test Reactor.[21–23]

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[20]P. A. Haas and C. C. Haws, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 62–69.

[21]Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, pp. 183–86.

[22]J. W. Snider, F. L. Daley, J. R. Parrott, R. J. Shannon, F. J. Furman, Jr., and R. A. Bowman, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 3–10.

[23]J. R. Parrott, F. L. Daley, F. J. Furman, and J. W. Snider, "Demonstration of $^{233}UO_2$-ThO_2 Microsphere Production by the Sol-Gel Process," presented at the 1969 Annual Meeting of the American Nuclear Society, Seattle, Wash., June 15–19, 1969.

Eight 1-kg-metal batches of ThO_2-$^{235}UO_2$ (Th/U = 4.2) were processed through the solvent extraction equipment[24] for the preparation of hydrosol having a nitrate-to-metal ratio of 0.1. The first run was necessary to obtain equilibrium, and the sol was of poor quality. Excessive amounts of nitrate ion were extracted. To prevent overdenitration of the sol, the extractant (Amberlite LA-2 in an n-paraffin diluent) flow rate had to be reduced 15% from the established flowsheet rate used for the HTLTR Program.

Microspheres were formed in the cell 4 facility. The drying agent was 2EH containing 0.1% Ethomeen S/15 and 0.1 M HNO_3. The two-fluid nozzle was replaced with a perforated plate (bucket-type),[25] which permitted the use of an air-lift feed device rather than the syringe pump. However, it became obvious that the microspheres were not being dried sufficiently in the column, and a new column with a smaller throat was installed. The increased solvent velocity corrected the difficulty, and operation was excellent during the remainder of the program. A total of 6.98 kg of ThO_2-UO_2 microspheres was transferred to the Metals and Ceramics Division for coating.

The material containing thorium and ^{235}U in the ratio Th/U = 2.0 required the preparation by solvent extraction of nitrate from four batches (1 kg of Th + U each) of thorium-uranyl nitrate solution. It was denitrated in the same sol-forming equipment used for the material richer in thorium. However, spheres from sol of this low a thorium-to-uranium ratio had not been prepared on a large scale, and initial efforts to form this material into microspheres were unsuccessful. Various combinations of surfactants and sol "aging" steps failed to reduce the cracking during drying in the sphere-forming column. The direct method — the forming of microspheres directly from the red sol — was abandoned in favor of an indirect method in which carbon was added to the oxide sol

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[24] J. W. Snider, The Design of Engineering-Scale Solex Equipment, ORNL-4256 (April 1969).

[25] P. A. Haas, C. C. Haws, Jr., F. G. Kitts, and A. D. Ryon, Engineering Development of Sol-Gel Processes at the Oak Ridge National Laboratory, ORNL-TM-1978, pp. 37–40 (January 1968).

before sphere forming. This method was adopted to eliminate cracking since past experience had shown that cracking tendencies were greatly minimized when carbon was present. The carbon can then be burned out before final densification.[26]

Preliminary laboratory tests indicated that at least 3 g-atoms C/mole oxide was necessary to obtain good spheres, and a ratio of 4 was desirable. The carbon was added by ultrasonic agitation of the oxide sol containing the weighed amount of carbon black. Microspheres were formed from the carbon sols by maintaining the following concentrations in the 2EH:

0.3 to 0.4% Ethomeen S/15,
0.004 M HNO_3,
0.2 to 0.4% Pluronic L-92, and
0.5 to 1% H_2O.

The carbon can cause a number of exothermic reactions during drying and calcining; therefore, the microspheres were allowed to dry in air overnight. They were then heated slowly in argon to 300°C over a period of 8 hr. This was followed by an 8-hr heating period at a decreased argon flow, an 8-hr cooling period, and calcination to 1000°C at 300°C/hr in air. After this treatment the carbon content was 0.003 wt %. The surfaces of these microspheres are rough, and the microspheres are not true spheres, but are spheroidal. They retain their general shape during calcination, and require sintering at 1450°C to attain a density greater than 95% of theoretical. These sintered spheres are shown in Fig. 3.18(a). Approximately 4.6 kg of this material was transferred to the Metals and Ceramics Division for coating and subsequent use in preparing the RTE's.

Although the above technique provided material acceptable for use in preparing the RTE's, frequent plugging of the sol disperser and other handling problems led to a desire to produce microspheres directly from the red sol. Nine experimental runs, varying in size from 10 to 100 g (as metal), were made in the development laboratory. A satisfactory yield (71%) was attained by forming directly from the red sol if the Ethomeen S/15 content was maintained at 0.2 vol %, the water content at 1.5 vol %,

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[26]K. J. Notz, Preparation of Porous Thoria by Incorporation of Carbon in Sols, ORNL-TM-1780 (December 1968).

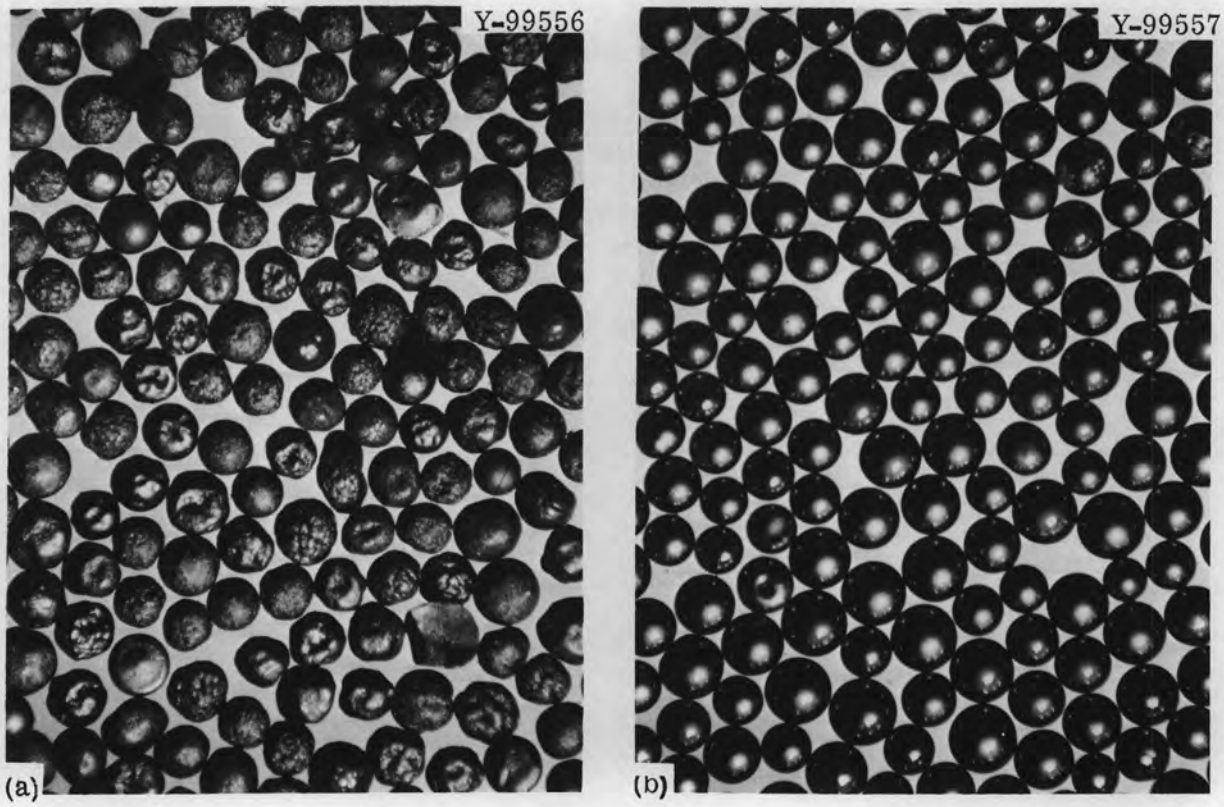

Fig. 3.18. Microspheres of $(Th,U)O_2$ with Th/U = 2.0 Prepared for Recycle Test Elements. 17×. (a) First batch. (b) Material formed directly from red sol in modified facility.

and the pH of the alcohol between 3.5 and 4.5. The facility was modified to incorporate the necessary controls to meet the above requirements, and 5.7 kg of material made in this manner was transferred to the Metals and Ceramics Division. A representative sample of this material, after rounding and screening, is shown in Fig. 3.18(b).

The $^{235}UO_2$ material was prepared by forming the sol using the previously described[27] precipitation-peptization technique. The data relating to the four lots of sols are given in Table 3.12.

Operation of the microsphere column during sphere forming was good; however, interparticle sintering was severe during the 1150°C calcination of the first two batches, resulting in a low (46%) yield. The final two

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[27]J. P. McBride, Laboratory Studies of Sol-Gel Processes at the Oak Ridge National Laboratory, ORNL-TM-1980, pp. 25–29 (September 1967).

Table 3.12. Enriched Urania Sols for RTE Program

Lot	Uranium Content (g)	Uranium Concentration (g/liter)	U(IV) (%)	Mole Ratio	
				NO_3^-/U	$HCOO^-/U$
93-21	277.5	245.5	90	0.14	0.24
93-26	286.0	280.4	92	0.15	0.42
93-30	295.8	197.4	88	0.14	0.24
93-31	295.3	190.6	79	0.15	0.27

batches were first fired to 800°C, cooled, stirred thoroughly, and then refired to 1100°C. The yield on the final two batches was 81%. We transferred 635 g to the Metals and Ceramics Division for coating.

4. FUELED-GRAPHITE FABRICATION DEVELOPMENT

F. J. Furman J. D. Sease

Our objective is to perform the development necessary to design and operate the remote refabrication line to be installed in TURF to demonstrate the recycle of HTGR fuel. This period our major efforts were in testing the prototype remote coating furnace and developing bonded beds. Significant quantities of coated particles and bonded beds were prepared for the Recycle Test Elements (RTE's) for irradiation testing in the Peach Bottom Reactor. Other development areas are particle handling, particle inspection, and fuel particle bonding. A general review of our fueled graphite development has been presented.[1,2]

Particle Handling

F. J. Furman

The fabrication of HTGR recycle fuels requires the transfer and classification of kilogram amounts of 150- to 850-μm-diam ^{233}U-bearing particles. Most commercial materials handling equipment is not suitable since either it is designed to handle ton quantities or it is laboratory equipment and thus not readily adaptable to remote or automatic operation. We have developed equipment to perform these tasks.[3]

The transfer equipment includes gravity and pneumatic transfer lines, transfer line valves and connections, storage hoppers, and feed devices.

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[1]F. J. Furman, J. D. Sease, and A. L. Lotts, "Economics and Technology of High-Temperature Gas-Cooled Reactor Fuel Refabrication," pp. 281–308 in Proceedings of the Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tennessee, May 4–7, 1970, CONF-700502.

[2]J. H. Coobs, A. R. Olsen, J. L. Scott, D. M. Hewette II, and E. L. Long, Jr., "Irradiation Performance of $(U, Th)O_2$ Coated Fuels for HTGR's," pp. 567–84 in Proceedings of the Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tennessee, May 4–7, 1970, CONF-700502.

[3]F. J. Furman, J. T. Meador, and J. D. Sease, Microsphere Handling Techniques, ORNL-TM-2782 (March 1970).

Previously we transferred the particles by feeding them continuously into 1/4- to 3/8-in. metal or plastic lines through which a steady stream of air is moving. This type of transfer line was successful on tests of up to 50 ft of line and elevation changes of 15 ft. However, during routine laboratory use this type of transfer system would occasionally be blocked at bends with radii of less than 2 to 3 in. during transfer of particles with low-density and hence compressible outer coatings. We modified the system to use a technique developed at the British Ministry of Technology's Warren Spring Laboratory, Stevenage, Hertfordshire, England. Air, in addition to that already flowing through the line carrying particles, is pulsed into the line downstream from the material inlet. This action breaks the material stream into plugs. These plugs can then pass through sharp bends before enough material can build up to cause blockage.

Classification of microspheres includes both the separation of nonspherical particles and over- and undersized particles. To separate nonspherical particles, a shape separator is used. This is a flat plate that is vibrated in one direction and slightly tilted in a direction approximately 90° to the vibration direction. The particles are fed onto the plate at one point. The spherical particles move in the direction of the slope and the nonspherical particles move with the vibration. With 350-μm-diam $(Th,U)O_2$ particles, the reference recycle fuel, a shape separator with one feeder can process about 0.5 kg/hr.

We plan to modify an 18-in.-diam SWECO gyratory separator[4] for screening in the hot cells. Normally the various parts of this separator are assembled piece by piece in place. We have modified the design so that all parts can be preassembled into modules. The parts that make up a module and the assembled module are shown in Fig. 4.1. A module can be available for each screen size and quickly installed. To facilitate the installation we substituted toggle clamps for the clamp rings that held the screens together. The toggle clamps can be seen in the fully assembled separator in Fig. 4.2.

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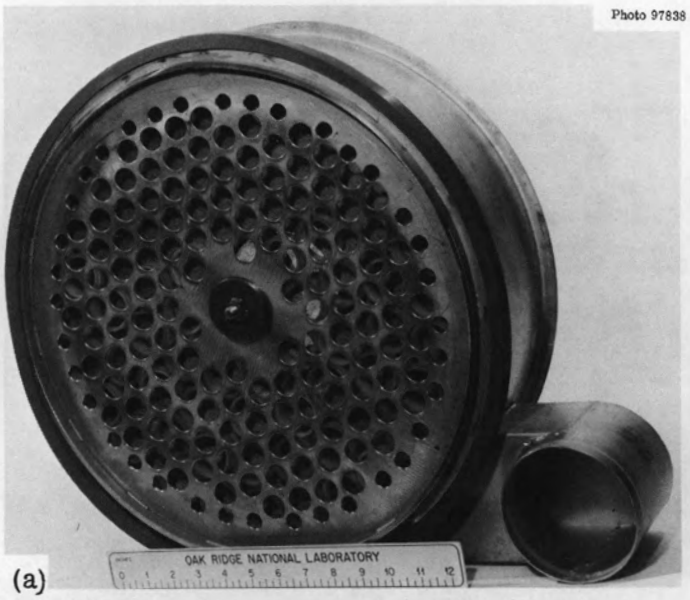
[4]Southwestern Engineering Co., Los Angeles.



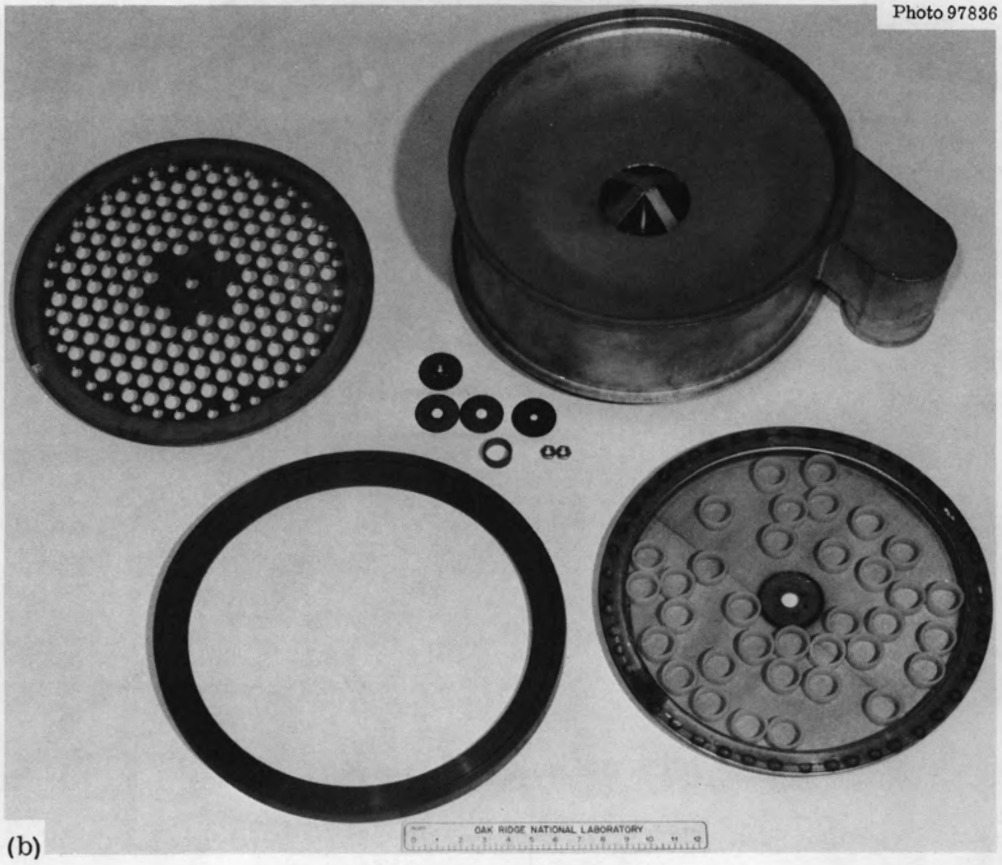


Fig. 4.1. Gyratory Separator Module Modified for Remote Assembly. (a) Assembled module. (b) Component parts.

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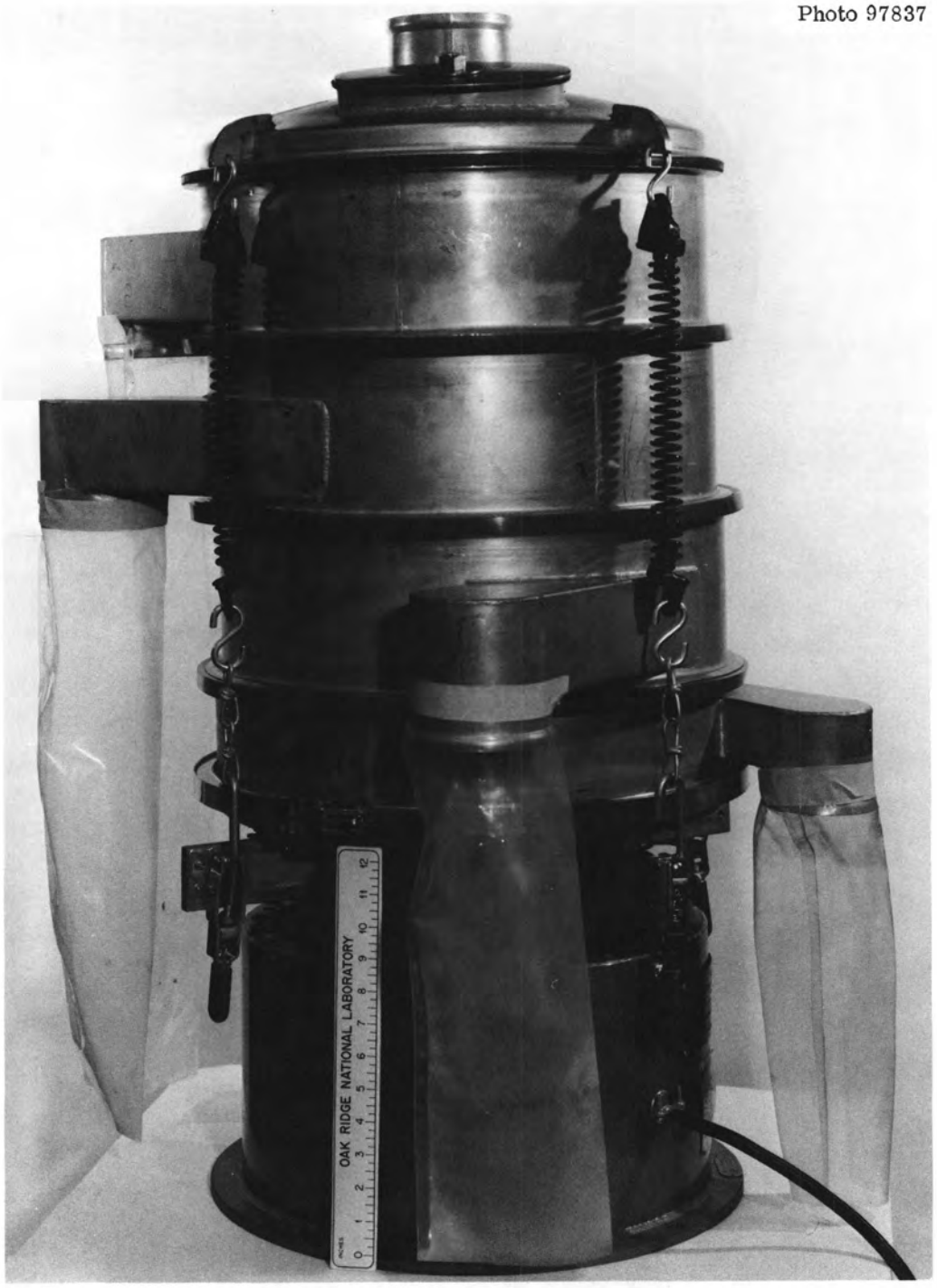

Fig. 4.2. Fully Assembled Gyratory Separator.

With a series of tests we determined the most advantageous setting for the adjustment on the separator. The adjustments include top motor weights, bottom motor weights, and lead angle between the top and bottom motor weights. We could split sol-gel microspheres with an average diameter approximately 350 μm into two size ranges with over 85% screening efficiency[5] at feed rates between 250 and 750 g/min.

The development of particle handling equipment is essentially complete; we now plan to begin design and fabrication of equipment to be installed at TURF.

Particle Coating

F. J. Furman

Of central importance to the current HTGR fuel design is the containment of the fission products in the fuel bodies. To contain them the fuel particles are encapsulated in pyrolytic carbon or silicon carbide shells or coatings. The reference design for the recycle particles calls for 350-μm-diam (Th–20% $^{233}U)O_2$ microspheres to be coated with two layers. The inner layer is 80 μm of low-density pyrolytic carbon to provide void volume for fission products and to protect the outer layer from fission recoil damage. The outer layer is 120 μm of moderately high-density, isotropic pyrolytic carbon and will contain most of the fission products.

Although the application of this type of coating is well understood, only limited experience exists[6] in applying the coating to particles containing ^{233}U. The recycle fuel to be used in large HTGR's must be fabricated in hot cells because of its high gamma activity. Since no production-scale coating equipment has been operated in hot cells we

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[5]F. J. Furman, J. D. Sease, and R. A. Bowman, Thorium Fuel Cycle Development Progress Report September 1969 No. 2, ORNL-TM-2705, pp. 9–11.

[6]J. R. Parrott, F. J. Furman, F. L. Daley, J. W. Snider, and J. D. Sease, Preparation by the Sol-Gel Process and Pyrocarbon Coating of 32 kg of 25% $^{233}UO_2$–75% ThO_2 Microspheres for the High Temperature Lattice Test Reactor, ORNL-4594, in preparation.

constructed a prototype of the remotely operable coating furnaces planned for TURF. This furnace and its operation to coat fuel for Recycle Test Elements (RTE's), which will be irradiated in the Peach Bottom Power Reactor, are described below.

Prototype Remote Coater

We completed the construction and initial testing of the prototype remote coating furnace. The design of this coating system has been described.[7] The particles to be coated are levitated by injection of gas into the apex of a 5-in.-diam inverted cone. Temperatures over 1600°C can be obtained. The total heat capacity of the furnace is low to permit accurate temperature control during rapid change in conditions in the coating region and allow rapid cool-down to facilitate routine maintenance. Both pyrolytic carbon and silicon carbide coatings can be applied in this furnace. The furnace is shown in Fig. 4.3, and a cross section explaining the various parts is shown in Fig. 4.4. The control panel is shown in Fig. 4.5. The entire system is diagrammed in Fig. 4.6.

The silicon carbide coating system, which was not included in the original prototype furnace design, consists of two major components: the silane injection system and the off-gas scrubbing system. Silicon carbide coatings are applied by the thermal decomposition of methyltrichlorosilane in hydrogen. The silane, normally a liquid at room temperature, must be vaporized before it can be fed into the furnace. We chose to flash evaporate a metered stream of the silane directly into flowing hydrogen. This approach has several advantages. The flow rate of the silane, important for the control of coating properties, is easily adjusted, and the equipment is relatively inexpensive compared to the alternative, an evaporator–reflux condenser system.[8]

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[7]R. B. Pratt and S. E. Bolt, Status and Progress Report for Thorium Fuel Cycle Development Dec. 31, 1966, ORNL-4275, pp. 61–78.

[8]R. L. Beatty and C. F. Sanders, GCR Program Semiann. Progr. Rept. Mar. 31, 1968, ORNL-4266, pp. 3–5.

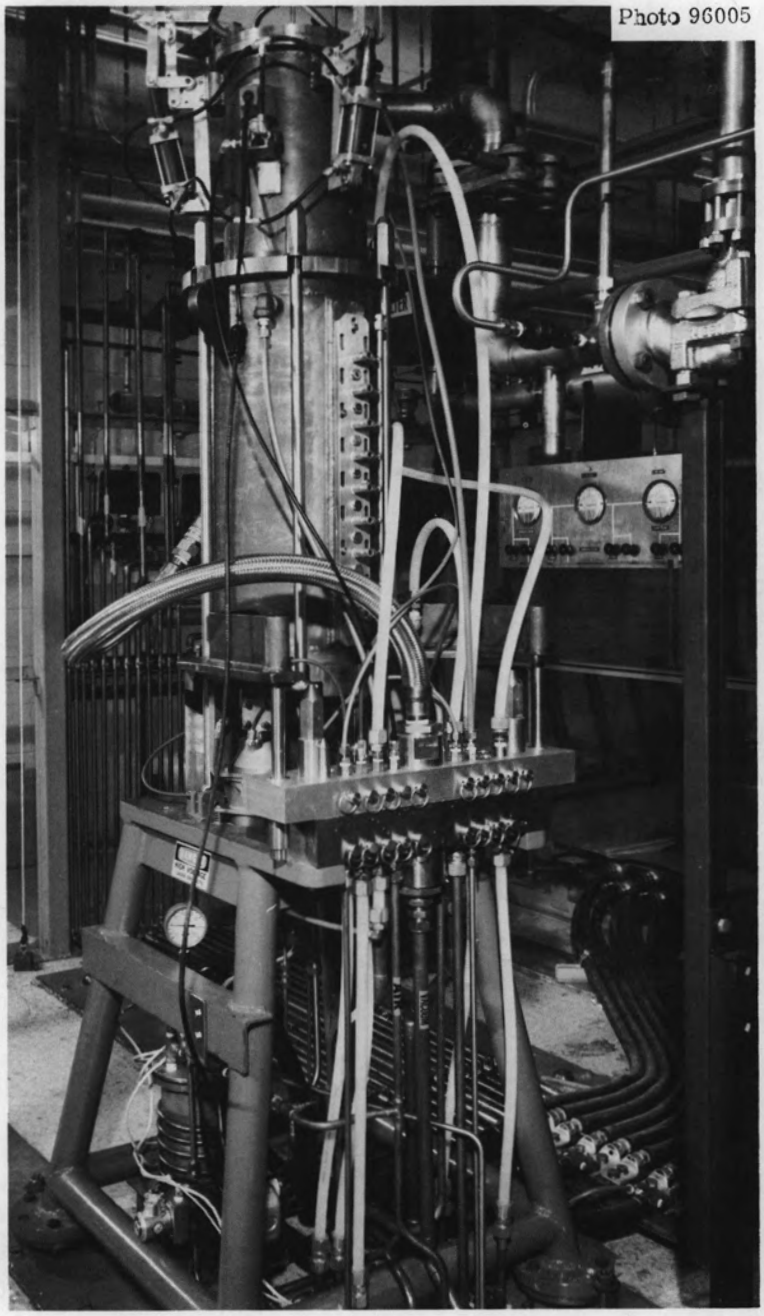

Fig. 4.3. Prototype Remote Fluidized Bed Coating Furnace.

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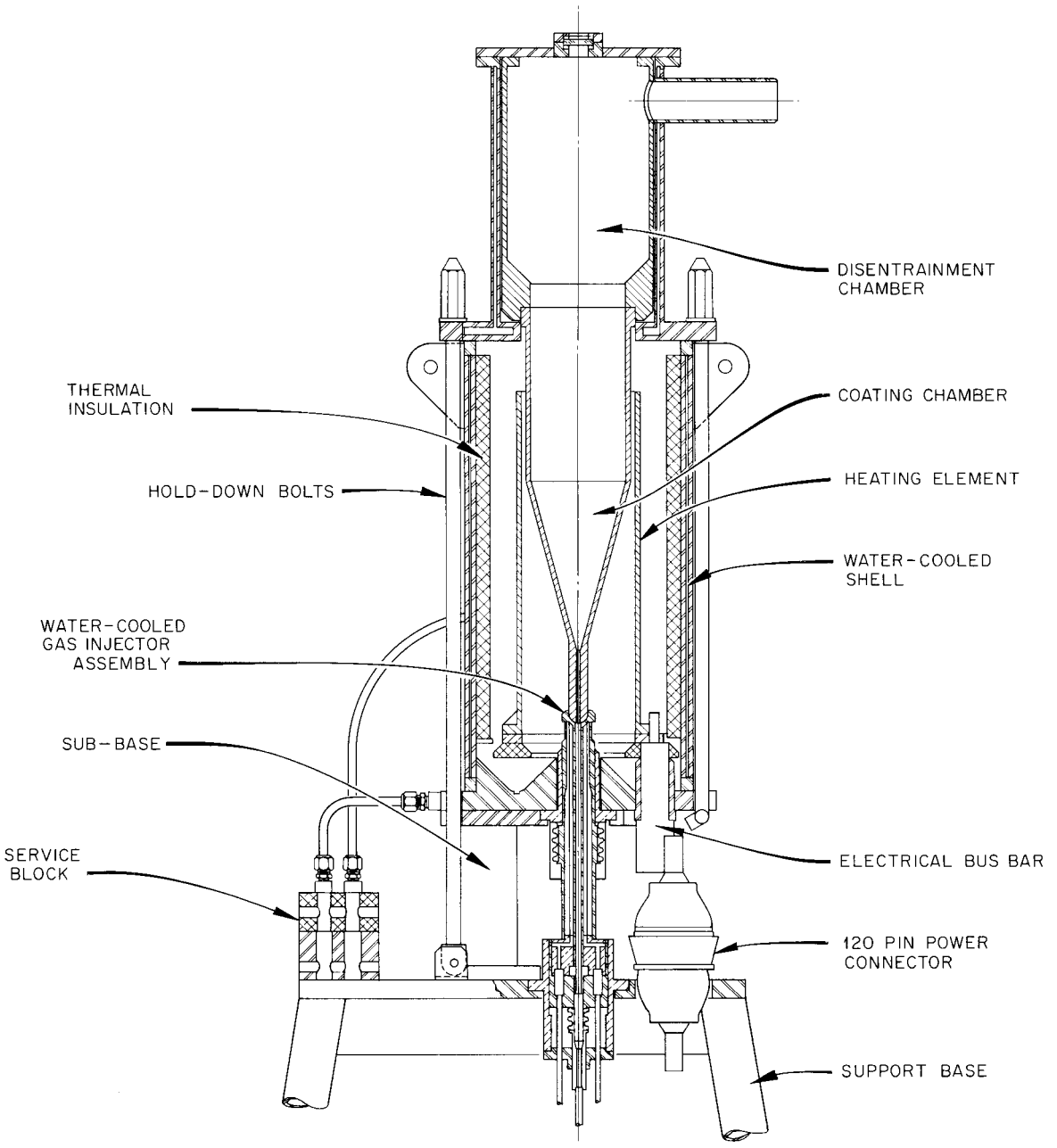

Fig. 4.4. Arrangement of Prototype Remote Fluidized Bed Coater.

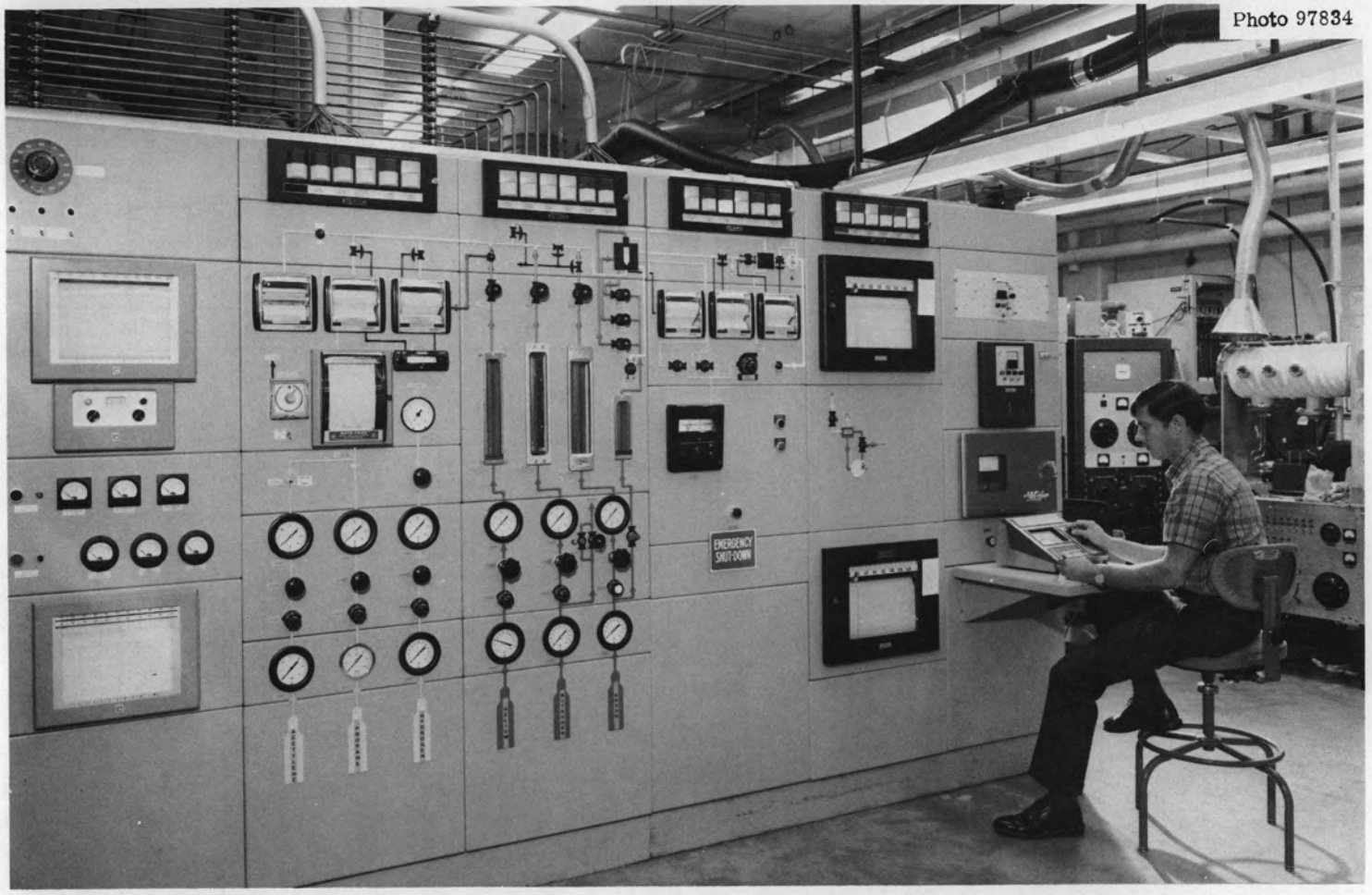

Fig. 4.5. Control Panel for Prototype Remote Coater.

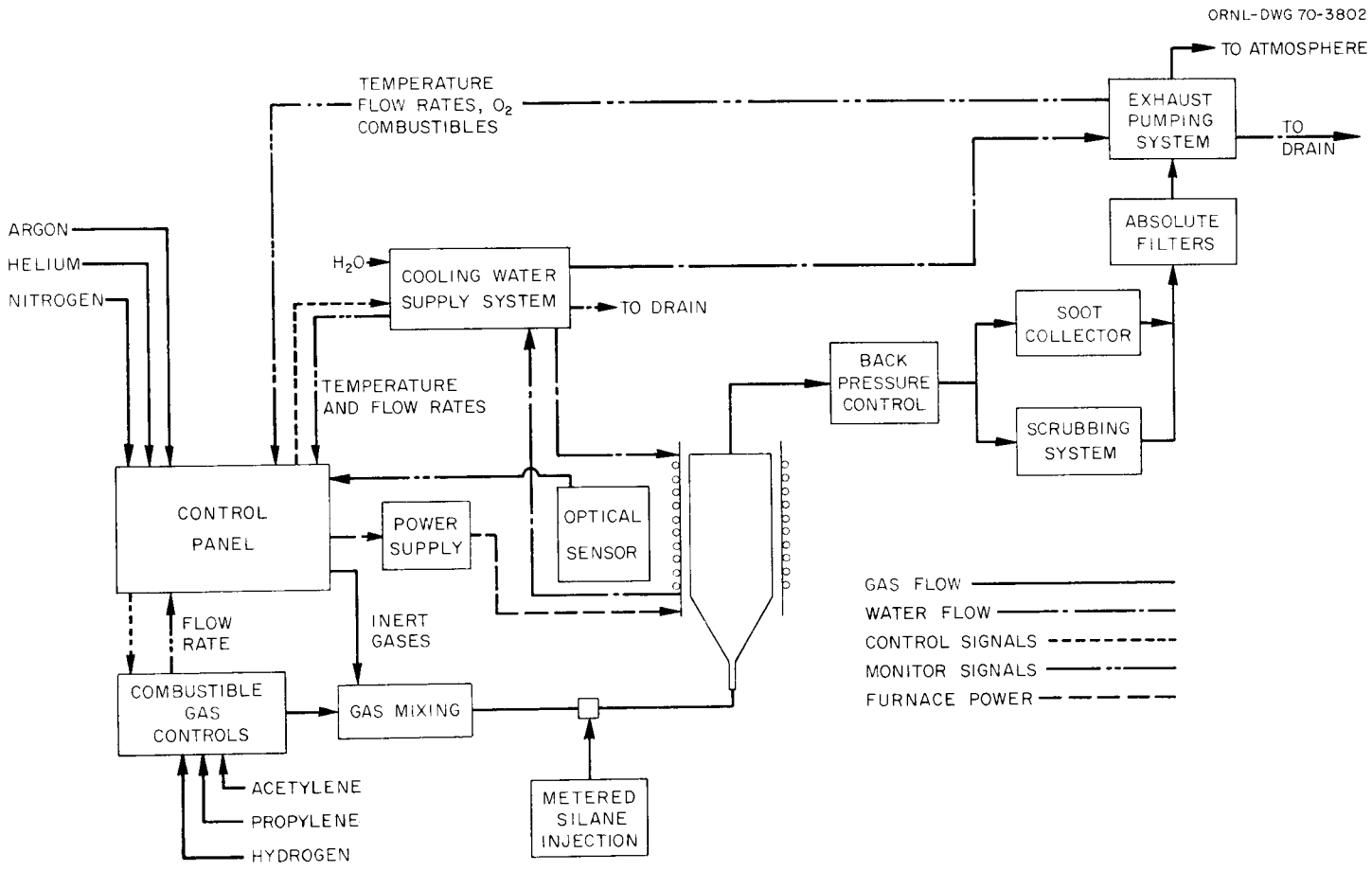

Fig. 4.6. Block Diagram of Prototype Coating System.

The reaction of the silane in hydrogen produces hydrogen chloride, which must be removed from the off-gas. We will do this with an ejector-venturi scrubber using a mild caustic solution. The off-gas from the scrubber will be separated from residual liquid by passage through a centrifugal-action purifier. The gas is then passed through absolute filters and a pumping system into the atmosphere. Preliminary tests show that the gas-liquid separation is sufficient to prevent plugging of the filters.

Coating Recycle Test Element Particles

We are coating sol-gel oxide particles for use in Recycle Test Elements (RTE's) that will be irradiated in the Peach Bottom Reactor. These elements, of the reference recycle design, are intended to evaluate the behavior of fuel prepared by TURF processes and prototype equipment and to provide irradiated fuel for reprocessing studies. Further details of the irradiation experiments are presented in Chapter 5.

The particles being coated and their purpose are listed in Table 4.1. Although the $(Th\text{–}20\%\ U)O_2$ is the reference particle, full burnup with this composition will not be achieved. Hence, the $(Th\text{–}33\%\ U)O_2$ particles, which will simulate full HTGR burnup after the three-year irradiation in Peach Bottom, are being produced. Both kinds of mixed oxide particles

Table 4.1. Particles Being Prepared for Recycle Test Elements

Kernel	Diameter of Kernel (μm)	Use
$(Th\text{–}20\%\ U)O_2$	350 ± 100	Reference recycle particle
$(Th\text{–}33\%\ U)O_2$	350 ± 100	Full burnup particle
UO_2	100 ± 30	Alternate recycle particle
ThO_2	400 ± 100	Alternate fertile particle

will be coated in the prototype remote coating furnace described above. The ThO_2 particles will also be coated in the prototype coater, while the UO_2 particles will be coated in a 1.5-in. laboratory coater. The coatings being applied are detailed in Table 4.2.

Table 4.2. Recycle Test Element Particle Coating Specifications

Kernel	Inner Layer[a] Thickness (μm)	Outer Layer[b] Thickness (μm)
$(Th,U)O_2$	80 ± 20	120 ± 20
UO_2	50 ± 10	70 ± 10
ThO_2	50 ± 10	70 ± 10

[a]Density 1.2 ± 0.2 g/cm^3.

[b]Density 1.85 ± 0.05 g/cm^3; anisotropy should not exceed 1.09.

The inner layer will be applied by the decomposition at 1100°C of acetylene diluted with helium. The outer layer will be applied by the decomposition of propylene at about 1400°C. Argon will be used to fluidize the bed of particles before the hydrocarbon gas is injected.

Particle Inspection

F. J. Furman W. H. Pechin R. A. Bowman[9]

Proper process control and quality assurance for the product require inspection of the bare and coated fuel particles at several points during the process. The process control will be based as much as possible on rapid automatic equipment such as the particle size analyzer described below. The quality of the fuel, however, depends to a large extent on the physical characteristics of the various pyrolytic carbon coatings. The coating characteristics of interest are anisotropy, density, and thickness.

[9]Present address: 1410 SW 8th Street, Pompano Beach, Florida 33061.

Anisotropy

The degree of preferred orientation of the crystal structure of the carbon in the high-density outer coating has a great effect on the strength of this coating and thus on the useful life of the fuel particle. Currently the only quantitative measurement of the coating anisotropy is a lengthy and difficult x-ray diffraction analysis; we normally judge the anisotropy of the coating from its reaction to plane polarized light in the metallographic sample. Past experience with coating runs for which the x-ray diffraction analysis was carried out indicates that the absence of a "Maltese Cross" formation when the coatings are viewed under plane polarized light is indicative of a Bacon Anisotropy Factor less than 1.1.

Coating Density

We routinely determine the densities of the buffer coating and the kernel by a calculation from the particle density as determined by mercury displacement and the carbon weight by combustion. The high-density coating can be determined similarly if the buffer coating is not infiltrated during the application of the high-density coating.

An alternate method for determining the high density is to remove some of the coating from the particle and place it in a density gradient column. Figure 4.7 illustrates the difference between density determined in the column and that calculated from mercury displacement. The higher values from the gradient density column are attributed to the fact that the fluids in the column wet the carbon and penetrate any open porosity. Apparently the difference is negligible above approximately 1.90 to 1.92 g/cm^3.

We have been characterizing the pyrolytic carbon with the scanning electron microscope. Figure 4.8 illustrates the surface morphology of the three different types of coating. The only conclusions to be drawn so far are that the denser carbon has a coarser structure, and a rather striking transition to a well defined crystallite structure occurs between 1.85 and 1.95 g/cm^3.

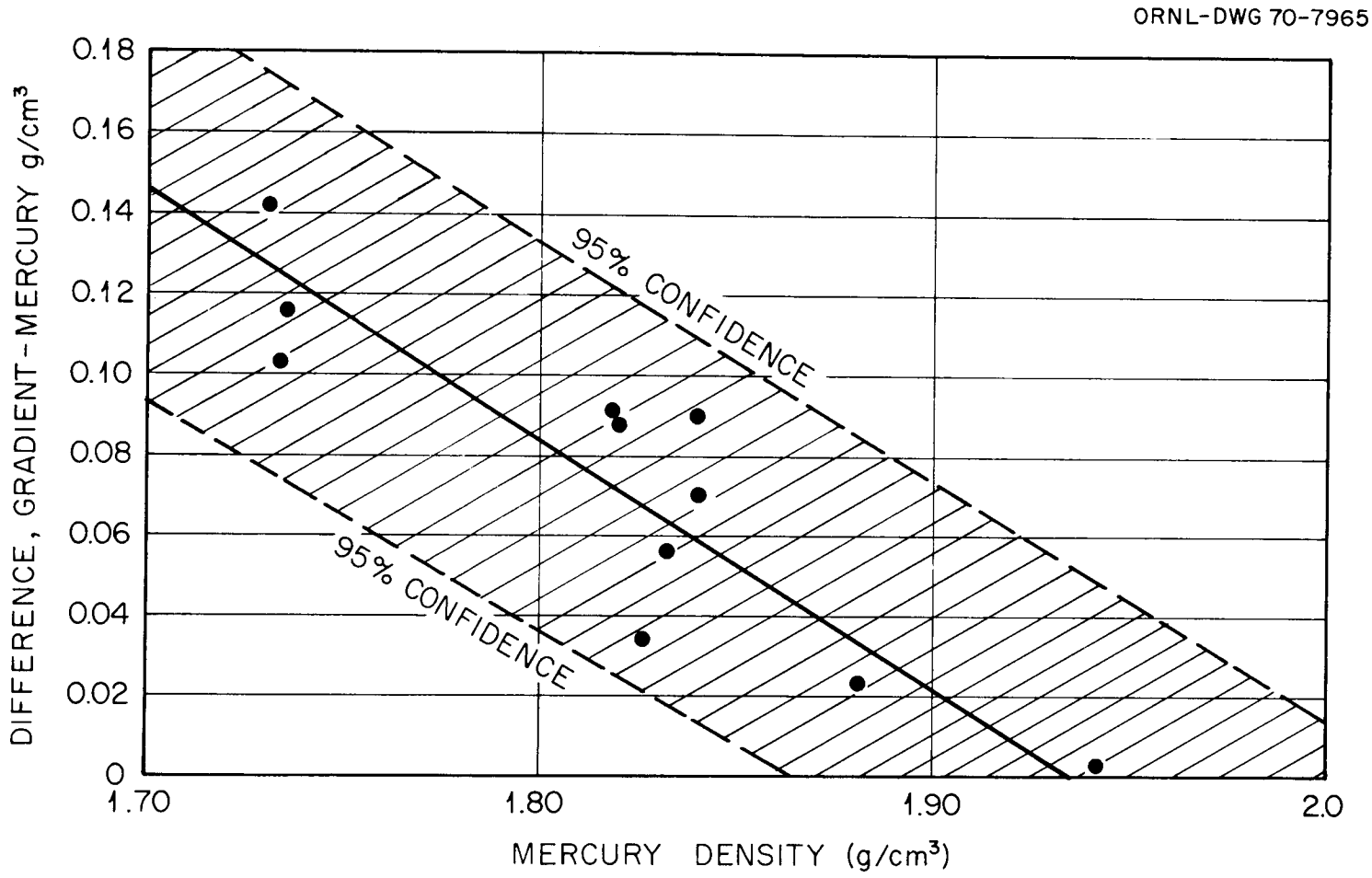

Fig. 4.7. Comparison of Density from Density Gradient Column with that from Mercury Displacement.

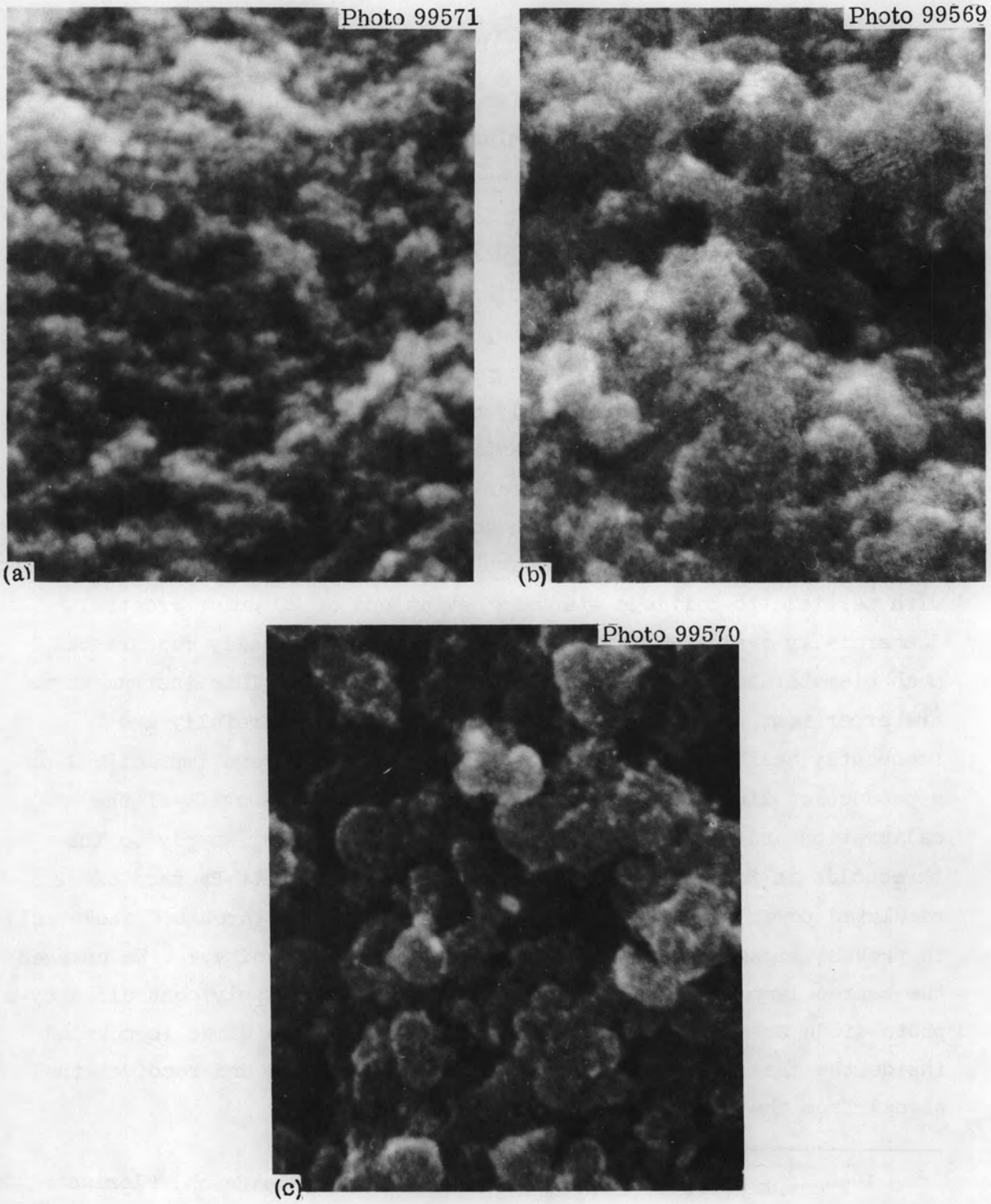

Fig. 4.8. Surface Structure of Pyrolytic Carbon Coatings. 10,000×. (a) Deposited from acetylene, 1.2 g/cm^3. (b) Deposited from propylene, 1.85 g/cm^3. (c) Deposited from propylene, 1.95 g/cm^3.

Size Analysis and Counting (F. J. Furman, R. A. Bowman[10])

To control the particle coating process in an HTGR fuel fabrication facility such as the Thorium-Uranium Recycle Facility (TURF), the size of the particles must be quickly and accurately determined both before and after coating. A HIAC particle size analyzer[11] was obtained to fulfill this need. The instrument functions by measuring the amount of light blocked by the passage of single particles between a light source and a photodetector. The current pulses of the photodetector are counted by a pulse height analyzer. With proper calibration of the threshold voltages of the pulse height analyzer, the size distribution of particles in relatively large samples of particles can be determined. Further details of the instrument have been reported.[12]

We expect to measure with an accuracy of 1% the mean size of batches of particles with diameters in the range of 250 to 850 μm and with particle-to-particle standard deviations of 20 μm or greater. Commercially available particle size analyzers typically measure the mean diameter to within 2 to 5% of the true value. This instrument we are experimenting with will give 1% accuracy when carefully and frequently calibrated. Since frequent calibrations are impractical on a production line, we have attempted to minimize the drift of the calibration and base voltages. We replaced the power supply to the thresholds in the pulse height analyzer with a Hewlett-Packard 6205B regulated power supply, connected to the thresholds through a choke coil to prevent signal pulses from affecting the supply voltage. We changed the source lamp power supply to a regulated power supply controlled by a photo diode observing the lamp intensity. The photo diode is mounted inside the chassis in a region of stable temperature and receives the signal from the lamp by fiber optics.

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[10]Present address: 1410 SW 8th Street, Pompano Beach, Florida 33061.

[11]High Accuracy Products Corporation, 141 Spring Street, Claremont, Calif. 91712.

[12]W. H. Pechin, S. E. Bolt, and F. J. Furman, Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 79–83.

Initial tests indicate significant improvement in stability, particularly with respect to the minute-to-minute fluctuations that have been observed in the past. Further tests will determine if the feedback loop from the lamp has sufficient gain to prevent long-term fluctuations and determine the absolute accuracy of the instrument over the range of particle sizes we wish to measure.

Blending and Bonding Fuel Particles

J M Robbins F. J. Furman

The fabrication of fuel particles into fuel sticks has received considerable attention during this report period. Most of the work on these problems is developmental and is described in Chapter 5 under "Development of Bonded and Blended Beds of Coated Particles for HTGR Fuel Elements." An intimate part of the program has been irradiation tests of simulated fuel sticks, also described in that chapter. A large quantity of fuel is being prepared for irradiation in the Peach Bottom Power Reactor. The main purpose of these Recycle Test Element (RTE) experiments is to provide kilogram quantities of irradiated material for experiments in head-end reprocessing of HTGR fuels.

Blending fissile and fertile particles in the fuel stick process requires accurate control of particle feed rate. We describe below a prototype filler-blender that was designed and is being fabricated to achieve this objective.

Fuel Sticks for Recycle Test Elements (J M Robbins)

Oak Ridge National Laboratory was asked to supply a portion of the RTE's to be operated in the Peach Bottom Reactor starting in July 1970. Our portions are being fabricated by bonding beds of mixed coated particles with 30 to 40 wt % Poco grade AXM graphite flour in 15V pitch. Particle beds are blended by coincident feeding of weighed charges. The requirement of RTE's from ORNL is shown in Table 4.3. All uranium-bearing particles are 93% enriched in ^{235}U.

Table 4.3. Fuel Stick Fabrication Requirements for Recycle Test Elements

Type Particles	Number of 2.14-in.-long Sticks		
	1st Group	2nd Group	Total
$(Th-20\%\ U)O_2$	72	96	168
$(Th-33\%\ U)O_2 + ThO_2$	72	96	168
$(Th-33\%\ U)O_2 + ThC_2$	168	144	312
$UO_2 + ThO_2$	120	96	216
TOTAL	432	432	864

Blending Equipment Development (F. J. Furman)

To make acceptable fuel sticks, the recycle particles must be accurately blended with fertile (ThC_2) particles. Since the particles differ in size and density, this step is extremely difficult. To facilitate this operation, we have designed and are now fabricating a loader-blender, a device for concurrently blending two or more types of particles while loading a fuel stick mold. The particles pour out of hoppers with orifices adjusted by stepping motors, which permit the particle flow rate to be accurately set remotely. We will use the loader-blender for fabricating the fuel sticks required by head-end reprocessing studies and irradiation tests.

5. IRRADIATION OF HTGR FUELS

J. H. Coobs J. L. Scott T. N. Washburn

Coated particle fuels for use in high-temperature gas-cooled reactors have been irradiation tested for a number of years. As part of a cooperative effort with the Advanced Gas-Cooled Reactor Program at ORNL, we have been testing the performance of coated sol-gel-derived UO_2 and $(Th,U)O_2$ microspheres. During the past year we began tests in support of the HTGR Fuel Recycle Program in cooperation with Gulf General Atomic. In most tests the sol-gel-derived fuel performance is compared directly with that of similar coated particles having sintered oxide or melted carbide fuel kernels. All tests are compared with performance predicted by our mathematical model of coated particle behavior.[1]

HTGR Fuel Recycle Irradiation Program

T. N. Washburn R. B. Fitts 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 total program includes capsule irradiation tests in a thermal test reactor, pilot-scale irradiations in the Peach Bottom Reactor, and a series of tests, eventually including remotely fabricated recycle test elements, in the Fort St. Vrain Reactor. The first two stages of this program are currently being implemented. They are (1) accelerated burnup-rate capsule irradiations and (2) eight test fuel elements to be irradiated in the Peach Bottom Reactor.

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[1] J. W. Prados and T. G. Godfrey, STRETCH, A Computer Program for Predicting Coated-Particle Irradiation Behavior: Modification IV, December 1967, ORNL-TM-2127 (April 1968).

Capsule Tests (A. R. Olsen, R. B. Fitts)

The accelerated-burnup capsule tests are designed to test the performance of coated particles processed in Thorium-Uranium Recycle Facility prototype equipment and provide small samples for chemical reprocessing studies in advance of the Peach Bottom Recycle Test Elements. To achieve these objectives, a capsule was designed for irradiation in the Advanced Test Reactor (ATR) starting January 1970. However, the test positions were not available, so alternate testing locations were examined. The use of an Oak Ridge Research Reactor partial fuel element[2] was examined and found to have insufficient experimental space without significant modification.

We are proceeding with the final design of a capsule to be irradiated in an X-basket position in the Engineering Test Reactor. The conceptual design is shown in Fig. 5.1. The basic design is similar to previous X-basket capsules[3] in that each capsule will contain two graphite sleeves. The sleeves are machined to vary the thickness of the helium gap between the sleeve and the stainless steel containment tube to provide the desired fuel operating temperatures of 750, 950, 1050, and 1300°C.

Detailed physics calculations for a 0.5-in.-diam fuel bed loaded with equal numbers of $(Th–20\%\ U)O_2$ and ThO_2 coated particles were completed. These calculations together with the currently reported peak thermal flux of 5.67×10^{14} neutrons cm^{-2} sec^{-1} for a J8 position in the ETR yield a calculated peak linear heat rate of 32 kW/ft. This heat generation rate is too high since the surface-to-center temperature differential, even for a bonded bed, would be greater than 900°C. Reducing the uranium content of the fuel bed by adding more coated ThO_2 particles will lower the heat generation rate, but it will also eliminate the possibility of doing duplicate reprocessing tests.

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[2]H. A. O'Brien, Jr., Fast and Thermal Neutron Flux Measurements in the ORR and LITR, ORNL-TM-1163 (January 1966).

[3]A. R. Olsen, J. H. Coobs, J. W. Prados, and E. L. Long, Jr., Status and Progress Report for Thorium Fuel Cycle Development 1967–1968, ORNL-4429, pp. 95–108.

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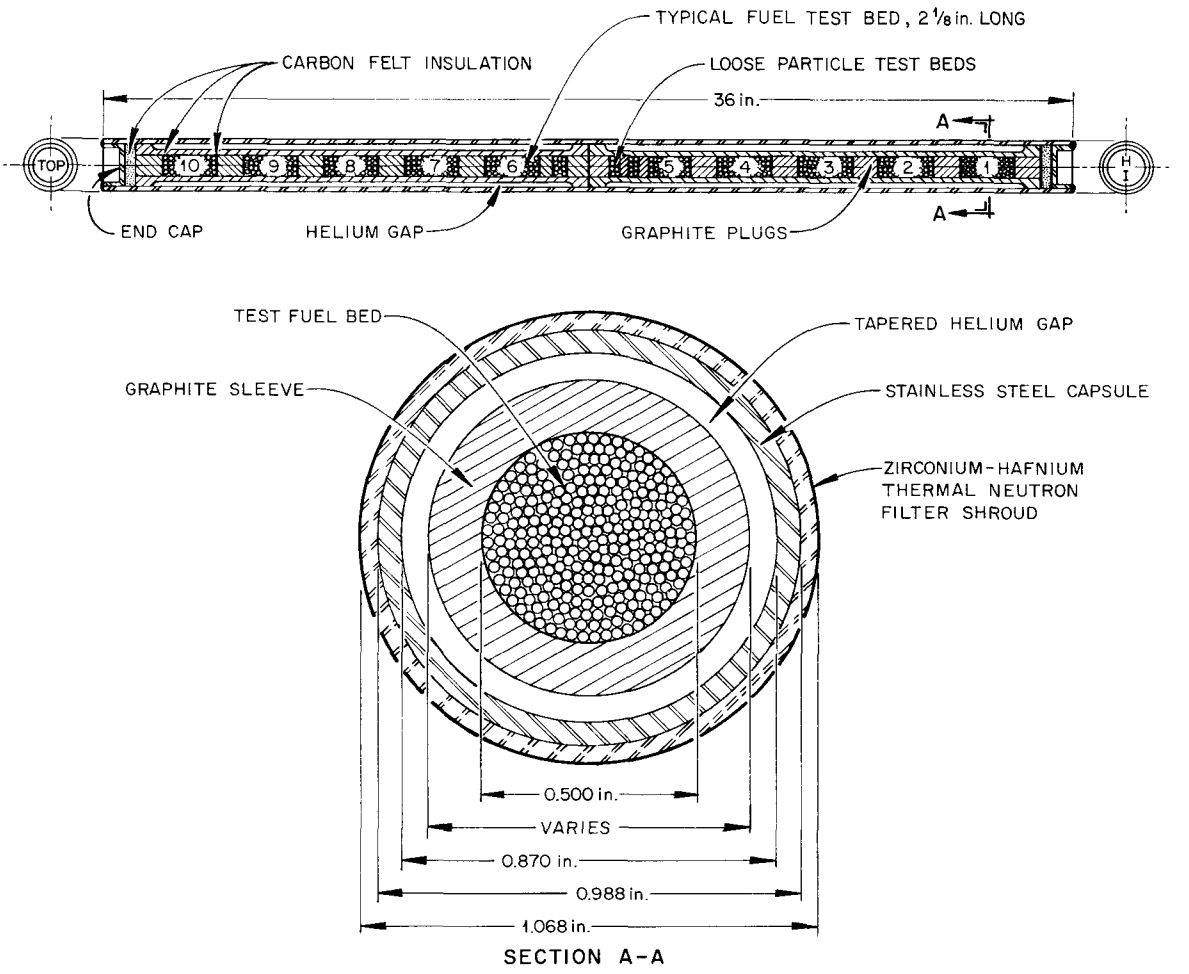

Fig. 5.1. Schematic of Proposed HTGR Recycle Irradiation Capsule.

Therefore, we are currently investigating the possibility of adding a thermal neutron filter to the outside of the capsule. This will lower the thermal flux in the fuel without seriously disturbing the fast flux level of approximately 3.4×10^{14} neutrons cm^{-2} sec^{-1} (> 0.18 MeV). We have contacted the Bettis Atomic Power Laboratory (BAPL) on their experience with zirconium-hafnium filters.[4] We have not yet done the physics calculations for this design modification, but the BAPL data suggest that reductions in fission rates up to half are

[4]R. M. Lieberman, "A System for Calculation of Fission Power in Irradiation Tests," pp. 473–490 in National Symposium on Developments in Irradiation Testing Technology, CONF-690910 (1970).

possible. This will permit utilization of the ETR capsules and still allow us to obtain fast fluence (> 0.18 MeV) exposures on the coated particles between 6 and 8 × 10^{21} neutrons/cm^2 in one year. We plan to start irradiation of the first two capsules in June or July 1970. The loadings as currently planned are given in Table 5.1. These fuels are from the same production batches as those used in the Recycle Test Elements.

Table 5.1. Fuel Loadings for HTGR Irradiation Test Capsules

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

[a]As shown in Fig. 5.1.

[b]These are combinations selected from those used in the RTE's and are described later in Table 5.3.

[c]Containers of loose particles for extensive metallographic examination and performance analysis.

[d]Blended beds (all others are bonded beds).

Recycle Test Elements (R. B. Fitts)

Eight test fuel elements, known as 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 (electrical) HTGR's. The test will serve three purposes:

1. provide irradiated fuel in gram quantities for head-end reprocessing development,

2. provide irradiated fuel blocks to test engineering-scale recycle process equipment,
3. provide irradiation proof tests of recycle fuel particles prepared with TURF processes and prototype equipment.

In cooperation with Gulf General Atomic, a final plan has been prepared for the loading and utilization of the RTE's. This plan is summarized and explained below.

Figure 5.2 is a cross-section diagram of an RTE body; six 15-in.-long bodies are stacked vertically to form one element. The RTE's are to be discharged in pairs. Of these pairs, one element will contain fuel bodies each filled with a single particle mixture, while the other will contain bodies each filled with four different particle mixtures. The multiple-mixture bodies will be quartered to separate these mixtures after irradiation. The single-mixture bodies will be used primarily for the larger scale reprocessing studies, while the multiple-mixture elements will provide material for hot cell reprocessing studies and fuel performance characterization.

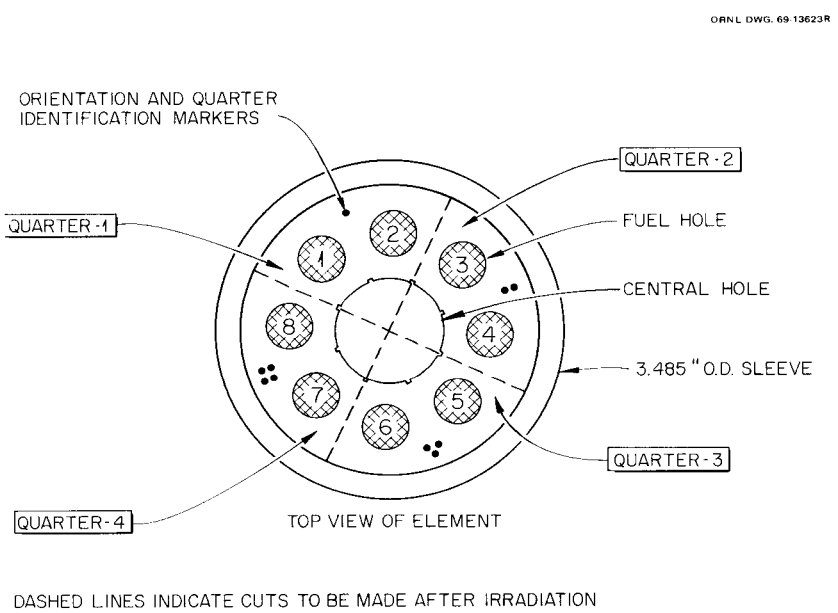

Fig. 5.2. Recycle Test Element.

Fuel Mixtures. — The fuel particles of interest to the HTGR Recycle Program are listed in Table 5.2 along with the possible uses of each. Of the various particle combinations that can be formed with these particles, the most promising are listed in Table 5.3 along with the HTGR use for each.

Table 5.2. Particles of Interest to the HTGR Recycle Program

Particle	Coating[a]	Possible Uses
$(Th-20\%\ U)O_2$	BISO	Reference recycle fissile particle
$(Th-33\%\ U)O_2$	BISO	Stand-in to provide faster burnup
UO_2 (buffer diluted)	BISO	Alternate recycle fissile particle Alternate makeup fissile particle
ThO_2	BISO	Alternate recycle fertile particle Alternate makeup fertile particle
UC_2	TRISO	Reference makeup fissile particle
UC_2	BISO	Alternate makeup fissile particle
ThC_2	BISO	Reference recycle fertile particle Reference makeup fertile particle

[a]The details of the BISO (two-layer pyrolytic carbon) and TRISO (three-layer pyrolytic carbon plus a SiC layer) coatings are given in GGA Specifications RF-1-1, 1002-4040-2, and 1002-4040-3.

Fuel Element Loading. — Each element is composed of six 15-in.-long blocks, and each block contains eight 0.5-in.-diam holes to be loaded with fuel. These holes are identified in Fig. 5.2. The reference design calls for the coated particle fuel to be bonded into fuel sticks,[5] and most of the fuel is tested in this form. Some loose beds of particles are included for comparison. Table 5.4 shows the particle loading for each RTE, identifying the stick and loose (or blended) beds. The fuel in the required forms, loose coated particles or sticks (bonded beds), is being fabricated. The finished fuel will be assembled into the test element blocks by Gulf General Atomic.

[5]Chapter 4 reports bonded stick development.

Table 5.3. Particle Combinations of Interest

Combination	Fissile	Fertile	HTGR Application
a	$(Th–20\%\ U)O_2$	ThO_2[a]	Reference recycle
b	UO_2	ThC_2	Advanced recycle or advanced makeup
c	$(Th–33\%\ U)O_2$	ThO_2	Alternate recycle with accelerated burnup
d	$(Th–33\%\ U)O_2$	ThC_2	Reference recycle with accelerated burnup
e	UC_2	ThC_2	Alternate makeup
f	UC_2[b]	ThC_2	Reference makeup
g	UO_2	ThO_2	Alternate makeup Alternate recycle
h	UC_2	ThO_2	Alternate makeup
i	UC_2[b]	ThC_2[b]	Fort St. Vrain fuel

[a]The RTE's containing $(Th–20\%\ U)O_2$ will actually contain no ThO_2 particles so as to maximize the uranium content of the particle bed.

[b]TRISO coating; all others are BISO.

These test elements are to be discharged in groups of two. The fact that we can quarter the elements after irradiation permits us to define eight pairs of holes at each axial location in each pair of elements. Thus, we can test the most likely particle combinations under all the available conditions of temperature, time, and burnup. Positions are also available for the tests of loose particle beds and of 15-in. blocks containing only one combination of particles.

The overall loading pattern of the pairs of elements is illustrated by the first discharge pair in Table 5.4. The odd-numbered elements (1, 3, 5, 7) contain blocks that will be quartered, and the even-numbered elements (2, 4, 6, 8) contain blocks with only one particle mixture each. Thus, the odd-numbered elements will provide tests of four different mixtures of particles at each axial position and furnish quarter blocks for reprocessing studies. The even-numbered elements will provide single-fuel blocks for larger scale reprocessing studies and help in evaluating the performance of prototypic single-fuel blocks. These

Table 5.4. RTE Loading Combinations[a]

Position of Fuel Body in Element	Center-Line Temperature (°F)	Discharge of Various RTE's							
		First		Second		Final			
		1	2	3	4	5	6	7	8
6 (Top of reactor)	2050–1950	*bdei*	*f*	*bdei*	*e*[b]	*bdei*	*g*	*acfg*	*f*
5	2250–2050	*bdeh*	*a*[b]	*bdeh*	*d*	*bdeh*	*f*	*acfg*	*i*
4 (Max flux)	2250–2300	*acfg*	*e*	*acfg*	*f*	*acfg*	*f*	*bdeh*	*d*
3 (Max flux)	2050–2250	*acfg*	*f*[b]	*acfg*	*a*[b]	*acfg*	*d*	*bdhi*	*e*
2	1650–2050	*acfg*	*d*	*acfg*	*f*[b]	*acfg*	*f*	*bdhi*	*i*
1 (Bottom of reactor)	1050–1650	*acfg*	*e*[b]	*acfg*	*e*	*acfg*	*e*	*bdhi*	*f*[b]

[a]Loadings are indicated by letters, as defined in Table 5.3. Four letters indicate the different loadings in elements to be quartered after irradiation. All beds are bonded except where noted otherwise.

[b]Blended beds.

even-numbered elements will also furnish backup samples if more material is needed than is available in the quarter blocks to study the particles or reprocessing techniques.

The first three odd-numbered blocks are loaded with emphasis on particle combinations *a*, *c*, *f*, and *g* (see Table 5.3). These combinations contain all of the particles of interest except the alternate makeup fissile particle (BISO-coated UC_2), are used as the key combinations, and are placed in the lower four positions in the odd-numbered elements. These positions, as can be seen in Table 5.4, cover all of the available temperatures, and they also cover the full range of available fast and thermal flux and burnup.

The single-fuel blocks emphasize the makeup fuels. The recycle of these fuels requires separation of the particles containing makeup ^{235}U from those containing bred ^{233}U and therefore requires more extensive development of the head-end recycling process procedures.

This arrangement of the eight RTE's will meet all three of the test objectives quite well. The head-end crushing and separation development studies can be adequately conducted on quarter blocks, and the dissolution studies require only 1/20 of the material in a quarter block. Larger quantities of fuel will be available from the even-numbered elements, as needed for engineering-scale work. The prime candidate fuels will be tested under all available conditions so that, in the event of unexpected particle failure, the failure regime and cause may be analyzed. In addition, most of the candidate particle mixtures will be tested to full test burnup and fast fluence (4×10^{21} neutrons/cm^2) in RTE's 5 and 7. This arrangement allows early characterization of fuel and development studies using only the odd-numbered elements, permitting storage of the even-numbered elements until larger quantities of fuel are required.

Results of Tests of HTGR Fuels

J. H. Coobs J. L. Scott

Development of Bonded and Blended Beds of Coated Particles for HTGR Fuel Elements (J. H. Coobs, D. M. Hewette II, J M Robbins)

The results of irradiation experiments show that the stability of particle bonding in HTGR fuels needs to be improved.[6] The objective of this program is to develop a fuel body that will withstand irradiation to the exposure required for Fort St. Vrain and larger HTGR's; that is, 20% burnup at 600 to 1250°C and fast-neutron (> 0.18 MeV) fluences up to 8×10^{21} neutrons/cm^2. Two possible ways of improving the stability are the careful selection of bonding materials and the addition of large amounts of graphitic or other filler material to the matrix or voids among the particles.

In keeping with these objectives, we developed techniques for fabricating bonded beds of coated particles with thermoplastic binders that

[6] J. H. Coobs, J. M. Robbins, J. A. Conlin, C. L. Segaser, R. L. Hamner, R. L. Senn, D. M. Hewette II, and S. C. Weaver, GCR Semiann. Progr. Rept. Sept. 30, 1968, ORNL-4353, pp. 28–54.

yield graphitizable coke. These binders along with Poco graphite[7] as the filler should yield a desirable matrix. Poco grade AXM graphite flour was chosen as the filler because recent irradiation tests[8] show the relative stability of this material. Also, we found that additional filler material could be added as Thermax[9] because of its size distribution and wettability.

The preparation and loading of bonded-bed specimens for HFIR target experiment HT-4 were completed. The specimens contain pyrolytic-carbon-coated carbon microspheres and were injection bonded with furfuryl alcohol or 15V pitch. Filler materials in the binders consist of 40 wt % Poco graphite or a mixture of 29 wt % Poco graphite and 29 wt % Thermax carbon black. The specimens used in the experiment and their preirradiation heat treatment are listed in Table 5.5. The locations and operating conditions of the specimens and magazines are given in Table 5.6.

After irradiation and disassembly, all bonded beds were intact and could be handled in-cell. The typical postirradiation appearance is illustrated in Fig. 5.3 by the group of specimens that were irradiated at 800°C to a fluence as great as 6×10^{21} neutrons/cm^2. The average dimensional changes that occurred at the low and high irradiation temperatures were −1.4 and −2.6%, respectively. At the low irradiation temperature the shrinkage increased with increasing fluence; at the high irradiation temperature the shrinkage seemed to decrease with increasing fluence. The shrinkage did not seem to be influenced at either temperature by the composition of the binder phase or the preirradiation heat treatment.

Blended Beds of Loose Coated Particles (J. H. Coobs, J M Robbins, J. L. Scott)

The poor results from early irradiation tests of bonded beds to full design HTGR fast neutron (> 0.18 MeV) fluences (about 8×10^{21} neutrons/cm^2) led to renewed interest in the use of loose beds of

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[7]An isotropic graphite flour from Poco Graphite, Inc.

[8]C. R. Kennedy, Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1969, ORNL-4470, pp. 193–195.

[9]A spherical carbon black from R. T. Vanderbilt Co.

Table 5.5. Bonded Particle Specimens for HT-4 Experiment

Specimen	Materials		Heat Treatment[a] Temperature (°C)	Magazine
	Binder	Filler		
JF78-1	Varcum 8251[b]	AXM + Thermax[c]	2100	CP-15
-2	Varcum 8251[b]	AXM + Thermax[c]	2100	-15
-4	Varcum 8251[b]	AXM + Thermax[c]	2100	-16
-5	Varcum 8251[b]	AXM + Thermax[c]	2100	-16
-8	Varcum 8251[b]	AXM + Thermax[c]	1500	-13
-9	Varcum 8251[b]	AXM + Thermax[c]	1500	-14
-10	Varcum 8251[b]	AXM + Thermax[c]	1500	-15
-11	Varcum 8251[b]	AXM + Thermax[c]	1500	-16
-21	15V Pitch[d]	AXM + Thermax[c]	1500	-13
-22	15V Pitch[d]	AXM + Thermax[c]	1500	-13
-23	15V Pitch[d]	AXM + Thermax[c]	1500	-14
-24	15V Pitch[d]	AXM + Thermax[c]	1500	-14
-14	15V Pitch[d]	AXM + Thermax[c]	2100	-15
-16	15V Pitch[d]	AXM + Thermax[c]	2100	-15
-19	15V Pitch[d]	AXM + Thermax[c]	2100	-16
-20	15V Pitch[d]	AXM + Thermax[c]	2100	-16
-25	15V Pitch[d]	40 wt % Poco AXM	2100	-13
-27	15V Pitch[d]	40 wt % Poco AXM	2100	-13
-28	15V Pitch[d]	40 wt % Poco AXM	2100	-14
-29	15V Pitch[d]	40 wt % Poco AXM	2100	-14

[a]Heated in argon for 30 min.

[b]Prepolymerized furfuryl alcohol from Varcum Chemical Co.

[c]29 wt % Poco AXM graphite flour (< 40 μm) from Poco Carbon Co. plus 29 wt % Thermax (a soft spherical carbon black from R. T. Vanderbilt Co.).

[d]Grade 15V coal tar pitch from Allied Chemical Co.

Table 5.6. Description of HT-4 Irradiation Capsule

Magazine	Types of Specimen	Axial Distance from Horizontal Midplane for Magazine, in.		Design Operating Temperature (°C)	Range of Expected Fluence (> 0.18 MeV)
		Bottom	Top		
					$\times 10^{21}$
CP-13	Bonded bed, matrix, and SiC temperature monitor	−10	−5.5	750	3–6.5
M-2	SiC temperature monitor and loose particle controls	−5	−4	750	6.5–7
CP-14	Bonded bed and matrix	−3.5	−0.125	1050	7–8
CP-15	Bonded bed, matrix, and SiC temperature monitor	+0.125	+4.5	1050	7–8
M-4	SiC temperature monitor and loose particle controls	+5	+6	1050	6.5–7
CP-16	Bonded bed and matrix	+6.5	+10	750	3–6.5

R-50105A

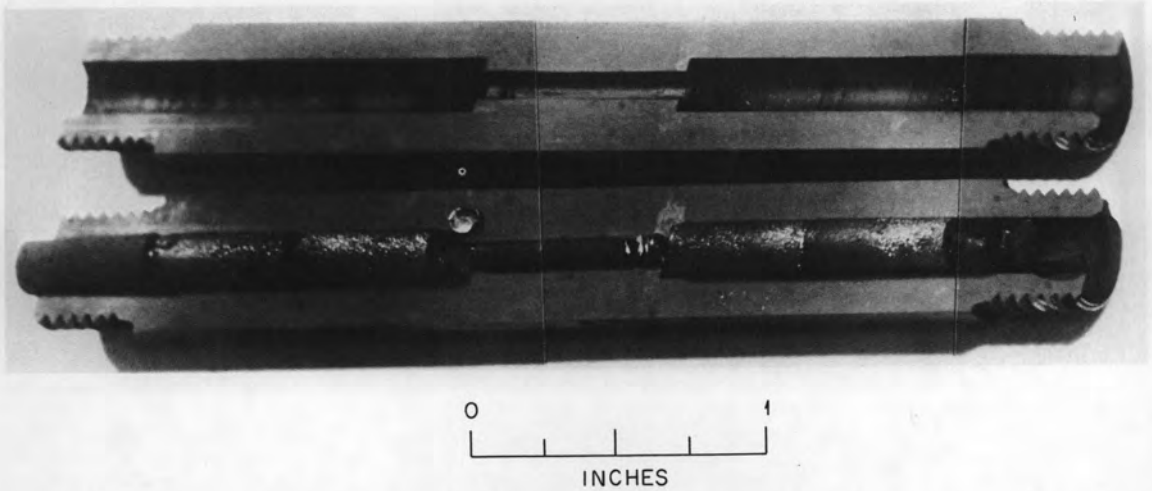

Fig. 5.3. Appearance of Bonded Beds of Coated Particles after Irradiation in Capsule HT-4 to a Fluence of 6×10^{21} neutrons/cm^2 at 800°C.

particles in HTGR fuel elements. Such fuel elements would require that two or more types of particles be blended in each fuel hole and form a stable bed that would not segregate or settle severely during transport and irradiation. We performed several experiments to study the behavior of loose beds of particles in graphite tubes and confirmed that beds will "lock" in place when force is applied from the bottom of the column, provided the length-to-diameter ratio of the column is at least 7. Additional force on the column does not move the particles but is transmitted to the tube wall and may rupture the tube.

This behavior indicated that a critical feature of such loose beds would be their interaction with the needle-coke graphite tube or fuel element during irradiation. In an HTGR environment the graphite will shrink in the axial (extrusion) direction throughout its life and will shrink initially and then expand transversely. This behavior and the net volume change postulated in an element operating at 1020°C are shown in Fig. 5.4. On the other hand, a bed of coated particles will shrink

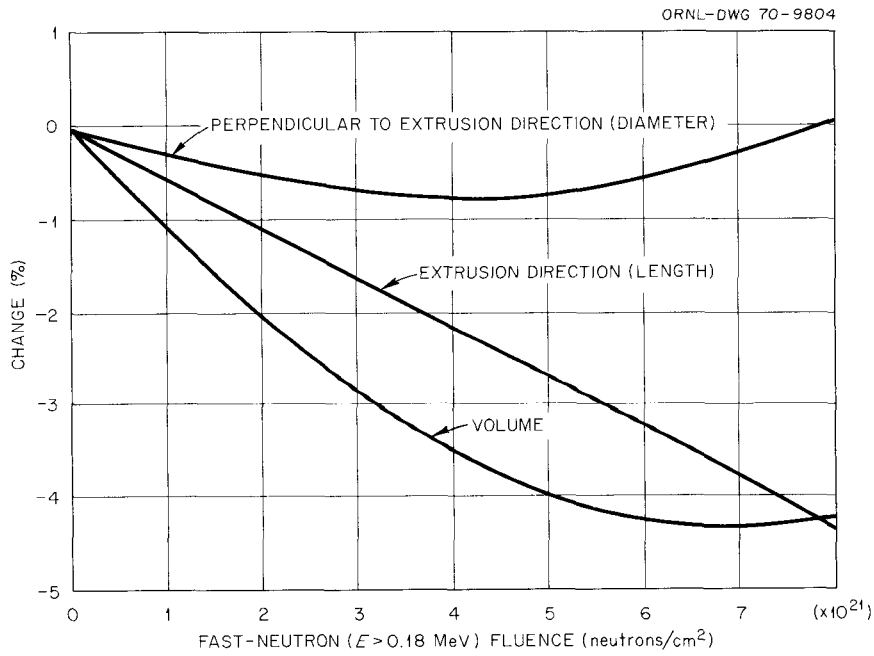

Fig. 5.4. Change in Dimensions and Internal Volume of H-327 Graphite Magazine at 1020°C (Conditions for HT-5 Experiment).

initially, as the outer isotropic coating densifies under irradiation, and will assume a stable volume at about 0.6 times the design fluence. The continuing axial shrinkage of the graphite must then lead to interaction with the bed.

Therefore, we designed an irradiation experiment to test the behavior of loose beds contained in a needle-coke graphite tube. Two loose blended beds with length-to-diameter ratios exceeding 11 were specified. One would consist of about 600-μm-diam particles with high-temperature isotropic carbon outer coatings and about 400-μm-diam particles with low-temperature isotropic (LTI) outer coatings. The second would have LTI outer coatings on both large and small particles. The properties of the coated particles prepared for this experiment are given in Table 5.7. The larger particles have inert kernels because the experiment was designed to be tested in the HFIR target region, in which the flux is too high to permit more than traces of fissile material.

Both loose beds were blended by coincident feeding of weighed charges and were loaded slowly and vibrated to a constant volume. In an attempt to stabilize the beds very small (50 to 75 μm diam) coke or carbon particles were loaded with the coated particles in sufficient

Table 5.7. Properties of Coated Particles Prepared and Used for Irradiation Experiment on Loose Beds

	OR 1062	OR 1078	OR 1083
Kernel	SiC on carbon seed	ThO_2	SiC on carbon seed
Diameter of kernel, μm	400 ± 100	103	400
Fuel	Inert	Th	Inert
Heavy metal content, wt %	0	7.22	0
Thickness of layer, μm			
Inner	54	90.8	56.6
Outer	91	69.2	107.6
Density of layer, g/cm^3			
Inner	0.9	0.9	0.9
Outer	1.75	1.85	1.80
Total particle density, g/cm^3	1.53	1.6	1.5

quantity to add about 0.15 g/cm^3 to the bed density. Both beds were held in place with several pieces of graphite felt that were compressed about 50% during loading.

The two blended beds were irradiated in HFIR target capsule HT-5 for 70 days at 1020°C to a fast-neutron (> 0.18 MeV) fluence of 7.5×10^{21} neutrons/cm^2. Examination by neutron radiography and gamma scanning indicated that both beds shrank more than 18% in length. This shrinkage is illustrated in Fig. 5.5. This was about twice the expected maximum shrinkage that could be accounted for by densification of the coatings (Fig. 5.4), indicating that some other mechanisms are responsible for part of the setting. Further examination is in progress.

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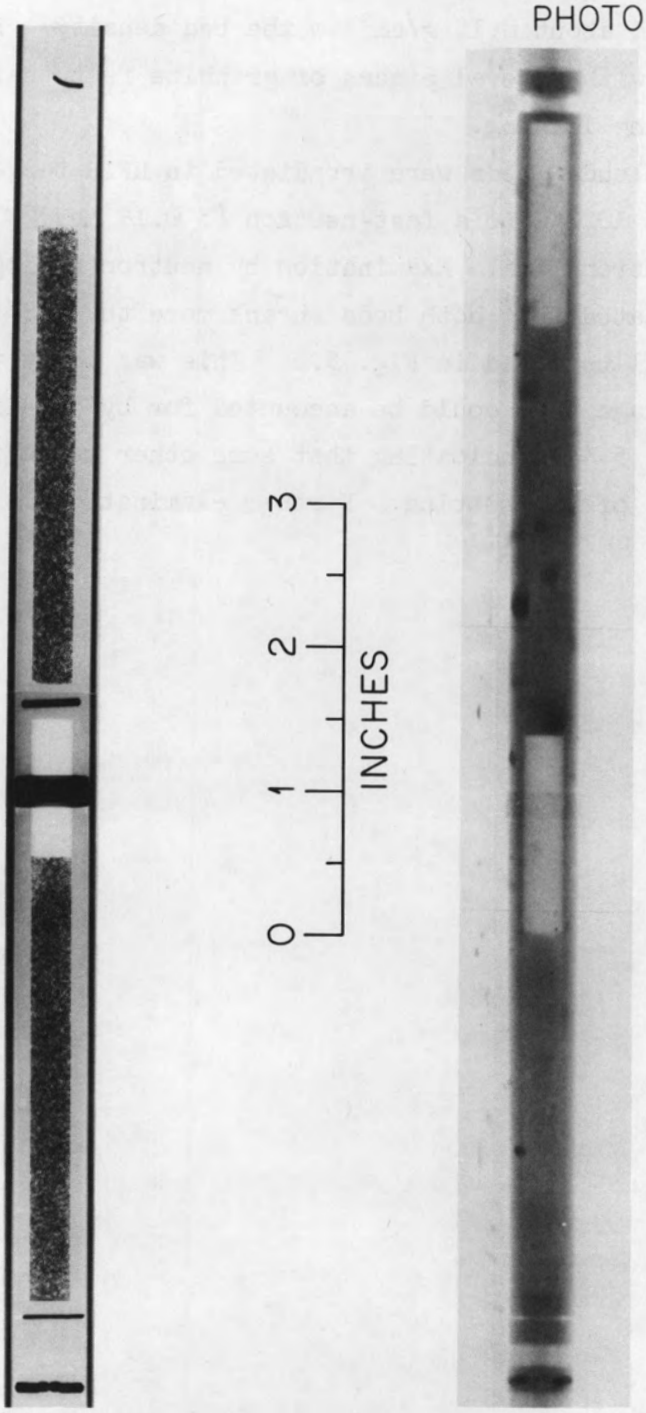

BEFORE IRRADIATION AFTER IRRADIATION

Fig. 5.5. Irradiation Shrinkage of Blended Beds of Loose Coated Particles. The left neutron radiograph shows the unirradiated capsule. The right radiograph shows the decreased length of particle beds after exposure at 1020°C to 7.5×10^{21} neutrons/cm^2.

6. FUNDAMENTAL SOL-GEL STUDIES

W. D. Bond

Drying studies on ThO_2-UO_3 gel spheres showed that the heating rates of fixed beds under steam purge must be both slow and uniform to control the rate of chemical reaction of nitric acid with the alcohol and, thus, the rate of heat liberation by the reaction. A steam purge flow through the bed of spheres enhances the desorption and vaporization of the organic reactants and thus reduces the quantity of organic materials that react with the nitric acid. Washing the gel spheres in ammonia solutions before drying removed the nitric acid and prevented the nitrate-organic reaction, but the washing processes broke about 50% of the spheres.

Steam drying to 200°C does not remove all of the carbon-bearing materials. The spheres still contain about 1% C, which is subsequently removed during calcination by combustion in air. Firing studies showed that the carbonaceous materials and other volatiles (nitrates and water) remaining after drying are removed before the ThO_2-UO_3 gel spheres shrink or densify appreciably; thus, no problems are encountered in attaining the density and chemical specifications on calcined products.

Drying Studies

Further laboratory studies on the drying of ThO_2-UO_3 spheres were required because the gel spheres produced in the 10-day continuous demonstration of the ORNL ThO_2-UO_2 sol-gel process were more sensitive to initiation of deleterious exothermic reactions than had been anticipated from earlier smaller scale work.[1,2] Also, the gel spheres prepared in the demonstration run contained 4.5 atoms thorium per

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[1] Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, pp. 187–90.

[2] C. C. Haws, W. D. Bond, and B. C. Finney, Engineering-Scale Demonstration of the Sol-Gel Process: Preparation of 100 kg of ThO_2-UO_2 Microspheres at a Rate of 10 kg/day, ORNL-4344, in press.

atom uranium, compared with 3 in our earlier developmental work. The spheres of the higher thorium content were considerably more sensitive to drying conditions.

Even when temperature rise rates as low as 25°C/hr were used in the drying of gel spheres (Th/U = 4.25) in a 2-in.-diam fixed bed, exothermic reactions occurred at 190 to 200°C and broke more than half the spheres during the almost instantaneous temperature rise to 250 to 300°C. During drying at 25°C/hr in the 100 to 200°C range, the central bed temperature lagged the heated dryer wall temperature by 10 to 20°C. Introduction of soaking periods between 100 and 200°C prevented the exothermic reaction and avoided breakage of the spheres (Table 6.1). Even though we did not observe any exothermic reaction in these dryings, the nitrate-to-metal ratio is substantially lowered by the process (from an initial value of 0.1 to as low as 0.005), showing that the organic is reacting with nitric acid during drying but at rates that do not liberate excessive amounts of heat. Conductivity measurements on the effluent steam condensate showed that material producing a conducting electrolyte, probably NO_2 or NO, was liberated throughout the drying in the 100 to 200°C range. Steam purge flow rates as low as 0.1 g/min prevented the exothermic reaction. No detectable breakage of spheres occurred when the dryings were conducted under conditions shown in Table 6.1. The 16-hr soaking period at some of the temperatures was used because it was convenient to carry out this stage of the drying overnight.

Washing the spheres in ammonia solution before drying very effectively removed the nitrate and prevented the exothermic reaction during drying. However, the washing caused spalling and cracking of the spheres. The cracking and spalling were independent of ammonia concentration from 0.1 to 15.0 M and of addition of ammonium nitrate to the ammonia before washing. Separation of the cracked spheres with a Roundometer showed that 50 to 60% of the spheres were broken or chipped in the ammonia washing step. For this reason it was given no further consideration as a process step.

Table 6.1. Effect of Soaking Times at Various Temperatures on Steam Drying of ThO_2-UO_3 Gel Spheres

Initial $NO_3^-/(Th + U) = 0.105$.
100-g samples heated to 100–110°C in argon (0.7 scfh) at 50°C/hr.
Steam flow rate was 1 g/min and rise rate was 25°C/hr between holding temperatures.

Sample	1	2	3	4	5	6[a]	7	8
Holding Temperature (°C)								
110	2	16	2	2	3.5	3.5	16	16
125	2	0	16	2	16	16	0	2
150	16	2	2	16	1	1	2.5	16
175	13	16	3	3	2.5	2.5	16	2
200	2.5	4	2	3	2	2	4	3
Analysis of Dried Gel								
$NO_3^-/(Th + U)$	0.024	0.025	0.009	0.022	0.006	0.005	0.008	0.027
NO_3^-, %	0.54	0.56	0.20	0.48	0.14	0.11	0.17	0.60
C, %	1.14	0.92	0.73	0.85	0.96	1.99	0.76	0.97
O/U	2.95[b]	2.81	2.93[b]	2.93[b]	2.96	2.72	2.84	2.94

[a]0.1 g/min used instead of usual 1 g/min.

[b]Samples were exposed to air during unloading after firing.

Firing Studies

To effect carbon removal and densification, the dried gel spheres are heated in air to 1150°C. The oxide is then reduced in Ar–4% H_2 to the desired oxygen-to-uranium ratio. The calcined spheres are then cooled to room temperature in argon. On calcination, the gels shrank about 65% in volume and 30% in diameter.

The firing procedure has been used throughout our work on ThO_2-UO_3 gels beginning with the Kilorod Program.[3] In laboratory studies several samples of the dried gel spheres were heated to 1150°C at 300°C/hr in air and held for 1 hr. They were then heated for 3 hr in Ar–4% H_2. The products had densities 95 to 98% of theoretical, carbon contents of 20 to 40 ppm, and oxygen-to-uranium ratios of 2.001 to 2.020. They were solid solutions of UO_2 in ThO_2, as determined by x-ray lattice parameter measurement, and had a crystallite size between 1000 and 2000 A. The gel spheres used in these studies had a good shrinkage pattern for ease of removal of the remaining volatiles. The density was only about 40% of theoretical at 850°C, and the pores were all open. Thus, the sorbed carbon-bearing materials, nitrates, and water could be removed easily before the pores closed.

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[3]C. C. Haws, J. L. Matherne, F. W. Miles, and J. E. Van Cleve, Summary of the Kilorod Project — A Semiremote 10-kg/day Demonstration of $^{233}UO_2$-ThO_2 Fuel-Element Fabrication by ORNL Sol-Gel Vibratory-Compaction Method, ORNL-3681 (August 1965).

7. THORIUM CERAMICS DATA COMPILATION

Sigfred Peterson

Data on the physical, mechanical, and chemical properties of ceramic compounds of thorium are being compiled from the literature. The collection has been completed[1] on oxides through October 1969 and nitrides through January 1970. That on carbides has been drafted, and information is being collected on other systems (borides, sulfides, etc.) and on the completed parts for future extensions and revisions. The collection is being issued in loose-leaf form so additions and revisions can be easily incorporated.

"Volumes" on the different systems contain major divisions on the useful compounds; divisions so far are on ThO_2, ThN, Th_3N_4, ThC, and ThC_2. Under each are "Parts" dealing with the compound, its binaries with uranium, with plutonium, and with other elements, more complex systems, and in some cases with other negative elements. The parts contain sections on composition, preparation, crystal properties, thermodynamic properties, change of state, electrical and magnetic properties, heat and mass transport, mechanical properties, chemical properties, and surface properties.

Volume I cites 256 references but defers systems with a second negative element (such as oxysulfides) to later volumes. Volume II cites 35 references and includes information on systems with added negative elements, such as carbonitrides. Many gaps exist in the characterization of the thorium nitrides. The most serious deficiencies in the carbides are the lack of reliable thermodynamic properties of ThC and the sparsity of mechanical and transport property data for both carbides.

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[1]S. Peterson and C. E. Curtis, Thorium Ceramics Data Manual Vol. I, Oxides and Vol. II, Nitrides, ORNL-4503, Vols. I, II (September 1970).

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