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CHEMICAL TECHNOLOGY DIVISION
METALS AND CERAMICS DIVISION

LMFBR FUEL CYCLE STUDIES PROGRESS REPORT FOR AUGUST, NO. 6

I. AQUEOUS FUEL REPROCESSING

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II. FUEL MATERIAL PREPARATION

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III. FUEL FABRICATION AND EVALUATION

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LMFBR FUEL CYCLE STUDIES PROGRESS REPORT FOR AUGUST, NO. 6

ABSTRACT

This report continues a series outlining progress in the development of methods for the reprocessing and fabrication of LMFBR fuels. Development work is reported on problems of irradiated fuel transport to the processing facility, the dissolution of the fuel and the chemical recovery of the $\text{PuO}_2\text{-UO}_2$ values, the containment of volatile fission products, product purification, preparation of fuel material by the sol-gel process, conversion of fuel processing plant product nitrate solutions to solids suitable for shipping and for fuel fabrication, fuel fabrication of sol-gel materials, and fuel evaluation studies, both in-pile and out-of-pile. Pertinent experimental results are presented for the information of those immediately concerned with the field. Detailed description of experimental work and data are included in topical reports and in the Chemical Technology Division and Metals and Ceramics Division Annual Reports.

HIGHLIGHTS

Division I

In impact tests on the radial spokes for the "bird cage" crash frame design rectangular spokes anchored by welding suffered cracking in the welds, whereas round spokes with threaded anchors survived with no visible failures. (Sect. 1.2)

Shearing, voloxidation, and dissolution experiments with four short-cooled LMFBR fuel rod specimens were completed but accumulation and interpretation of the data are only partially finished. The leachability of plutonium was adversely affected by the voloxidation treatment. (Sects. 4.1 and 5.1)

Very efficient trapping of methyl iodide from air was obtained with silver zeolite at 100 to 200°C but not at 25°C. The presence of n-dodecane in the air decreased the trapping efficiency slightly at 200°C but had no detectable effect at 100°C. (Sect. 10.1)

The efficiency in scrubbing of n-octyliodide and n-dodecyliodide from air with mercuric nitrate solutions was much more effective when the nitric acid concentration in the scrub solution was 5 M than 1 M. (Sect. 10.1)

Division II

The solvent extraction contactor using a packed-bed column of Berl saddles has been successfully used for the preparation of CUSP sol. Because of its simplicity of operation, it offers advantages over the mixer-settler contactor for use in remotely operated facilities. Sol prepared with the packed-bed contactor appears to be as good in every way as other CUSP sols. (Sect. 2.1)

Solvent extraction apparatus consisting of two identical contactor-separator sections has been fabricated and installed in a glove box to study the preparation of plutonia sols. This apparatus which closely simulates the operations to be carried out in engineering scale equipment will be used to obtain information required for plutonia sol preparation and it will provide a convenient source of plutonia sol for the development studies. (Sect. 2.2)

Division III

A procedure was developed for calcining sol-gel-derived (U, Pu)O₂ and for pressing and sintering this material into annular pellets for the Oak Ridge Research Reactor instrumented capsule test series. The densities of the pellets ranged from 83.1 to 85% of theoretical density with an average of 84.0% T.D. (Sect. 1.1.2)

Two instrumented TREAT capsules, which are designed to compare sol-gel Sphere-Pac fuels with pelletized fuels, were completed and await shipment to the Transient Test Facility. (Sect. 1.2.1)

Preliminary plans were developed for the fabrication of a set of unencapsulated fuel rods to be irradiated in a 37-rod subassembly in the EBR-II Reactor. The primary objective of this test series is to establish the performance characteristics and limitations of (U, Pu)O₂ fuels fabricated by different processes. The subassembly is to be shared with the Babcock and Wilcox Company. (Sect. 1.2.2)

The analytical chemistry data show that sol-gel-derived pellets have less than 0.10 cm³/g gas release when the pellets are initially removed from the furnace, but that this value increases with time. The increase in the gas content is probably caused by the adsorption of water from the atmosphere during storage and indicates the importance of proper storage and prompt loading of the fuel. (Sect. 2.1.1)

Five fuel rods containing Sphere-Pac fuels being irradiated in the EBR-II in subassembly X050 have been exposed to 4710 Mwd of reactor operation. Thus the highest heat rate fuel rod has accumulated a calculated 2.6% FIMA burnup. (Sect. 2.2.5)

I. AQUEOUS FUEL REPROCESSING

(W. E. Unger, R. E. Blanco, D. J. Crouse, A. R. Irvine, C. D. Watson)

1. SHIPPING (TASK 1)

(A. R. Irvine, J. D. Rollins, R. S. Lowrie,
D. C. Watkin, J. H. Evans)

The objective of Task 1 is to assure that an economic and safe method of shipment of LMFBR spent fuel will be available when needed for transport of fuel from the demonstration and early commercial LMFBR's. The work involves analytical studies of the various facets of the problem; design, construction, and test of components, and of assemblies; and preliminary design of prototype casks.

The bulk of the effort on this task is directed toward expanding the store of information on the effectiveness of sodium as a primary coolant and of cask design features which can assure containment of coolant (and fission products) within the cask fuel cavity. Other coolants (including gases, liquids, and solids) have been considered, but they do not appear to be as attractive as liquid sodium.

Work performed during this report period was almost entirely in the areas of Tasks 1.1 through 1.4, which deal with evaluation and test of heat dissipation methods and of cask integrity.

Reportable accomplishments include the following:

1.1 Heat Dissipation Tests (Task 1.2)

- A. A new electrical heater was obtained and installed in the reduced scale cask mockup and the test program continued using mercury as the heat transfer medium. The orientation of and the temperature profiles obtained in the first 24 in. of 7 tubes in the mockup are shown in Fig. 1-1. Tubes 1, 2, and 3 pass through only the third partial baffle plate (farthest from the heated end). Tubes 4, 5, 6, and 7 pass through both the second (center) and the third baffle plates. The rather pronounced temperature drop across the baffled section indicates that the baffles exert a considerable mixing effect on the fluid. Additional tests and temperature measurements will be required to determine the extent that the baffles interfere with the thermal convective flow within the fuel cavity.
- B. On the basis of delivery schedules for replacement tube heaters now on order, a two-to-three week hiatus is anticipated prior to the second startup of the electrically heated mockup of an Atomics International Reference Oxide Reactor fuel subassembly (test device). The initial operation of the test device was aborted due to faulty tube heaters which

ORNL DWG 69-8480

Fig. 1-1 Temperature Profile of Tubes 1-7 in the Reduced Scale Cask Mockup Heat Transfer Device.

resulted in erroneous temperature readings of the simulated fuel pin clads. Subsequent investigations (by the heater manufacturer) of the tube heaters indicated that the problem was due to high impurity content in the filament insulation (MgO). The heater manufacturer will replace the heaters at no charge.

During shutdown of the test device, five additional thermocouples are being attached to the external surface of the hexagonal shroud which surrounds the fuel subassembly. Temperature readings from the above locations will obviate calculations of the temperature gradient between the shroud and the wall of the outer container (10 in. pipe), thereby providing a more precise temperature profile for purposes of analytical correlation.

- C. Fabrication of the full-scale, half-length, 37-subassembly, sodium-cooled, electrically-heated cask mockup is continuing, with completion anticipated for late September. The planned startup of operation for November 1969, is consistent with the present schedule.

1.2 Cask Integrity Studies and Tests (Tasks 1.3 and 1.4)

- D. Radial spoke impact specimens which consisted of 1/8 in. thick 304L stainless steel sheet welded to low carbon steel end blocks were tested in a fixture which stresses the spoke specimens in bending as well as tension. This arrangement simulates more closely the actual loading in the "bird cage" crash frame. Although the specimens experienced 60% elongation and almost 90,000 psi ultimate stress, cracking in the welds occurred in every specimen regardless of whether the end flare was 38%, 50%, or 75%.
- E. Round cross-section (1/4-in.-diam) spokes impacted in the same fixture as above performed exceptionally well. All failures were in the gage lengths of the specimens with very uniform elongations throughout. These specimens were attached to the fixture by way of threaded ends; half were 3/8 - 24 NF and half were 1/2 - 20 NF. None of the specimens showed any evidence of cracking in the threads.
- F. As a result of the successful tests with round spokes, the design of the "bird cage" crash frame test specimen has been simplified to utilize fixed tangential spokes of circular cross-section. Fabrication is scheduled to begin shortly.
- G. The cask modeling study tests are ready to begin. Load cells are being modified for utilization in recording the impact loads with respect to time. Deformation of the cask specimens will also be compared on the basis of scale and drop height.

- H. The metal-to-metal seals fabricated by the Gray Tool Co. have been leak tested to a He leak rate sensitivity of 10^{-9} cc/sec with no indication of leaks. The seal flanges are presently being welded in the 1/6 scale model casks.

Also, Gamah seals and plugs to be tested in the full size cask closure test program have been received from the vendor. These components will be installed in the test facility as soon as craft time becomes available.

- I. Scouting tests were continued in an effort to determine the energy absorption capability of tubular specimens consisting of different materials and having various dimensions. Some seventy 1-1/2 in. long specimens were tested. These included 3/8-in.-diam stainless steel tube, 1/4 in. steel pipe (sched 40), 1/8 in. steel pipe (sched 40), and 1/4 in. steel pipe (sched 80). Results of these tests confirmed the expectation that stainless steel specimens will absorb considerably more energy during deformation than will steel specimens.

Additional specimens consisting of tube-filled pipes were prepared for subsequent testing. These include 3-in.-long sections of 1-1/4 in.-, 2 in.-, and 3 in. pipe (sched 40).

- J. Design of crash frame test specimen predicated on tube-filled pipes as energy absorbers is complete and construction drawings are being made.

During the next report period work will continue along the same general lines. Extensive test data will be compiled on impact deformation and corresponding energy absorption of various sizes of tube-filled pipes. Construction of the crash frame test specimens will be given top priority. The extent of heat dissipation work will be dependent on the arrival of replacement electrical heaters.

2. RECEIVING AND STORAGE (TASK 2)

(A. R. Irvine and C. D. Watson)

This task is concerned with the means for rapid, effective economical, and safe operation of receiving and storage facilities for LMFBR fuels. The character of the work to be performed under this task will be determined largely by the outcome of investigations performed for the shipping and for the head-end processing tasks. Conversely, these other two tasks will be required to take into consideration the effect of variables in their area on the task of receiving and storage. This work will take cognizance of related work on fuel handling and sodium

removal that will be performed under Elements 3 and 5, respectively, of the LMFBR program plan.

The work being done on this task is limited to sodium deactivation, which is reported under Task 3.5.

3. HEAD-END PROCESSING OF LMFBR FUELS (TASK 3) (C. D. Watson)

The objective of this task is to develop economic head-end processing steps, in preparation for Purex recovery methods, of long- and short-decayed fuels.

In this report period: an ORNL report of computer code, HEX, was continued; a confirmation of the theoretical calculations made by HEX is being delayed pending receipt of replacement heaters; a plasma torch appears sufficiently promising to warrant scoping evaluation tests for shroud removal; hold-down clamps for slitting studies were completed but fabrication of mounting fixtures and prototype assembly is temporarily delayed by machinists' vacations; the stroke of the ORNL 250-ton bundle shear is being lengthened and new fixed and moving blades designed in preparation for shear tests to shred a shrouded intact LMFBR assembly into discrete pieces; work on multirod and single rod shears is being suspended in deference to work on the bundle shear; an analysis of interstage seals and valves to isolate the head-end equipment units has begun; installation of sodium deactivation equipment delayed during this report period because of limited cell space will be started in September; and melt-declad experiments curtailed in August will be renewed in September.

Reportable accomplishments include:

3.1. Decay Heat Dissipation (Task 3.1) (R. L. Cox)

Experimental work to check the validity of the theoretical calculations of the temperatures in hexagonal fuel rod arrays is still being held up by a lack of replacement heaters for the simulated fuel sub-assembly. It now appears that the heaters will be received by the middle of September. In the meantime several more thermocouples have been installed to facilitate data analysis.

Work on an ORNL report to document the theoretical studies and the computer code HEX is continuing and is expected to be essentially complete, in rough draft, by the end of the September report period.

3.2. Dismantling of Multitubular Assemblies (Task 3.2) (G. A. West, R. S. Lowrie, F. C. Davis)

In keeping with the program objective of developing information applicable to the near term processing of FFTF fuel in an existing plant such as NFS, Inc., information was obtained on the use of two modes of torch cutting for possible removal of the shroud from LMFBR

fuel assemblies. They are: (1) A carbon arc-air which uses an electric-arc in conjunction with a blast of high pressure air, at approximately 100 psi, to cut through steel. This method produces a "ragged" cut and the melt (stainless steel) is blown for a distance of several feet from the work material, and (2) A plasma-arc torch which uses an argon gas flow and produces a smoother more precise cut than the carbon arc-air torch. Tests are being devised to ascertain if the plasma torch can cut off (melt) opposite corners of a shrouded hexagonal AI prototype assembly in an axial direction without damaging the fuel rods.

Equipment components for the cropping tests on end fittings and slitting tests on shrouds are being fabricated. The hold-down clamps have been completed and the mounting fixtures and prototype assemblies are scheduled to be fabricated in September.

3.3. Shearing (Task 3.3)

(G. A. West, R. S. Lowrie, C. H. Odom, J. H. Evans, E. I. Wroblewski)

Emphasis on shearing is being shifted from the longer range development of multirod shearing and single rod shearing to the near term use of a bundle shear for FFTF and Demo fuel in existing reprocessing facilities.

Assembly or Bundle Shear. - In LMFBR fuel, warpage of 8 in. to 12 in. can be expected in fuel assemblies, depending on length, and 1% to 5% swelling of the stainless steel cladding, shrouds, etc. will occur. Consideration has been given to the intact shearing of the fuel assemblies. For single rod or multipin shearing, the warpage and swelling of the assemblies may require that each assembly be reasonably straightened by using a series of heavy duty clamps. The shroud would have to be loosened or removed either by longitudinal slitting with an abrasive wheel or milling cutter, or by burning off of the corners of the shroud with a plasma torch. All of these techniques are being investigated, and the most promising will be demonstrated. After the fuel rods are removed from the shroud, rod warpage will probably require an extra operation in order to straighten them prior to their entering a rod singulator.

The two major problems to be solved in intact shearing are: (1) Clamping the assembly with enough force to squeeze out the voids between rods in order to prevent long pieces of fuel rods from being produced at the terminal end of the assembly. Special clamps (or gags) have been designed with serrated faces which will concentrate the available clamping force on the thick shroud. (2) Breaking up of the shroud into small enough pieces to pass through the discharge line from the shear and through other process lines without jamming. Three special moving blades--Fig. 3-1--and three special fixed blades have been designed (an order has been placed with The American Shear

ENLONGATED STEPPED
TOOTH BLADE

INTERRUPTED SHARKS
TOOTH BLADE

STRAIGHT SHARKS
TOOTH BLADE

Fig. 3-1 Experimental Shear Blades.

and Knife Co. for these blades). The three moving blades are: (1) straight "shark's tooth"; (2) interrupted "shark's tooth", and (3) elongated stepped blade. The three fixed blades have stepped-teeth to match the stepped-teeth in the corresponding moving blades.

Since these moving blades are ~ 6 in. longer than the existing blades (5.75 in.) used in the 250-ton shear, it was necessary to increase the stroke from 10-3/16 in. to 12-1/2 in. To do this, it was necessary to remove 2-5/16 in. from the piston in the hydraulic cylinder and the same amount from the shear ram to which the moving blades are attached. This work is being done in the ORNL and K-25 shops and should be completed by about September 1.

The shear side cover plate, to which the feed magazine is attached, has been redesigned so the cover plate, gag guides and gags can be removed as one unit. This will provide a much faster means of changing moving blades during the test program than removing each of the components individually.

Tests have been designed for shearing AI prototype fuel assemblies at the following process conditions: (1) removal of both end adapters by sawing to produce loose fuel rods in the shroud, (2) removal of both end adapters leaving the restraining grid or lattice welded to the shroud, and (3) removal of only one end adapter leaving the terminal end adapter attached. The end adapter in this case will either be withdrawn from the feed magazine or pushed through the shear into a special discharge chute to the waste disposal system.

During the next report period, the 250-ton shear will be re-assembled with new and revised parts added. However, some delay may be encountered, since the delivery of the shear blades is 8-10 weeks from receipt of order. Also, drawings will be prepared of the three types of prototype fuels and fabrication should be started by October 1.

Multirod Shearing. - Data compiled during the shearing of solid stainless steel rods, 0.250-in. OD, with the UNOP multipin shear operating with the 125 hp hydraulic pump and 0.75 in. OD supply lines is presented in Table 3-1. The unit was capable of operating at 150 cycles/min by removing the cylinder's hydraulic cushion rings and increasing the sequencing unit setting.

Single Rod Shearing. - It was decided to design and fabricate the parts required to convert the spring powered high-speed experimental shear to a low-speed hydraulic unit. This was accomplished by modifying the load cell design and designing additional cylinder mounting brackets. The nine-ton hydraulic cylinder which will be used to cock the spring for high-speed operation will also be used to provide the force for low-speed studies. These modifications will essentially provide a second device for basic shearing studies at an absolute minimum cost.

Table 3-1. UNOP Multirod Shear Characteristics
(Shearing 0, 1 and 11 solid stainless steel rods, 0.250-in.-diam each)

Operating		Pump		Cutting Stroke			Reverse Stroke		
(Cycles per Min)	Efficiency: ($\frac{\text{Cutting Load}}{\text{Pump Head}}$)	Head (psi)	HP	Time (sec)	Flow (gpm)	Load (psi)	Time (sec)	Flow (gpm)	Pressure (psi)
20 ¹	80	2300	16	0.8	13	1900	0.4	24	200
30 ¹	67	2400	32	0.4	24	1600	0.4	24	400
75 ²	--	2200	30	0.4	24	1800	--	--	400
50 ¹	75	2400	32	0.4	24	1800	0.4	24	300
60 ³	71	2100	40	0.3	34	1500	0.4	24	300
150 ²	--	1700	50	0.2	50	900	0.2	50	800

¹Cutting eleven rods.

²Cycling, no load.

³Cutting a single rod.

During the next report period it is anticipated that the drawing revisions on the experimental shear will be completed; fabrication is to be deferred.

3.4. Isolation of Shearing Operations (Task 3.4)
(R. S. Lowrie, C. H. Odom, E. I. Wroblewski, G. A. West)

The basic objective of this task is to study, evaluate, and establish the feasibility of sealing off the shear while fuel is being sheared. However, in keeping with the program objectives, an examination of other steps in the mechanical head-end has indicated an overall need for equipment isolation seals between:

1. The storage area and the fuel assembly cleaning equipment,
2. The fuel cleaning step and the cropping and dismantling step,
3. The cropping and dismantling step and the shear,
4. The shear and the voloxidizer, and
5. The voloxidizer and the dissolver.

In addition, it will be necessary to devise a method of moving the fuel, regardless of its physical configuration through these isolation devices.

A preliminary design of a seal valve has been made which will be located between the feed magazine and the shear. This seal valve is required during reloading of the feed magazine. In addition, emphasis in current conceptual studies is being given to the interstage sealing devices located between the shear and the voloxidizer and the voloxidizer and the dissolver.

Next month, the preliminary background information necessary for designing, developing, and evaluating various interstage valving, sealing, and fuel transport mechanisms and techniques will be reviewed and analyzed.

3.5. Sodium Handling and Removal (Task 3.5)
(R. S. Lowrie)

Fabrication of most of the experimental sodium deactivation equipment¹ was completed during the month. During the next report period, installation of the equipment will be started. This operation is dependent upon the completion of the decontamination and cleanup of the C cell, east cell bank in Bldg. 3503.

3.7. Alternative Head-End Processes (Task 3.7) (S. D. Clinton, A. R. Irvine)

Melt-decladding is being considered as a backup process for the mechanical head-end. By heating the fuel assemblies above the melting point of stainless steel (1450°C), it may be possible not only to volatilize iodine, xenon, krypton, and tritium but also the separate UO_2 - PuO_2 quantitatively from the molten cladding.

No experiments were conducted during the past month.

Runs to attempt to skim UO_2 particles floating on the surface of the flowing molten stainless steel are scheduled during the next report period.

References

1. W. E. Unger, R. G. Wymer, A. L. Lotts, et al., LMFBR Fuel Cycle Studies Progress Report No. 5, ORNL-TM-2671, p. 14.

4. VOLATILE FISSION PRODUCT REMOVAL (TASK 4) (D. J. Crouse, C. D. Watson)

The objective of Task 4 is to develop a head-end processing method for removing iodine, xenon, krypton, and tritium from the fuel prior to aqueous processing. Early removal of these gases from the fuel into a relatively small volume of gas would greatly facilitate off-gas treatment. This is of particular importance with respect to iodine control because of the very high plant retention factors that will be required for ^{131}I when treating short-cooled fuels.

This month the processing steps of shearing, voloxidation, and dissolution were completed for four short-cooled LMFBF fuel rod specimens and accumulation and interpretation of the data were partially completed. Thermogravimetric oxidation studies were begun to determine if $\text{UO}_2\text{-CeO}_2$ and $\text{UO}_2\text{-ThO}_2$ are suitable stand-in fuels for simulating head-end processing of $\text{UO}_2\text{-PuO}_2$.

4.1 Volatilization from Oxide Fuels (Task 4.1) (V. C. A. Vaughen, J. H. Goode, O. L. Kirkland, L. A. Byrd, G. D. Davis, W. B. Howerton, R. C. Lovelace)

We completed the hot cell experiments on the shearing, oxidation, and dissolution of four short-cooled (30 to 60 days) rods containing sol-gel 15% PuO_2 --85% UO_2 that had been irradiated to a nominal 20,000 Mwd/ton (U + Pu). Analyses are not complete but preliminary interpretation of the data indicates the following:

- 1) Shearing the 3-in. fuel column of a rod into 1/4-in. lengths dislodged nearly all of the sol-gel microspheres from the stainless steel cladding, but shearing into 3/4-in. lengths dislodged only part (~1/6th) of the oxide. An average of 19% of the ^{133}Xe and 56% of the ^{85}Kr were released when the first two fuel rods were sheared.
- 2) In the first run only about 0.4% of the total ^{131}I was found in the shear bowl; it was associated with a dust comprising about 1% of the fuel. We found 61% of the total ^{131}I in the cooler plenum section and adjacent to the bottom end plug. Oxidation of the sectioned (1/4-in.) fuel and cladding for 4 hr at 750°C volatilized about one-half each of the ^{85}Kr , ^{133}Xe , and ^{131}I remaining in the fuel after shearing. After dissolution of the oxide in 8 M HNO_3 using a reflux condenser, about 15% of the total ^{131}I was found in the fuel solution.
- 3) All of the oxidation and dissolution off-gases were treated in a single 2-in.-diam by 2-ft tall glass scrubber column filled with protruded stainless steel packing. The packing was wetted with 0.1 M HNO_3 --0.05 M $\text{Hg}(\text{NO}_3)_2$ solution flowing at the rate of 1 liter per hour. The scrubber gave an overall decontamination factor for ^{131}I during the first run of 6.5×10^3 , as

measured by iodine absorption on a charcoal trap at the exit of the scrubber.

Analysis of Equipment Requirements (S. D. Clinton)

A suitable stand-in fuel for $\text{UO}_2\text{-PuO}_2$ is desired for use in evaluating process parameters and developing engineering-scale equipment for the shearing, voloxidation, and dissolution processing steps. A stand-in fuel would permit experimental work to be conducted in facilities that are not adequate for handling and containing plutonium. Stand-in fuels under consideration are $\text{UO}_2\text{-CeO}_2$ and $\text{UO}_2\text{-ThO}_2$.

During the next month, thermogravimetric studies will be initiated to compare the oxidation characteristics of $\text{UO}_2\text{-CeO}_2$, $\text{UO}_2\text{-ThO}_2$, and $\text{UO}_2\text{-PuO}_2$ pellets as a function of temperature and time. Previous oxidation tests with $\text{UO}_2\text{-20% PuO}_2$ pellets at 850°C showed a weight gain equivalent to 77% conversion of UO_2 to U_3O_8 in 7 min and 91% conversion in 20 min.¹ The oxidation reaction was 97% complete in 2 hr.

Reference

1. Personal communication with R. G. Haire of ORNL, July 1969.

5. DISSOLVING (TASK 5) (D. J. Crouse, C. D. Watson)

The objective of Task 5 is to ensure that LMFBR fuels can be dissolved in nitric acid with high metal recoveries. Since the dissolution characteristics of the fuels can vary widely depending on their plutonium content, method of preparation, and irradiation histories, extensive leaching data are being obtained to define the effects of the many variables. A thorough understanding of iodine chemistry in the dissolver system is needed as a guide for providing effective iodine control. The dissolver equipment must be designed and operated within rather narrow limitations imposed by criticality control and off-gas considerations. It appears that satisfactory solution of these problems can best be accomplished using a continuous dissolver and this approach is being emphasized. Evolution of a successful dissolver will require development of equipment for dependably moving the sheared stainless steel hulls and other solids through the system, and development of seals for isolating the system to prevent excessive in-leakage of diluent gases.

This month dissolution of the short-cooled LMFBR fuel specimens was completed. The preliminary data indicate that the oxidation treatment of the fuel to remove volatile fission products prior to dissolution had an adverse effect on plutonium recoveries in the dissolution step. Preliminary studies of the feasibility of transporting sheared fuel through a continuous dissolver using a wire brush attached to a rotary screw were completed.

5.1 Dissolution Data (Task 5.1)

(V. C. A. Vaughen, J. H. Goode, L. A. Byrd, G. D. Davis,
W. B. Howerton, O. L. Kirkland, R. C. Lovelace)

Preliminary data on leaching the oxidized (and non-oxidized) sheared fuel rod segments in the short-decay experiments (see Task 4.1) indicate that the oxidation treatment at 750°C severely decreased plutonium recoveries in the subsequent dissolution step. For example, in four dissolution tests with portions of the oxidized fuel, the amounts of undissolved plutonium after 12 hr of leaching with boiling 8 M HNO₃ were in the range of 16 to 25%, compared to about 0.8% when the fuel was not oxidized. Oxidizing at 450°C also decreased plutonium recoveries but the effect was much less severe (~2% undissolved Pu). In each case, a leach of the residue with 8 M HNO₃--0.05 M HF satisfactorily dissolved the plutonium along with smaller quantities of uranium, cerium, zirconium, and niobium. A residue of ^{103,106}Ru (and daughters) and oxidized stainless steel components remained.

We do not understand why the oxidation treatment had such a strong adverse effect on the leachability of the plutonium since this effect was not observed in previous tests. Additional analyses for fission products and thorium (the thorium insulator pellets melted into the fuel) may help clarify the problem before next month's report. Complete leaching data will be presented at that time.

Dissolution of (Pu,U)C Fuels (ERRATA)

Table 5.1 of last month's report (ORNL-TM-2671) was in error. The results for the first three dissolution tests apply to the dissolution of oxidized fuel rather than to the direct dissolution of (U,Pu)C as shown in the table. The better plutonium recoveries (last 3 tests) were obtained by direct dissolution of the (Pu,U)C fuel.

5.4 Equipment Development and Testing (Task 5.4) (W. S. Groenier)

Preliminary studies of the feasibility of transporting sheared fuel via a spiral brush using an available screw-type leacher prototype were concluded. To summarize, both of the brushes tested (8-mil or 22-mil-diam bristles, ~1080 or ~130 bristles/in. of brush) were effective in transporting intact fuel pieces but neither was effective in transporting powdered fuel when using porcelain-filled 1/4-in. stainless steel tubing sheared to a length of 1 in. to simulate core region AI Reference fuel. With respect to wire spacers, which vary in diameter from 91 mil for core region fuel down to 22 mil for blanket region fuel, transport is a function of the spacing between brush wire bristles. The 91-mil spacers were moved satisfactorily with the closely-woven brush but not with the larger brush; the 22-mil spacers lodged within the first few flights of either brush.

In conclusion, the use of a spiral brush as the sole transporting device in a dissolver is not recommended. A brush having a close enough spacing so as not to entangle fine wire spacers would have to be woven of a fine wire itself. If fabricated by conventional means, this type of brush would probably not withstand the corrosive dissolver solution for a reasonable operating period. At this time, we prefer the concept of using a perforated sheath to surround the screw flights containing fuel pieces and wires and depending on a brush to agitate, but not to transport the fines that fall through the perforations.

6. FEED PREPARATION (TASK 6) (D. J. Crouse)

The aqueous feed discharged from the dissolver will contain solids (undissolved fission products, corrosion products, etc.) and will probably require clarification prior to solvent extraction. Preparation of the feed for solvent extraction also will include adjustment of the plutonium valence and the nitric acid concentration, and possibly, a treatment to remove iodine. This task also covers feed preparation for subsequent process cycles.

No reportable progress was made on this task this month.

7. SOLVENT EXTRACTION (TASK 7) (D. J. Crouse, C. D. Watson)

The objective of Task 7 is to establish that LMFBR fuels can be processed successfully by solvent extraction methods. Initial emphasis is on development of solvent extraction flowsheets suitable for interim processing of LMFBR fuels in existing plants. Present Purex flowsheets are being modified where necessary to provide for the high plutonium content of these fuels. The wide solvent extraction experience accumulated at production sites is being assessed and factored into these studies. Particular emphasis is being given to experimental evaluation of iodine behavior in solvent extraction and to the effect of solvent damage on process performance, especially when processing short-cooled fuels. Different solvent extraction contactors are being evaluated with respect to their relative merits for processing LMFBR fuels.

This month our computer code for predicting the maximum concentrations of fission products and actinides that will be in the aqueous feed to solvent extraction was modified to provide additional information.

7.1 Flowsheet Development (Task 7.1)

(W. Davis, Jr.)

Computer programs are now being widely used to calculate the quantities of the various fission products, actinide elements, etc., that are formed in nuclear reactors. The parameters of these calculations include fuel composition, reactor power or flux, irradiation time, and out-of-reactor time. When several nuclear-fuel types are dissolved together to produce a feed solution for a solvent extraction process (whether in small quantities for hot-cell tests or in large quantities as in the combining of core, radial blanket, and axial blanket fuel materials of LMFBR's), the manipulation of the large number of calculated quantities can become very tedious. For this reason we previously¹ modified the RIBDOR Code (RIBDOR is a modification, prepared by E. D. Arnold,² of the RIBD subroutine of the ISOSHL program of Engel, Greenborg, and Hendrickson³) so that it produced decks of punched cards of the quantities of fission products. These cards were then used as input to data-manipulating subroutines which we had written.

More recently, M. J. Bell⁴ described a more sophisticated program, RABBIT, that calculates the quantities of actinide elements and of activation products of construction materials, as well as of fission products. We have modified our data manipulating subroutines so that they are called by ORIGEN. One of the types of output from the subroutines is shown in Table 7-1. This example shows the contents of one liter of solution, containing 72 g (U + Pu), made by dissolving core, radial, and axial blanket materials from the AI Reference oxide fuel⁵, after 30 days out-of-reactor time, according to the conditions specified in the table headings and assuming all of each element would be dissolved. Data on several isotopes as well as totals for elements are included. While the latter are a standard part of the output, the programmer must specify the isotopes for which he also wants data.

References

1. W. Davis, Jr., and H. F. Soard, A Computer Program for Handling and Comparing Fission Product Data from RIBDOR for Mixtures of Reactor Fuels Irradiated Under Different Conditions: Application to Atomic International LMFBR Fuel, ORNL-TM-2393 (November 1968).
2. Chem. Technol. Div. Ann. Progr. Rept. May 31, 1968, ORNL-4272 (September 1968).
3. R. L. Engel, J. Greenborg, and M. M. Hendrickson, ISOSHL-A Computer Code for General Purpose Isotope Shielding Analysis, Battelle Memorial Institute, Pacific Northwest Laboratory (June 1966).
4. Aqueous Processing of LMFBR Fuels - Program Plan, Compiled and Edited by the Staff of the Chemical Technology Division, Oak Ridge National Laboratory, ORNL-4436 (in preparation).

FISSION PRODUCTS AND ACTINIDES

AI REFERENCE OXIDE LMFBR CORE 80300.9 MWD/MT IN
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 AI REFERENCE OXIDE LMFBR AXIAL BLAN 2500.1 MWD/MT IN
 540.0 DAYS. THE COOLING TIME FOR THIS FUEL IS 30.0 DAYS
 AI REFERENCE OXIDE LMFBR RADIAL BLA 8099.9 MWD/MT IN
 970.0 DAYS. THE COOLING TIME FOR THIS FUEL IS 30.0 DAYS
 THESE ARE COMBINED IN THE WEIGHT RATIO 0.3617 TO 0.2108 TO 0.4274
 THE FOLLOWING NUMBERS APPLY FOR 1 LITER OF SOLUTION CONTAINING
 72.0 GRAMS(U+PU)/LITER

ELEMENT	CURIES	GRAM- ATOMS	GRAMS	BETA POWER WATTS	GAMMA POWER WATTS
1 H	6.942E-02	2.388E-06	7.165E-06	2.470E-06	0.0
1 H 3	6.943E-02	2.388E-06	7.164E-06	2.470E-06	0.0
2 HE	0.0	1.249E-05	4.995E-05	0.0	0.0
30 ZN	8.395E-07	1.246E-14	8.968E-13	1.122E-09	1.029E-10
31 GA	1.275E-06	5.421E-15	3.903E-13	3.460E-09	2.126E-08
32 GE	0.0	1.625E-07	1.187E-05	0.0	0.0
33 AS	6.655E-08	1.853E-08	1.389E-06	9.079E-11	1.951E-12
34 SE	2.925E-06	6.046E-06	4.901E-04	1.110E-09	0.0
35 BR	1.532E-08	2.056E-06	1.665E-04	1.266E-11	2.405E-10
36 KR	7.608E-01	2.758E-04	2.332E-02	1.213E-03	9.779E-06
36 KR 85	7.608E-01	2.290E-05	1.946E-03	1.213E-03	9.781E-06
37 RB	7.630E-02	1.534E-04	1.327E-02	3.175E-04	4.167E-05
38 SR	5.072E-01	4.464E-04	3.981E-02	1.751E-01	2.035E-23
38 SR 89	4.747E-01	1.891E-05	1.683E-03	1.709E-01	0.0
38 SR 90	3.236E-00	2.544E-04	2.290E-02	4.222E-03	0.0
39 Y	7.186E-01	2.177E-04	1.944E-02	2.781E-01	1.567E-03
40 ZR	1.563E-02	2.216E-03	2.076E-01	1.465E-01	6.718E-01
40 ZR 95	1.563E-02	7.779E-05	7.390E-03	1.465E-01	6.717E-01
41 NB	2.023E-02	5.344E-05	5.076E-03	5.250E-02	9.067E-01
41 NB 95	1.990E-02	5.333E-05	5.067E-03	5.250E-02	9.021E-01
42 MO	1.345E-01	2.651E-03	2.591E-01	4.293E-04	1.753E-04
43 TC	1.297E-01	6.504E-04	6.439E-02	1.097E-04	0.0
44 RU	2.272E-02	2.248E-03	2.310E-01	5.708E-02	3.768E-01
44 RU 103	1.311E-02	3.975E-05	4.092E-03	5.139E-02	3.767E-01
44 RU 106	9.612E-01	2.701E-04	2.863E-02	5.700E-03	0.0
45 RH	2.272E-02	5.929E-04	6.107E-02	8.485E-01	1.115E-01
46 PD	3.745E-10	1.166E-03	1.239E-01	2.132E-13	0.0
47 AG	1.055E-00	2.481E-04	2.704E-02	2.320E-03	1.829E-03
48 CD	2.946E-02	8.442E-05	9.400E-03	8.214E-05	1.203E-05
49 IN	2.092E-04	1.310E-06	1.507E-04	5.983E-07	3.684E-08
50 SN	5.554E-01	4.475E-05	5.529E-03	2.923E-03	2.747E-04
51 SB	1.699E-00	1.988E-05	2.453E-03	2.933E-03	3.620E-03
52 TE	3.212E-01	3.143E-04	4.063E-02	6.078E-02	8.189E-03
53 I	1.061E-01	2.557E-04	3.286E-02	1.915E-02	2.824E-02
53 I 127	0.0	6.643E-05	8.434E-03	0.0	0.0
53 I 129	3.968E-06	1.887E-04	2.434E-02	1.717E-09	0.0
53 I 131	1.729E-01	6.343E-07	8.311E-05	1.804E-02	2.431E-02
53 I 132	3.150E-01	2.312E-10	3.052E-08	1.109E-03	3.933E-03
54 XE	5.155E-00	2.777E-03	3.175E-01	5.514E-03	0.0
54 XE 131	0.0	3.864E-04	5.061E-02	0.0	0.0
54 XE 133	4.596E-00	1.895E-07	2.520E-05	5.065E-03	0.0

FISSION PRODUCTS AND ACTINIDES

A1 REFERENCE OXIDE LMFBR CORE 80000.9 MWD/MT IN
 540.0 DAYS. THE COOLING TIME FOR THIS FUEL IS 30.0 DAYS
 A1 REFERENCE OXIDE LMFBR AXIAL BLAN 25000.1 MWD/MT IN
 540.0 DAYS. THE COOLING TIME FOR THIS FUEL IS 30.0 DAYS
 A1 REFERENCE OXIDE LMFBR RADIAL BLA 8699.9 MWD/MT IN
 970.0 DAYS. THE COOLING TIME FOR THIS FUEL IS 30.0 DAYS
 THESE ARE COMBINED IN THE WEIGHT RATIO 0.3617 TO 0.2108 TO 0.4274
 THE FOLLOWING NUMBERS APPLY FOR 1 LITER OF SOLUTION CONTAINING
 72.0 GRAMS(U+PU)/LITER

ELEMENT	CURIES	GRAM- ATOMS	GRAMS	BETA POWER WATTS	GAMMA POWER WATTS
55 CS	1.243E-01	2.122E-03	2.865E-01	1.764E-02	5.133E-02
55 CS 137	8.123E-00	6.818E-04	9.343E-02	1.315E-02	0.0
56 BA	4.653E-01	6.978E-04	9.624E-02	6.962E-02	9.156E-02
57 LA	4.480E-01	6.131E-04	8.523E-02	1.711E-01	5.727E-01
58 CE	2.755E-02	1.426E-03	2.016E-01	2.781E-01	2.254E-02
59 PR	1.431E-02	5.753E-04	8.112E-02	7.952E-01	1.699E-02
60 ND	1.379E-01	1.734E-03	2.516E-01	3.694E-02	1.660E-03
61 PM	2.976E-01	1.938E-04	2.848E-02	1.873E-02	3.705E-02
62 SM	3.500E-01	4.029E-04	6.047E-02	6.103E-04	3.939E-09
63 EU	8.271E-00	7.046E-05	1.084E-02	1.088E-02	1.888E-02
64 GD	3.290E-01	8.414E-05	1.321E-02	1.120E-03	1.913E-15
65 TB	1.101E-00	1.795E-05	2.855E-03	3.382E-03	4.863E-03
66 DY	4.593E-05	6.607E-06	1.065E-03	3.894E-08	0.0
67 HO	6.856E-05	9.996E-08	1.649E-05	3.004E-07	0.0
68 ER	0.0	7.006E-08	1.163E-05	0.0	0.0
81 TL	1.238E-08	2.741E-19	4.246E-17	4.313E-11	1.992E-10
82 PB	3.440E-08	2.850E-14	5.928E-12	2.427E-11	3.671E-11
83 BI	3.440E-08	1.109E-17	2.350E-15	5.350E-10	1.769E-11
84 PO	5.641E-08	4.575E-22	9.882E-20	2.574E-09	0.0
86 RN	3.440E-08	1.707E-19	3.756E-17	1.304E-09	0.0
88 RA	3.440E-09	9.588E-16	2.148E-13	1.177E-09	2.358E-12
90 TH	3.766E-08	6.696E-12	1.541E-09	1.161E-09	1.349E-12
91 PA	2.014E-09	1.922E-13	4.441E-11	9.834E-13	4.187E-12
92 U	6.372E-01	2.756E-01	6.560E-01	3.973E-04	9.709E-04
92 U 232	2.228E-07	4.487E-11	1.041E-08	7.154E-09	0.0
92 U 233	5.581E-10	2.574E-10	5.998E-08	1.654E-11	0.0
92 U 234	3.898E-06	2.693E-06	6.302E-04	1.122E-07	0.0
92 U 235	2.274E-09	4.516E-04	1.061E-01	6.313E-11	0.0
92 U 236	1.785E-07	1.193E-05	2.816E-03	4.841E-09	0.0
92 U 238	2.181E-05	2.752E-01	6.549E-01	5.520E-07	0.0
93 NP	5.352E-01	3.978E-05	9.428E-03	5.553E-04	1.031E-03
93 NP 236	3.171E-14	2.226E-22	5.254E-20	8.950E-17	0.0
93 NP 237	6.644E-06	3.977E-05	9.423E-03	0.0	0.0
94 PU	4.608E-01	2.678E-02	6.413E-00	4.761E-02	0.0
94 PU 235	3.058E-05	2.437E-10	5.753E-08	1.064E-06	0.0
94 PU 238	8.353E-01	2.180E-04	4.949E-02	2.767E-02	0.0
94 PU 239	2.630E-01	1.795E-02	4.290E-00	8.175E-03	0.0
94 PU 240	3.172E-01	5.995E-03	1.439E-00	9.881E-03	0.0
94 PU 241	4.465E-01	1.624E-03	3.914E-01	1.854E-03	0.0
94 PU 242	9.490E-04	1.006E-03	2.435E-01	2.803E-05	0.0
95 AM	1.263E-01	2.312E-04	5.589E-02	3.899E-03	1.069E-05

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72.0 GRAMS(U+PU)/LITER

ELEMENT	CURIES	GRAM- ATOMS	GRAMS	BETA POWER WATTS	GAMMA PCWER WATTS
96 CM	4.975E 00	1.102E-05	2.677E-03	5.658E-03	1.264E-02
TOTAL RE	4.022E 02	4.511E-03	6.512E-01	1.145E 00	1.020E-01
TOTAL FP	1.494E 03	2.197E-02	2.603E 00	3.057E 00	2.928E 00
ACTINIDES	5.235E 01	3.027E-01	7.208E 01	5.812E-02	1.466E-02
TOTAL	1.546E 03	3.247E-01	7.469E 01	3.115E 00	2.943E 00

5. K. Buttrey, O. R. Hillig, P. M. Magee, and E. H. Ottewitte, Liquid Metal Fast Breeder Reactor (LMFBR) Task Force Fuel Cycle Study, NAA-SR-MEMO-12604, Atomics International Division, North American Aviation (January 10, 1968).

8. PLUTONIUM PURIFICATION (TASK 8) (D. J. Crouse)

This task covers the process steps in purifying plutonium, starting with the plutonium product solution from the first Purex cycle and continuing through preparation of a product solution of adequate purity and concentration for delivery to the fuel refabrication operation.

Plutonium chemistry is reasonably well-known although the high plutonium content of LMFBR fuels makes some process revisions desirable. The large amounts of plutonium to be handled provide strong incentive for improving the efficiency of the plutonium purification processes since the cost of these operations will represent a much larger fraction of the total reprocessing costs than previously. In particular there appears to be a need for a higher capacity process than ion exchange for final decontamination of the plutonium.

This month studies were continued of third phase formation in the TBP--plutonium nitrate--nitric acid system.

8.2 Second TBP Cycle (Task 8.2) (D. E. Horner, J. R. Collins)

In continued tests to define the conditions under which a third phase forms, the maximum plutonium concentration obtainable in the solvent without third phase formation was found to increase as the acidity, the total nitrate concentration, or the ionic strength of the aqueous phase were increased. Data showing the correlation with the ionic strength are shown in Fig. 8-1. The maximum concentration obtainable for 30% TBP was approximately 1.7 times that for 15% TBP. In these tests a third phase was formed by contacting the solvent at about 23°C with an aqueous feed containing different concentrations of nitric acid and plutonium at a concentration high enough to overload the solvent and form a third liquid phase. A small amount of fresh solvent was then added in increments and the phases were re-equilibrated and centrifuged. This procedure was repeated until there was no evidence of a third phase at which point the phases were sampled for analysis.

For the conditions that we have outlined for the second TBP cycle, maximum plutonium loading of the 15% TBP solvent (at the feed stage) is about 22 grams per liter, whereas the data of Fig. 8-1 indicate that the solvent could be loaded to 26 grams per liter without formation of a third phase. Thus, third phase formation would not be expected for normal conditions of operation. It is not unlikely, however, that formation of a

Fig. 8-1 Maximum Plutonium Loading of TBP--n-Dodecane Solvent Without Third-Phase Formation. Aqueous Phase: $Pu(NO_3)_4$ -- HNO_3 .

third phase could occur for maloperation conditions, i.e. conditions that provide excessive plutonium reflux.

Additional tests are planned to define the maximum concentrations obtainable at elevated temperatures and those obtainable when a small amount of a diluent modifier, such as tridecanol, is used.

9. WASTE TREATMENT AND STORAGE (TASK 9)

Progress on this task is reported separately.

10. OFF-GAS TREATMENT (TASK 10) (D. J. Crouse, C. D. Watson)

Retention of iodine is the major problem in treating the off-gas from processing of short-cooled LMFBR fuels since plant retention factors of 10^7 to 10^8 would be required. Retention of most of the xenon and krypton, and eventually tritium, also may be required for future large processing plants. Process option diagrams illustrating alternative processing methods, based on present knowledge, for removing the gases from off-gas streams were presented previously.¹ All promising methods will be evaluated and additional chemical and engineering data developed where necessary. Studies are active in the areas of (1) scrubbing iodine species from gas streams with mercuric nitrate--nitric acid and alkaline solutions, (2) decomposition of organic solvent vapors and organic iodides by catalytic oxidation, and (3) testing of solid iodine adsorbents.

This month additional data were obtained for the trapping of methyl iodide with silver zeolite and for the rate of reaction of methyl iodide with mercuric nitrate solutions. Efficient scrubbing of *n*-butyliodide, *n*-octyliodide, and *n*-dodecyliodide from air with mercuric nitrate solutions was demonstrated. Iodine in the form of iodine monochloride in nitric acid was readily reduced to I^- with either nitrite or iodide ions.

10.1 Iodine (Task 10.1)

Trapping of Methyl Iodide by Silver Zeolite (R. E. Adams, R. D. Ackley, Zell Combs)

Recently, it was found that material referred to as silver zeolite is remarkably effective for trapping iodine in the form of CH_3I at 200 and 400°C.² This agent, which is prepared by treating Linde Molecular Sieves (Type 13X) with silver nitrate solution, represents a development of Idaho Nuclear Corporation reported by Maeck, Pence, and Keller.³ The aforementioned results were obtained with zeolite material furnished by Maeck. Some additional data have since been obtained with material

prepared at ORNL using Type 13X Sieves supplied as 1/16 in. pellets.

One group of trapping experiments, using ^{131}I -labeled CH_3I , was performed to check the quality of the newer preparation at 200°C and also to investigate the applicability of the silver zeolite at lower temperatures. The CH_3I concentration in the air stream was 3 ppm and the air was moisturized to the extent of 2.9% (both by volume). In those cases where the tests were at 25°C , the relative humidity (R.H.) was 90%. The CH_3I injection period was 2 hr. The results of the tests are listed in Table 10-1. Comparison of the results with earlier results indicates that the ORNL material was prepared satisfactorily. In addition to being effective at 200 and 400°C , the silver zeolite is also effective at 100°C , but it is not highly effective at 25°C , at least not for the condition of 90% R.H. For the case of operation at 25°C , prolonged exposure to humid air is, as expected, somewhat deleterious; however, exposure to humid air at 25°C followed by subsequent testing at 100°C did not reveal an adverse effect.

Behavior of the zeolite when organic vapors are present in the gas stream represents, of course, a situation of considerable interest. Experiments, generally similar to those described above and involving silver zeolite beds at 100 and 200°C were performed regarding this aspect. The beds were pre-exposed to flowing air containing n-dodecane for 18 hr prior to CH_3I injection. (Exposure to dodecane continued during the injection.) We estimate that the amount of dodecane introduced, relative to the amount of zeolite (in a 2-in. bed depth) was about 20% by weight. For each bed, the temperature during pre-exposure was the same as during CH_3I injection. The silver zeolite was effective at 100°C , despite the exposure to dodecane vapor, but moderately less effective at 200°C (Table 10-2). This behavior can probably be ascribed to greater decomposition of the organic with more extensive associated poisoning at 200°C than at 100°C . This observation appears to be substantiated by the colors of the silver zeolite beds after the experiment. The bed that was held at 100°C was only slightly discolored while the one held at 200°C was medium brown. Further experiments of this type are planned.

Rate of Reaction of CH_3I with Mercuric Nitrate Solutions (R. E. Adams, R. L. Bennett, Ruth Slusher)

The kinetics of the reaction of CH_3I at very low concentrations (about 10^{-6} M) with aqueous mercuric nitrate-nitric acid scrubber solutions are being investigated. Previously it was shown that no detectable reaction occurs with nitric acid (1 M) alone. The reaction with $\text{Hg}(\text{NO}_3)_2$ -- HNO_3 solutions is apparently first order with respect to CH_3I and, since the mercuric nitrate was present in large excess in these tests, pseudo-first order rates were obtained from the observed half-lives. Division of the pseudo-first order rate constants by the mercuric nitrate concentration yielded second order constants (1.70 to 1.33 liter mole $^{-1}$ sec $^{-1}$) which decreased as the mercuric nitrate concentration was increased.

Table 10-1. Efficiency of Silver Zeolite for Trapping Methyl Iodide

Temperature (°C)	Pre-exposure to Entering Air (hr)	Face Velocity of Air (fpm)	Trapping Efficiency for 2-in. Bed Depth (%)
100	0.7	50	99.9+
200	0.7	63	99.9+
25	0.1	40	94.6
100	0.1	50	99.9+
25	18.	40	91.1
100	18. ^a	50	99.9+

^aSilver zeolite was at 25°C during most of pre-exposure period.

Table 10-2. Effect of Exposure to n-Dodecane Vapor on Methyl Iodine Trapping Efficiency of Silver Zeolite

Temperature (°C)	Face Velocity of Air (fpm)	Trapping Efficiency (%)	
		1-in. Depth	2-in. Depth
100	50	99.56	99.99+
200	63	95.45	99.86

The effect on the reaction of varying the nitric acid concentration was examined recently. Rate measurements were made on a series of 0.010 M $\text{Hg}(\text{NO}_3)_2$ solutions which had nitric acid concentrations varying from 0.005 to 0.10 M. The rate of CH_3I reaction was virtually constant over this range of acid concentration (Table 10-3); although no significant variation was observed, it should be noted that the hydrogen ion, nitrate ion and ionic strength of the solution all increased at the higher HNO_3 concentrations and compensating effects may have occurred. Another test series is planned in which the nitrate ion and ionic strength will be held constant while the acidity is increased

Table 10-3. Reaction Rate at 30°C of Methyl Iodide with Mercuric Nitrate^a with Varying Nitric Acid Concentrations

HNO ₃ Conc. (M)	Reaction Half Life (min)	Pseudo First Order Rate Constant (min ⁻¹)	Second Order Rate Constant (liter mole ⁻¹ sec ⁻¹)
0.005	0.63	1.10	1.80
0.010	0.59	1.18	1.93
0.020	0.62	1.12	1.83
0.030	0.65	1.06	1.73
0.100	0.65	1.06	1.73

^aThe Hg(NO₃)₂ and CH₃I concentrations were 0.010 M and 3.2 x 10⁻⁷ M, respectively, in all tests.

The reactions of other alkyl iodides with mercuric nitrate-nitric acid solution are also being examined. Higher organic iodides, in addition to methyl iodide, have been found in fuel processing off-gas. The initial study of the reaction of *n*-butyl iodide indicated that the reaction rate with 0.005 M mercuric nitrate solution was too rapid to measure with our present techniques. By decreasing the mercuric nitrate concentration, the reaction was slowed so that quantitative data can now be obtained. The relative reactivity of other organic iodides is currently being determined.

Scrubbing Alkyl Iodides from Air with Mercuric Nitrate Solutions (J. M. Schmitt)

In tests reported previously,² *n*-butyliodide and *n*-octyliodide were scrubbed efficiently (DF > 1000) from air streams with 0.2 M Hg(NO₃)₂--8 M HNO₃ solution. Additional scrubbing tests at lower Hg²⁺ and HNO₃ concentrations have now been completed with these compounds. The results, showing the decrease in the alkyl iodide concentration in the air stream on passing it through three scrubbers in series is shown in Fig. 10-1. The first scrubber contained 100 ml of scrub solution and the second and third scrubbers each contained 50 ml. The air stream, flowing at the rate of about 60 ml/min, was dispersed into the solution through coarse glass frits. The Hg²⁺ concentration in all tests was 0.1 M but the HNO₃ concentration was varied from 0.1 to 5 M.

Fig. 10-1 Scrubbing Alkyl iodides from Air with 0.1M $\text{H g}(\text{NO}_3)_2$ Solutions in a 3-Stage Scrub System.

Results with n-octyliodide were approximately the same for acid concentrations of 0.1 and 1 M (Fig. 10-1); the n-octyliodide concentration in the air was reduced to 4.5 to 6% of its original concentration, corresponding to a DF of 16 to 22. However, with scrub solution containing 5 M HNO_3 , about 99.999% of the n-octyliodide was removed (DF of $\sim 10^5$). Removal of n-dodecyliodide was also considerably more efficient when the scrub acidity was 5 M than when it was 0.1 M, the respective DF's for the two experiments being 2×10^4 and 410. A DF of about 1200 was obtained for n-butyliodide using a scrub solution containing 0.1 M HNO_3 .

In the above tests, the average concentrations of n-butyliodide, n-octyliodide, and n-dodecyliodide in the air streams fed to the scrub system were about 8, 0.4, and 0.04 mg per liter of air, respectively.

Removal of Methyl Iodide. - A series of four tests was made in which 100 cc/min of air containing about 15 mg of I-labeled CH_3I per liter was passed through 0.1 M $\text{Hg}(\text{NO}_3)_2$ --0.1 M HNO_3 solution contained in a 1-in.-diam cylinder. The volume of solution in the cylinder was changed in each test so as to vary the path length that the bubbles traveled before they emerged from the solution.

When the volume of scrub solution was such that the top level of the solution was about 4 in. above the gas dispersal point, about 95% of the iodine was removed from the air (Fig. 10-2). Increasing the solution depth above the dispersal point to 14 in. increased the amount of iodine removed to 99.85%; this corresponds to a DF of about 700. We estimate that with this volume of solution in the cylinder the average bubble residence time in the solution was about 3 sec. The slope of the straight line obtained by plotting the bubble path length (in the range of 4 to 14 in.) vs the CH_3I concentration in the air (Fig. 10-2), indicates that the CH_3I concentration is being decreased by a factor of 10 with each 6 in. of travel through the solution. Additional tests are being made with solution depths up to about 36 in. to see if this relationship persists to very low CH_3I concentrations.

In these tests the air was dispersed through a coarse glass frit to produce bubbles that were possibly about 1 mm in diam. There appeared to be little or no coalescence of the bubbles as they traveled up through the solution.

Formation of Uncommon Iodine Species (J. M. Schmitt)

We are studying iodine chemistry in acidic and alkaline solutions and attempting to form volatile species of iodine other than I^0 and the alkyl iodides. Previous tests² showed that, in the presence of small concentrations of chloride, iodine is oxidized slowly in HNO_3 apparently to form ICl or ICl_2 , which are not extractable with CCl_4 . Recent tests show that iodine in this form is readily reduced to extractable I^0 by adding sodium nitrite or potassium iodide to the solution. For these tests, a 6 M HNO_3 --0.0042 M KI --0.042 M NaCl solution was prepared and

Fig. 10-2 Effect of Depth of Scrub Solution on the Methyl Iodide Removal Efficiency.

aged 8 days. Only about 20% of the iodine was extracted from a sample of this solution with CCl_4 . Since iodide ion oxidizes readily to the extractable I° state in 6 M HNO_3 , this indicates that the balance (~80%) of the iodine had been converted to a higher oxidation state (presumably I^+). When samples of the solution were made 0.017 M in NaNO_2 or 0.017 M in KI and contacted almost immediately with CCl_4 , 93% and 97%, respectively, of the iodine was extracted. Three days after addition of the NaNO_2 and KI only 49% and 93% of the iodine was extractable, respectively, from these solutions indicating that the iodine was slowly reoxidizing as the solutions were aged.

References

1. W. E. Unger, et al., Aqueous Processing of LMFBF Fuels Progress Report March 1969, No. 1, ORNL-2552.
2. W. E. Unger, et al., LMFBF Fuel Cycle Studies Progress Report No. 5, ORNL-TM-2671 (July 1969).
3. W. J. Maeck, D. T. Pence, and J. H. Keller, "A Highly Efficient Inorganic Adsorber for Airborne Iodine Species," in Proceedings of the Tenth AEC Air Cleaning Conference, New York, August 28, 1968, USAEC Report CONF-680821, pp. 185-203.

11. RADIATION AND SHIELDING (TASK 11) (J. P. Nichols)

This task consists of analytical studies with the objective of developing information on the radiation properties and shielding requirements of LMFBR fuels outside the reactor. The work involves compilation and correlation of basic nuclear data including decay schemes, nuclear cross sections, radiation sources and energy spectra, and thermal power (Task 11.1); development of computer programs for calculating transient concentrations of radionuclides in LMFBR fuel (Task 11.2); calculation of dose attenuation kerma for shield materials of interest (Task 11.3); and applications of these data to LMFBR fuel cycle processes (Task 11.4).

11.4 Neutron and Capture Gamma Dose Rates from LMFBR Fuels (E. D. Arnold, H. F. Soard)

Several sets of calculations have been performed using the ANISN code to calculate neutron and capture gamma dose rates in LMFBR cask shield configurations. The results indicate that a hydrogenous outer shield will be necessary to reduce neutron dose rates to an allowable level. Approximately 7 cm of water should be ample to reduce the neutron dose rate to approximately 10% of the fission product gamma level; i.e., to 5 mrem/hr at the carrier surface. However, under these conditions in which only water is placed on the outside of an iron shield, the capture gamma dose rate would be approximately 20 mrad/hr at the surface of the water shield. An additional 4-5 cm of iron would be necessary to further reduce the capture gamma dose rate. The total neutron source in a 36 element LMFBR carrier is approximately 4.75×10^9 n/sec. Additional neutron production due to subcritical multiplication has not been included.

Three summary tables of the computer data are included. These tables cover the cases of shields consisting of 50 cm iron + 5 cm H₂O + 5 cm iron (Fig 11-1), 50 cm iron + 10 cm H₂O + 5 cm iron (Fig 11-2), and 65 cm iron (Fig 11-3). In addition, we have run cases using shields of iron plus aluminum, iron plus magnesium, iron plus water only and iron plus polyethylene. These results have not been summarized and will be reported next month. We have asked for cross sections for lead, boron, uranium, and plutonium in order to cover new shield and core materials and to find the effect of adding boron to water or polyethylene on the capture gamma dose rate.

Fig 11-1. Dose Rate vs Position in Iron-Water-Iron Shield
for 36 Element LMFBR Cask

Case 1 (5 cm Water)

Basis: One neutron/sec in 75 cm core sphere

Zone No. and Material	Interval	Distance (cm)	Neutron Dose Rate (rem/hr)	Capture γ Dose Rate (rad/hr)
3 (Iron)	32	1.25	2.52481E-09	1.97189E-11
"	34	6.25	2.28669	1.39586
"	36	11.25	2.03937	1.04709
"	40	21.25	1.41260	6.65747E-12
"	44	31.25	7.86006E-10	4.21590
"	48	41.25	3.36230	2.94485
"	51	48.75	1.06673	5.33315
4 (Water)	52	50.25	5.90714E-11	6.19653
"	54	51.25	3.30865	6.22663
"	56	52.25	1.99800	6.34821
"	58	53.25	1.26540	6.31732
"	61	54.75	7.97127E-12	6.27746
5 (Iron)	62	55.5	7.72409	5.72820
"	64	57.5	5.83284	3.07852
"	66	59.5	3.30101	1.41004

Fig 11-2. Dose Rate vs Position in Iron-Water-Iron Shield
for 36 Element LMFBR Cask

Case 2 (10 cm water)

Basis: One neutron/sec in 75 cm core sphere

Zone No. and Material	Interval	Distance (cm)	Neutron Dose Rate (rem/hr)	Capture γ Dose Rate (rad/hr)
3 (Iron)	32	1.25	2.52472E-09	1.97164E-11
"	34	6.25	2.28659	1.39574
"	36	11.25	2.03926	1.04687
"	40	21.25	1.41249	6.65485E-12
"	44	31.25	7.85841E-10	4.21017E-12
"	48	41.25	3.35982	2.91873
"	51	48.75	1.06281	5.20143
4 (Water)	52	50.5	5.15843E-11	5.69449
"	53	51.5	2.89318	5.61139
"	54	52.5	1.73035	5.73912
"	55	53.5	1.05362	5.63086
"	56	54.5	6.42793E-12	5.36570
"	58	56.5	2.52619	4.82177
"	61	59.5	8.26481E-13	4.01087
5 (Iron)	62	60.5	7.55584	3.38722
"	64	62.5	5.79342	1.67411
"	66	64.5	3.34527	7.90379E-13

Fig 11-3. Dose Rate vs Position in Iron Shield for 36 Element
LMFBR Cask

Basis: One Neutron/sec in 75 cm core sphere

Zone No. and Material	Interval	Distance (cm)	Neutron Dose Rate (rem/hr)	Capture γ Dose Rate (rad/hr)
3 (Iron)	32	1.25	2.53557E-09	1.99908E-11
"	34	6.25	2.30102	1.42358
"	36	11.25	1.05894	1.07860
"	40	21.25	1.44763	7.13021E-12
"	44	31.25	8.46230E-10	4.90006
"	48	41.25	4.39144	3.19701
"	51	48.75	2.62645	1.11411
"	52	51.25	2.23298	1.95515
"	54	56.25	1.58458	1.49218
"	56	61.25	1.11681	1.11749
"	58	66.25	7.77467E-11	8.16174E-13
"	60	71.25	5.28498	5.73393
"	62	76.25	3.41948	3.75391
"	64	81.25	1.96768	1.10775
"	66	86.25	7.39965E-12	7.50162E-14

12. CRITICALITY (TASK 12) (J. P. Nichols)

The objective of this task is to develop evaluated criticality data for application to the aqueous processing of LMFBR fuels. The work involves compilation of basic data and liason with other critical experiment groups (Task 12.1); calculation of basic parameters (Task 12.2); the performance of select critical experiments with systems containing fixed and soluble neutron absorbers (Task 12.3); and the application of the critical data to the design of process equipment (Task 12.4).

12.4 Process Design Applications (S. D. Clinton)

The criticality study of the head-end processing of LMFBR fuel is continuing. Progress has been made on the analysis of information to determine the restrictions imposed by criticality upon process parameters and the design of equipment for the LMFBR dissolution step (1 to 5 metric tons of heavy metal per day). A preliminary analysis should be completed by the next report period. One of the principal objectives of the study is to identify the areas where basic criticality data are not available.

II. FUEL MATERIAL PREPARATION

R. G. Wymer, R. E. Brooksbank, R. E. Leuze,
J. P. McBride, W. D. Bond, P. A. Haas

1. CONVERSION STUDIES (R. E. Brooksbank)

In the LMFBFR fuel cycle, it would be highly advantageous to convert the product solutions from the fuel reprocessing plants to solid fuel materials that are suitable both for shipping and for direct use in re-fabrication of fuel elements. Earlier fuel cycle studies have not necessarily optimized the conversion to meet both of these requirements. In order to meet both requirements, the solids must be in the desired chemical form with the necessary purity. In this study, we hope to determine the best method for accomplishing the desired conversion. Although the major emphasis will be placed on conversions to oxides, the conversion to advanced fuel forms (such as carbides, nitrides, and carbonitrides) will be included in our studies. Conversion to these advanced fuel forms involves only a carbothermic synthesis step after conversion to the oxide.

We are studying processes that are currently in use or under development; an economic evaluation is being made prior to undertaking extensive laboratory and engineering process studies. The conversion processes being evaluated include a variety of approaches, such as fluidized-bed conversion, flame denitration, sol-gel, and numerous precipitation processes.

1.1 Sinterable Powder Preparation (W. D. Bond, P. A. Haas, R. E. Brooksbank)

Laboratory and engineering studies of the conversion of aqueous solutions of uranium and plutonium to powders will be initiated after our process evaluation studies (Sect. 1.2) have indicated which of the possible methods are the more promising.

1.2 Process Evaluation

Currently plutonium is shipped from chemical processing plants as a nitrate solution. While this is satisfactory at present, safety considerations will probably dictate that the increased quantities of plutonium that will result from LMFBFR fuel processing be shipped in a solid form. The objectives of this program are to define the most reasonable form for shipment to fabrication plants and to develop or adapt processes for this purpose. Processes currently used or being developed will be studied, and an economic evaluation will be made to establish the most promising approach. This work will, in turn, provide guidance for further experimental work.

The existing methods under study include those that are most likely to be used in production of first generation fast reactor fuel elements. They are: (1) dry powder blending of oxide powders for pelletizing,

(2) coprecipitation of plutonium and uranium to provide a mixed oxide for pelletizing, and (3) use of the sol-gel method to form either separate or blended UO_2 and PuO_2 microspheres or pelletizing stock. These are the most directly useful conversions, but if it appears desirable to convert to an intermediate solely for shipping purposes, this can also be considered.

In reporting comparative costs, we plan to show the costs of the various conversion methods separately from shipping and storage costs in order to provide more flexibility in the overall evaluation. As a need for further development work is recognized, it will be reported.

1.2.1 Chemical Conversion (F. E. Harrington, J. D. Sease, R. B. Pratt)

We are continuing the study of the costs involved in four alternative routes to the fuel preparation and fuel element fabrication for a specific LMFBR, as described last month.¹ The plants being studied would produce oxide fuel elements (containing 500 kg of heavy metal core material per day) from depleted UF_6 and $\text{Pu}(\text{NO}_3)_4$ solution. The four alternative routes are: (1) mechanical blending to produce pellets, (2) coprecipitation to produce pellets, (3) sol-gel to produce pellets, and (4) sol-gel using the sphere-pac technique for rod fabrication.

A detailed review of each processing step is nearing completion. In this review, the starting uranium feed is the same for all alternatives. The original approach, using purchased sinterable-grade UO_2 for the mechanical blending, raised the question of the comparability of the results.

We are attempting to evaluate cost differences that are associated with analytical work, quality assurance, and the safeguarding of materials. To date, definitive progress in this area has been disappointing.

1.2.2 Shipping and Storage (R. W. Horton)

The shipment and storage problems under study are connected with the procurement of feed materials that are used in fast reactor fuel fabrication plants. Two heavy metals are used in these fuel elements: ^{239}Pu as the fissile fraction, and ^{238}U as the fertile source of new plutonium. The supply of these materials is discussed below.

Fertile, depleted uranium is derived from isotopic separation in the gaseous diffusion cascade; it is stored and shipped as UF_6 . The fertile uranium that is recovered from fast reactor fuels in reprocessing plants will leave the separation process as a nitrate solution. There will be a large volume of solution produced for storage and eventual fabrication into blanket material. In some special cases, shipment of the nitrate solution is desirable. However, in most cases, it would be desirable to denitrate

¹LMFBR Fuel Cycle Studies Progress Report No. 5, ORNL-TM-2671 (August 1969), p. 38.

at the reprocessing plant and ship the resulting UO_3 for dry storage and further processing at the fabricator's plant. The trioxide can be readily dissolved in nitric acid if a solution is needed, or the trioxide can be reduced to a sinterable UO_2 powder.

Plutonium is a product of spent reactor fuel processing plants, and after final purification steps is usually available as a nitrate solution. The isotopic composition is a function of neutron exposure; the major fissile isotope, ^{239}Pu , may constitute 60%¹ to 95% of the total mass. There is no process for isotopic separation at reasonable cost and as a consequence the composition changes with each reactor exposure and refabrication. By a proper blending of available plutonium a pseudo-steady-state may be reached eventually. Some of the blending material will come from processing of LWR fuel, some from LMFBF combined core and blanket fuel, and some from LMFBF radial blanket processing. The need for blending plutonium from several sources makes a solution an attractive plutonium form, but the cost of shipping solution is very high.² A reasonable alternative is redissolution at the fabricator's plant; a "low-temperature" oxide might be used as the shipping form. The problems of preparing, shipping, and redissolving will be examined.

1.3 Advanced Fuel Studies (W. D. Bond)

Increasing demands on reactor fuels make the development of new or improved fuels important. Among the more promising advanced fuel materials for the LMFBF are the monocarbides, carbonitrides, and nitrides of plutonium and uranium. Sol-gel processes for the preparation of these materials are being developed on the laboratory scale. Stable, codispersed oxide-carbon sols are prepared by effecting dispersion of carbon black in UO_2 , PuO_2 , or $\text{PuO}_2\text{-UO}_2$ sols by ultrasonic agitation, and the oxide-carbon sols are then formed into gel microspheres or shards. After drying the gels to remove volatile materials, the gels are converted either to the monocarbide or to nitrides or carbonitrides, depending on the atmospheres used in carbothermic reduction. Monocarbides are formed when carbothermic reduction is effected under inert gas or vacuum atmospheres, whereas nitride or carbonitride conversion is effected under a nitrogen atmosphere.

Most of our work has been concerned with preparation of carbides. We had previously demonstrated the preparation of dense ThC_2 and $(\text{Th,U})\text{C}_2$ microspheres by sol-gel processes. In more recent work, laboratory-scale preparation of dense UC microspheres was demonstrated, and plutonium carbide microspheres were prepared. Work is now in progress on the preparation of other carbides. Kinetic studies are being carried out on the

¹Chem. Technol. Div. Ann. Progr. Rept. May 31, 1967, ORNL-4145, p. 195.

²Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, Sect. 9.1.

carbothermic synthesis step to better understand the rate controlling mechanism.

1.3.1 Sol-Gel Process Studies

Sol-gel process conversion development studies include the preparation of oxide-carbon sols that are suitable for forming gel shards or microspheres, and the conversion of these gels to carbides, nitrides, or carbonitrides by carbothermic synthesis. This month our work was concerned with studies on the preparation of (U, Zr)C.

Preparation of (U, Zr)C (K. J. Notz) - A number of approaches to stabilization of the carbon in UC fast reactor fuels are under consideration. On the one hand, two-component systems using either hypostoichiometric or hyperstoichiometric UC are being tested. On the other hand, two types of three-component systems are being studied: those which form a solid solution with UC (e.g., Zr, Nb, or N), and those which create a ternary phase field with UC at one corner (e.g., V or Cr).

As part of our development effort on the preparation of LMFBR fuels via sol-gel methods, we have previously made dense UC microspheres by the carbothermic reduction of $\text{UO}_2\text{-C}$ gels, in both hyper- and hypostoichiometric forms.¹ We have also demonstrated the preparation of U(C, N) shards using $\text{UO}_2\text{-C}$ gels,² and are extending this to include microspheres.

The sol-gel method is ideally suited for the addition of a second cationic component such as zirconium, which can be prepared in the form of an oxide sol.^{3,4} We have made zirconia sols that can be mixed with UO_2 and $\text{UO}_2\text{-C}$ sols,^{3,4} and it is probable that similar sols containing Nb, V, and Cr can also be obtained.

Preliminary tests with $\text{UO}_2\text{-ZrO}_2\text{-C}$ gel shards indicate that (U, Zr)C can be made by this sol-gel route. In one experiment, gel shards containing 22 cation % Zr were reacted at 1600 to 1900°C under argon, with a vacuum applied during the last 30 min of the 3-hr reaction period. The fact that the oxygen content of the product was only 190 ppm shows that elimination of oxygen was complete. X-ray diffraction showed a mixture of "UC" and "UC" phases, but the lines were too broad to determine a lattice parameter; a ZrC phase was not detected. Metallographic cross

¹Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, Sect. 7.5.1. Also presented at the 71st Annual Meeting of the American Ceramic Society, Washington, D. C., May 3-8, 1969.

²Metals and Ceramics Division Ann. Progr. Rept. June 30, 1968, ORNL-4370, p. 86.

³Chem. Technol. Div. Ann. Progr. Rept. May 31, 1967, ORNL-4145, p. 195.

⁴Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, Sect. 9.1.

sections showed well densified particles, despite the relatively low reaction temperature. Etching revealed a rather fine structure of regular grains 4 to 8 μ in size. This is a much smaller grain size (by an order of magnitude) than is observed for UC made by the analogous route;¹ Bocker² observed a similar effect with arc-furnace castings.

1.3.2 Kinetic Studies of Carbothermic Synthesis (T. B. Lindemer, R. L. Beatty, K. J. Notz)

Carbothermic synthesis of carbides, carbonitrides, and nitrides from oxide-carbon gels is an important process step in the preparation of these materials by the sol-gel process. An understanding of the rate-controlling mechanisms and kinetic equations of these carbothermic syntheses would be very useful for the determination of the best conditions for effecting these syntheses.

We have been doing exploratory work with the vacuum conversion of UO_2 -C sol-gel material at 1500°C. This approach would utilize fully the fine particle size of both the UO_2 and carbon in sol-gel material. Starting materials used thus far have been -100 + 120 mesh microspheres with a C/U ratio of either 7/1 or 3.1/1 and -35 + 100 mesh shards with a C/U ratio 4.3, 2.8, or 2.2.

A Debye-Scherrer film of the 7/1 microspheres reacted for about one min at 1500°C indicated that about 90% conversion to UC_2 was obtained. However, the 3.1/1 material appeared to react only on the surface in a reaction time of one min; the interior of the +50 mesh microspheres appeared to be unconverted. Particles crushed from microspheres to give -60 + 100 mesh material appeared to behave in the same manner as the original microspheres.

The shards appeared to be completely converted for all three C/U ratios after one min at 1500°C. No carbon was apparent in the interior of shards examined visually after reaction. As much as 25 g of material has been converted in one to two min. A portion of the vacuum-converted, 2.8 C/U shards were reacted subsequently in nitrogen in a fluidized bed at 1500°C to see if U(C,N) can be formed readily from this material.

We are presently awaiting the results of x-ray and analytical chemistry analyses on much of the material. These quantitative results will be reported later.

¹Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, Sect. 7.5.1.

²S. Bocker, "Study of Stabilization of Mixed Carbides of Uranium and Plutonium by Addition of Zirconium," CEA-R-3765 (March 1969).

2 - SOL-GEL PROCESSES FOR PREPARATION OF LMFBR RECYCLE FUEL (R. E. Leuze)

Sol-gel processes are ideally suited to the preparation of LMFBR recycle fuel since they can be readily adapted to continuous and remote operation for processing materials behind shielding. The processes under development prepare sols by controlled solvent extraction of nitrate from plutonium and uranium nitrate solutions, the products from fuel reprocessing plants. The sols are then converted to the desired ceramic forms, usually high density oxide microspheres, required for subsequent fabrication into recycle fuel elements. This section reports progress for all of the process development and demonstration, equipment design, and instrument development being carried out to obtain sufficient information for design of a full scale facility. Also included is the preparation of sol-gel materials required for testing and for use in other parts of the LMFBR fuel recycle program.

2.1 Urania Sol Process and Equipment Development (J. P. McBride)

Although the LMFBR recycle fuel under consideration is mixed urania-plutonia, study of urania sol preparation is important because urania is used as a fertile material in an LMFBR and is the major component in the mixed oxide. Urania sols are also useful for studying other phases of the program such as sphere forming and tray drying.

The CUSP process (Concentration Urania Sol Preparation) developed at ORNL has been selected as the method for preparation of urania sols since it is most amenable to scale-up and consistently produces good sols with desirable characteristics.¹ This section of the report covers all aspects of CUSP sol preparation including uranous nitrate feed preparation, laboratory- and engineering-scale process development, sol preparation, and equipment design and instrumentation.

Urania Sol Production (B. C. Finney, W. L. Pattison)

In the CUSP process, nitrate is extracted continuously at a controlled rate from a U(IV) nitrate-formate solution with a solution of Amberlite LA-2 (a high molecular weight secondary amine) in 75% diethylbenzene-25% n-paraffin (average length of carbon chain = 12). The amine is continuously regenerated by contacting it with Na_2CO_3 - NaOH solution. By following a prescribed conductivity-temperature-time path, a highly crystalline, very stable concentrated urania sol with a high U(IV) content is produced.

¹J. P. McBride, K. H. McCorkle, W. L. Pattison, and B. C. Finney, "Preparation of Concentrated, Crystalline Urania Sols by Solvent Extraction," presented at 15th Annual Meeting of the American Nuclear Society, Seattle, Washington, June 15-19, 1969; summary published in Trans. Am. Nucl. Soc. 12, 206 (1969).

Laboratory development of the CUSP process and an engineering-scale demonstration at a 4 kg UO_2 per batch level were described in the previous progress report.² To date, more than 45 engineering-scale production runs have been carried out: 12 during the development and refining of the engineering-scale operation, 26 during a sol-production demonstration, and the rest to supply specific needs or to investigate process variables and equipment performance. The results show that the CUSP process is relatively easy to control in engineering-scale equipment at the 4 kg per batch level and consistently produces fluid, 1 $\underline{\text{M}}$ UO_2 sols with shelf lives (i.e., periods of time before thickening or gelling) of 3 months or longer and with good microsphere-forming characteristics (see Sect. 2.3). The present report covers the 26 sol-production demonstration runs (CUSP-ES-13 through -38).

The production runs were made during a period of several weeks in which processing was carried out 2 shifts per day and 5 days per week. A run producing 4 kg of UO_2 sol was made each 8 hr shift. The 1 $\underline{\text{M}}$ U(IV) feed solution with NO_3^-/U and HCOO^-/U mole ratios of 2 and 0.5, respectively, was prepared by reduction with H_2 using a PtO_2 catalyst during one shift and used the following shift. Reduction times varied from 2.0 to 3.9 hr with an average time 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 by this procedure (through run CUSP-ES-18) showed distinct color differences, larger and less uniform micelles, and very poor performance in the formation of gel microspheres. By completely draining the solvent extraction system and flushing the equipment between batches with two water washes, these apparent differences between sols were largely eliminated. After run CUSP-ES-21, the system was thoroughly cleaned with HNO_3 and flushed with water; after CUSP-ES-29, in addition to the HNO_3 clean-up of the system, the solvent was cleaned by repeated cycling through HNO_3 -carbonate- H_2O cycles.

Numerous analyses were made at all phases of the operation, but only a summary of the results are presented here. Uranium concentrations in the sols were never more than 1% greater than in the uranous nitrate feed solution. The U(IV) content varied from 85 to 90% (with two exceptions, 82% and 84%) for an over-all average of 87%. An interesting observation is that sols produced from freshly prepared feeds were ~85% U(IV) and had smaller average micelle sizes (CUSP-ES-38, 260 Å) **than** those prepared from feeds that had aged overnight, in which the U(IV) contents were ~88% and the micelles were somewhat larger (CUSP-ES-37, 330 Å). The production of some "oxidizing" species during the U(IV) feed preparation step which decays out on standing has been noticed before. It appears that aging the feed a day or so prior to sol preparation is desirable. Further study of the reduction step is in progress.

²LMFBR Fuel Cycle Studies Progress Report No. 5, ORNL-TM-2671 (August 1969), pp. 52-60.

There was no apparent correlation between the conductivities and pH's of the final sols. The conductivities varied from 4000 to 6000 $\mu\text{mhos/cm}$; the pH's varied from 2.1 to 2.9 with most of the values being between 2.2 and 2.6. Aging studies showed that the conductivity increased 5 to 15% during the first one or two days standing. Average increases of 2 to 3% per day were noted for periods of 10 days. For additional two months aging, the average per day increase in conductivity was 0.4 to 0.8%.

The NO_3^-/U mole ratios varied from 0.08 to 0.12 with the average being 0.10. However, a previous investigation of nitrate analyses indicated that they are accurate to only $\pm 20\%$ at the 95% confidence level.³ The HCOO^-/U mole ratios varied from 0.40 to 0.50 with an average value of 0.47. The NH_4^+/U mole ratios varied from 0.0004 to 0.0016 (average 0.0011), and the Na^+/U mole ratios ranged from 0.0006 to 0.0030 (average 0.0013).

While x-ray diffraction data were not available to determine the degree of crystallinity of the sols, the long shelf lives and relatively small changes in conductivity on aging indicate they were highly crystalline. Electron micrographs showed uniform, spherical micelles with average sizes varying between 250 and 350 Å.

The solvent became discolored with entrained UO_2 during the production runs. This carry-over of urania into the organic phase was aesthetically unappealing but appeared to have no deleterious effects on the sols. Analysis showed that less than 0.5% of the UO_2 was lost to the solvent. Recent results indicate that the use of a $\text{NaNO}_3\text{-HNO}_3$ scrub followed by a caustic and then a water scrub in the solvent regeneration system eliminates the black color from the solvent with most of the uranium stripping into the acid scrub.

The molarity of the amine decreased from 0.21 to 0.11 during the 26 production runs, an average loss of 0.004 molar units per run (15 liters aqueous phase to 30 liters of amine) or from 2 to 4% loss per run. This was reflected in an increase of total run time per batch from an initial time of 4 hr to a final time of 6.4 hr.

Equipment Development (J. R. Parrott, F. L. Daley, F. G. Kitts)

Development of a contactor for use with the CUSP flowsheet for forming urania sols by amine solvent extraction is in progress in the Pilot Plant. A reductor for preparing the U(IV) feed solution, the contactor, and equipment for mixing the urania sol with plutonia sol will be added to the existing Solmix facility and used to prepare 80% UO_2 - 20% PuO_2 in 1 kg batches.

Our development work has been restricted to the testing of various mixing devices which might be used as the CUSP contactor. Although a satisfactory sol (JM-1, Table 2-1) was made with a standard 1/2 in. steam jet, used as the contactor, both aqueous and organic flow rates had to be higher than desired in order to achieve the mixing necessary

³J. G. Moore, "A Sol-Gel Process for Preparing $\text{ThO}_2\text{-UO}_3$ Sols from Nitrate Solutions by Solvent Extraction with Amines," ORNL-4095 (October 1967), p. 5.

Table 2-1. Conditions and Product Compositions for Urania Sol Runs

RUN NO.		JM-1	PC -1	PC -3	PC -4
CONTACTOR		1/2" jet	pack. col.	pack. col.	pack. col.
DIRECTION OF FLOW			down	up	up
CONTINUOUS PHASE		organic	organic	aqueous	aqueous
ORGANIC ^a FLOW (cc/min)		1500	400	225	225
AQUEOUS FLOW (cc/min)		1000	500	750	750
PRODUCT SOL					
Composition:					
U	(M)	1.00	1.00	1.03	1.03
U(IV)	(%U)	-	84	79	85
NO ₃ ⁻	(M)	0.11	0.07	0.12	0.11
HCOO ⁻	(M)	0.39	0.45	0.46	0.33
NH ₄ ⁺	(M)	0.001	0.002	0.006	0.004
pH		2.80	2.37	2.38	2.98
Density	(g/cc)	1.2518	1.2584	1.2650	1.2604
Conductivity @ 25°C		2900	2700	3000	2900
	(μmhos/cm)				
Impurities: ^b					
Na	(g/liter)	0.32	-	0.04	0.03
Fe	(g/liter)	-	-	0.007	0.006

^a0.2 M Amberlite IA-2 in 75% diethylbenzene-25% n-paraffin (average length of carbon chain = 12).

^bThese were the only elements found in significant quantities in routine spectro-graphic analysis.

- Not determined.

to denitrate at the specified rate. To obtain a longer contact time, a 1 in. ID glass pipe with a 3-1/2 in. length packed with 1/4 in. ceramic Berl saddles was installed. With this contactor the flow of both phases could be varied independently, and it was found that the rate of denitration was principally a function of the organic flow rate.

A run was made with co-current flow downward through the contactor in an effort to maintain the organic phase continuous and thus realize the maximum interfacial area. Although acceptable sol was made (PC-1, Table 2-1), gassing in the column was a problem, and constant operator attention was required. The most successful operation was achieved with co-current flow up the column and with the aqueous phase continuous. This eliminated the problem of gas accumulation. This mode of operation was used to make two runs (PC-3, -4) at identical conditions.

2.2 - Urania-Plutonia Sol Process and Equipment Development (R. E. Leuze)

This section of the report covers all aspects of mixed urania-plutonia sol preparation including preparation of high-nitrate plutonia sol, special treatment of CUSP sol prior to mixing with plutonia, techniques for mixing plutonia and urania sols, and treatments required to produce satisfactory mixed sol ready for subsequent processing into the desired ceramic form. Progress on equipment development and engineering-scale demonstration is also reported here.

All efforts at the present time are directed at setting process conditions and preparing equipment in order to demonstrate engineering-scale preparation of mixed UO_2 - PuO_2 and to produce several kilograms of irradiation test material during the first half of FY-1970. In the process selected for this demonstration, CUSP urania sol is pretreated to remove excess formate and is then mixed with a high-nitrate plutonia sol prepared by an alcohol extraction process (APEX). The mixed sol is contacted with a secondary amine to extract excess nitrate and is subsequently formed into microspheres or shards which can be dried and calcined to dense oxide product. This procedure was selected because CUSP and APEX sols have exhibited improved compatibility after mixing. It is believed that the highly crystalline characteristics of these sols are at least partially responsible for the improved behavior.

Plutonium Sol Preparation by Alcohol Extraction (L. E. Morse)

Solvent extraction equipment has been fabricated and installed in a glove box to study the preparation of plutonium sols from Pu(IV)-HNO_3 aqueous solutions by extraction with n-hexanol. The apparatus was designed by J. W. Snider of the Chemical Technology Design Section. The equipment was used in a demonstration run to prepare a dilute, high-nitrate plutonia sol.

The apparatus consists of two identical contactor-separator sections. In the first, or extraction section, nitric acid is extracted from the aqueous $\text{Pu(NO}_3)_4$ solution with n-hexanol. After phase separation, the alcohol is pumped to the second, or scrubbing section, where the acid is scrubbed from the alcohol into water. The regenerated alcohol is then recycled to the extractor. The plutonium nitrate solution is circulated through the extraction section only, and the water scrub is circulated through the scrubbing section only. All liquid circulation is obtained by means of gas-lift pumps using argon. The net result of this extraction-scrubbing cycle is to transport HNO_3 from the plutonium nitrate solution to the water scrub. When the acidity of the solution becomes sufficiently low, Pu(IV) polymer is formed. The progress of the extraction is monitored by a conductivity probe located in the circulating plutonium nitrate stream. The apparatus will be used to obtain information required to scale up the process and to provide chemical and physical data which will aid in a better understanding of the process. Operation of this equipment will also provide a convenient source of plutonia sol for the preparation of mixed urania-plutonia sols.

A solution of 0.088 M $\text{Pu}(\text{NO}_3)_4$ with a NO_3^-/Pu mole ratio of 13.1 was converted to a 0.070 M Pu polymer solution (with a NO_3^-/Pu mole ratio of 1.3) during about 9.0 hours operating time at room temperature. The entire sol preparation was spread out over about 29 hours, including the time to change the water scrub once and an overnight shutdown. Initially, extraction was continued until an almost constant conductivity value of the plutonium nitrate solution indicated that acid extraction virtually had ceased. This required about 3.5 hours of extraction. At this point, the NO_3^-/Pu mole ratio had been reduced from 13.1 to 3.6 and the specific conductivity decreased from 127×10^{-3} to 46×10^{-3} mhos/cm. During this period the color changed from brown to various shades of blue and finally to green, indicating that the plutonium had undergone disproportionation and then polymerization. The operation was suspended for about 1 hour while the water-scrub was replaced with fresh water. During this interval, the specific conductivity increased to 50×10^{-3} mhos/cm. Operation was resumed for about another hour before being shut down for the night. At this stage, the NO_3^-/Pu mole ratio was 2.4, and the specific conductivity was 34×10^{-3} mhos/cm.

After standing overnight (about 17 hours) the specific conductivity had increased to 39×10^{-3} mhos/cm. Extraction was resumed, and after about 5 hours the NO_3^-/Pu mole ratio decreased to 1.4 and the specific conductivity to 13.8×10^{-3} mhos/cm. After an additional 1.75 hours of operation, when the almost constant conductivity indicated again a virtual end to the acid extraction, the run was terminated. The product sol was 0.07 M Pu and had a NO_3^-/Pu mole ratio of 1.3 and a specific conductivity of 14×10^{-3} mhos/cm. On standing overnight at room temperature the specific conductivity was unchanged.

Mixed Plutonia-Urania Sol Compatibility Studies (O. K. Tallent)

The occurrence of thixotropic gelling is the principal indication of incompatibility in mixed CUSP-APEX sols. In past work it was found that mixed sol stability could generally be improved by partial extraction of formate from the urania sol and by increasing the crystallinity and crystallite size of either or both of the sols prior to mixing. In recent studies, the compatibility of mixed sols was found to be highly temperature dependent. The shelf life of mixed CUSP-APEX $[0.8 \text{ M } \text{UO}_2 - 0.2 \text{ M } \text{PuO}_2]$ sols increased from 5 min at 38°C , to 1 hr at 25°C , and to >5 hr at 0°C . Pre-extraction of formate from the CUSP sol with an equal volume of *n*-hexanol increased the shelf life to 4 hr at 24°C and to ~ 30 hr at 0°C . A shelf life of 24-36 hr after mixing is expected to allow adequate time for microsphere preparation. In future work the microsphere forming properties of sols which have been chilled at 0°C for several hours will be investigated.

In preliminary studies, the time required for mixed sol gelation was also found to be a function of sol concentration. Dilute sols take longer to gel, with the time to gelation being approximately inversely proportional to the sol concentration. Continued kinetic studies may help to determine which substances in the mixed sol are reacting to cause the gelation and to determine conditions for improving the stability of mixed sols.

2.3 - Sphere Preparation (P. A. Haas)

Information concerning the conversion of urania and urania-plutonia sols into microspheres of the desired size and with the desired properties is reported here. This includes studies on sphere-forming, chemistry of the sphere-forming column, recycle of the drying alcohol, drying and firing of gel spheres, and classification of the fired particles. The latest information on adapting these process steps and equipment to remote operation is also included.

Sphere Forming Column Chemistry (W. D. Bond, A. B. Meservey)

When sols are dispersed into 2-ethyl-1-hexanol (2EH) to form microspheres, not only is water transferred to the 2EH, but a number of dissolved materials (e.g., HNO_3 and HCOOH) are also partially extracted into the 2EH. If this drying alcohol is to be recycled, the extracted materials must be removed. Removal of HNO_3 and HCOOH by scrubbing the 2EH with aqueous solutions of ammonium hydroxide or sodium carbonate is being investigated. As part of this study, the distributions of materials between 2EH and various scrubbing solutions are being determined.

Batch extractions were performed to determine the distribution of ammonia and nitrate between a 0.1 M NH_4OH -0.02 M NH_4NO_3 aqueous solution and 2-ethyl-1-hexanol (2EH). Extractions were made with 2EH of four different compositions: pure 2EH; 2EH containing 0.5% Span 80; 2EH containing 0.12% Ethomeen S/15; and 2EH containing both 0.5% Span 80 and 0.12% Ethomeen S/15. After the phases were separated, the organic portions were analyzed for NO_3^- and NH_4^+ . The nitrate concentration was less than 2 parts per million, indicating a nitrate extraction coefficient (E_a^0) of $< 2 \times 10^{-6}$. From 4.0 to 4.5% of the NH_4^+ was extracted into 2EH containing either or both of the surfactants. Extraction of NH_4^+ into 2EH containing no surfactants appeared to be slightly less.

The amounts of Span 80 and Ethomeen S/15 transferred from 2EH to ammonium hydroxide solutions were determined. It was found that 1% to 4% of the surfactants can be lost to the aqueous phase by a process in which the organic phase is equilibrated with an equal volume of 0.005 M to 0.5 M NH_4OH . Each of three organic solutions (0.5% Span 80, 0.12% Ethomeen, and 0.5% Span-0.12% Ethomeen in 2EH) were shaken with equal volumes of three different ammonium hydroxide solutions (0.5, 0.05, and 0.005 M), for a total of nine cases investigated. After thorough mixing, the phases were separated by gravity or, if necessary, by centrifuging. A measured volume (~100 ml) of the aqueous phase was drawn off and carefully evaporated, leaving the surfactant as a residue. The amount of surfactant in the aqueous phase was determined by direct weighing, and the amount left in the organic phase was determined by difference. This method was validated by suitable controls. Results indicated that varying the concentration of NH_4OH did not significantly affect the extraction coefficient (E_a^0) of Span 80, which was 24 to 34. The Ethomeen extraction coefficients changed significantly with ammonium hydroxide concentration, decreasing from 90 ± 15

for 0.005 M NH_4OH to about 32 for 0.5 M NH_4OH . When the two surfactants were used in combination, the Ethomeen appeared to be effective in decreasing the amount of Span 80 scrubbed into the aqueous phase, with Span 80 extraction coefficients of about 60.

Formic acid concentrations as low as 0.01 M in the 2EH of the microsphere forming column caused a significant increase in clustering for a CUSP urania sol (ES-31, 1 M). Essentially no clustering occurred with 2EH containing 0.02% Span 80, 0.005% Ethomeen S/15, and 1% H_2O at pH 2.4 + 0.1 if formic acid was not present. Adding 0.05 M formic acid to the 2EH greatly increased the clustering. Very heavy and immediate clustering occurred at 0.75 M HCOOH (pH 3.5). Relatively large amounts of formic acid in the 2EH caused only small changes in pH; for example, 0.75 M HCOOH was required to lower the pH of 2EH from 5.0 to 3.5. The pH adjustments therefore are normally made by adding nitric acid. Clustering with 0.05 M HCOOH and 0.02% Span 80 in the 2EH was not appreciably decreased by increasing the Span concentration to 0.10%, but there was an increase in microsphere distortion from the increased Span.

Microsphere Preparation Development (P. A. Haas)

The gel spheres from CUSP sols prepared during a series of demonstration runs can be dried and fired into dense UO_2 spheres. Analyses of some calcined products are given in Table 2-2.

Table 2-2. Selected Properties of Microspheres Made from CUSP Sols

Sample	UO_2 Sol	Density g/cc (Hg at 210 psi)	BET Surface Area m^2/g
6-25-1337	CUSP-ES-29	10.36	0.007
6-26-1345	CUSP-ES-31	10.54	0.006
6-27-1517	CUSP-ES-37	10.56	0.005

These samples were prepared from 1 molar sols with 0.010-in.-diam orifice dispersers, and the mean diameters of the fired products were about 450 microns.

Additional results obtained during formation of CUSP sols into gel spheres have confirmed the need for a caustic scrub or other clean-up operation for the 2-ethyl-1-hexanol and the need to control entrainment of scrub solution. The clustering, which appears after accumulated operation at sol/2EH volume ratios >0.03 , is more severe for older sols. This could be caused either by an increasing sensitivity to clustering or a more rapid accumulation of formate or some other constituent from the sol in the 2EH.

We have purchased a liquid-liquid (Selas Corp.) separator and will test it for removal of entrained caustic scrub solution. Entrained NaOH from the scrub system does not appear to contaminate the UO_2 spheres with sodium, since the fired spheres contained only 250 to 1200 ppm Na. These values are less than the sodium content in the sols from which the spheres were formed, and there was no apparent increase in sodium contamination when the 2EH was scrubbed with caustic.

Analyses for HCOO^- show 26 to 44 mg/liter in the 2EH in the sphere forming column and 6 to 18 mg/liter in the 2EH returning to the column from the scrub columns and still. These analyses are consistent with the scrub solution analyses for HCOO^- . Both indicate that ~25% of the HCOOH in the CUSP sols is extracted into the 2EH.

2.4 - Preparation of Sol Gel Test Materials (W. T. McDuffee, P. A. Haas)

Preparation of sol-gel materials for use in other parts of the LMFBF fuel cycle program is reported here. This includes materials for irradiation capsules and for development of fuel fabrication techniques such as sphere-pac or pellet forming.

At the present time, there are fourteen requests for sol-gel material containing a total of 900 g of plutonium and 6,500 g of uranium. Most of the requests are for materials needed by members of the Metals and Ceramics Division for developing fuel fabrication methods and for TREAT, ETR, ORR, and SG3 irradiation specimens.

PuO_2 Sol Preparation

Four standard PuO_2 sols (150 g Pu each) were prepared. Sol containing 240 g of plutonium was transferred to the Metals and Ceramics Division for blending with UO_2 sol. The resulting mixed sol will be dried and converted into pellet fuel for the TREAT III and IV and the ORR and SG3 irradiation specimens.

Preparation of Enriched Urania Sol

Three urania sols containing a total of ~1 kg of 20% enriched uranium-235 were prepared from uranyl nitrate solution by the standard reduction-precipitation-peptization flowsheet. The sols were allowed to stand in order to remove those solids which readily settled. The sols were decanted from the dregs, combined, and then extracted twice with equal volumes of n-hexanol to remove formic acid. The resulting sol was quite fluid and remained so during the two weeks it was stored under argon. Analyses of the sol are as follows:

U (g/liter)	=	224.1	
U(IV)/U	=	0.86	
NO_3^- (g/liter)	=	5.79	(NO_3^-/U mole ratio = 0.1)
NH_4^+ (g/liter)	=	0.18	(NH_4^+/U mole ratio = 0.01)
Sp. G @ 25°C	=	1.2322	

This sol was mixed with plutonia and formed into microspheres (see below).

Pretreatment of CUSP Urania Sol for Mixing with Plutonia Sol

A portion of CUSP sol ES-33 containing about 1 kg of uranium was contacted twice in batch extractions with equal volumes of n-hexanol to remove formic acid. The extracted sol was very fluid and from all physical appearances was a good sol. It was stored under argon and in contact with n-hexanol for later use to prepare mixed UO_2 - PuO_2 sol. The purpose for storing the sol in this manner was to provide blanket-ing to prevent oxidation by air and to maintain the free formic acid at a low concentration.

Preparation of Microspheres from Mixed UO_2 - PuO_2 Sols

Dense microspheres of $\text{Pu}_{0.2}\text{U}_{0.8}\text{O}_2$ are being prepared for use in irradiation test specimens. In order to minimize aging effects of the mixed sols (such as gelation, increased viscosity, and increased tendency for microspheres to crack), only enough sol was mixed for one day of sphere-forming (~100 g of plutonium + uranium). These freshly mixed sols were immediately formed into microspheres.

In a series of runs, about half of the 20% enriched-urania sol was blended with plutonia sol, and the mixed sols were formed to produce dense oxide microspheres from 400 to 600 μ in diameter. Difficulties with clustering during sphere forming and with cracking during drying and calcining were encountered. Efforts were made to adjust the forming conditions to minimize these difficulties. The principal variable investigated was the acidity of the drying solvent (2EH). A summary of the results are given in Table 2-3. Attempts to start forming microspheres with 2EH at a pH of ~3 were unsuccessful because of severe microsphere clustering, coalescence into larger droplets, and sticking to the column walls. These difficulties were eliminated by acidifying the solvent to a pH of 1.5-2.0; however, the resulting spheres cracked upon drying and firing. It was possible to start sphere forming at a low pH and then to raise the pH to some higher level without recurrence of sticking and clustering (Run 3, Table 2-3). A larger fraction of good, sound spheres were produced in this run.

Intermittent additions of acid were required since ~90% of the acid added to the solvent was distilled into the aqueous condensate from the 2EH drying-still. If acid was not added, the pH of the 2EH rose to ~4.5.

Mixed plutonia-urania sols made from the pretreated CUSP sol had a shelf-life (with no apparent thickening) of at least four days and had sphere-forming properties superior to mixed sols made from the enriched urania sol. This mixed sol made from the treated CUSP sol could also be formed in a 2EH at a higher pH (starting at 3.0-3.5 and increasing to 3.5-4.0) without clustering or sticking. About 20% of the dried gel spheres formed at pH 3.0-3.5 were cracked compared to <10% of those formed at pH 3.5-4.0. Characterization of these products is not yet complete.

Table 2-3. Effect of Acidity on Formation of $\text{PuO}_2\text{-UO}_2$ Microspheres

Batch No.	Apparent pH of Solvent ^a	Sphere-Forming Behavior	Microsphere Drying Behavior	Character of Fired Microspheres
1(a)	3.2-3.5	sticking-clustering	-	-
1(b)	1.5-2.0	good; no clusters or sticking	severe cracking	100% cracked
2	1.5-2.0	generally good, but some sticking and clustering	mild cracking	~80% cracked
3	2.0-3.0	some sticking-clustering at startup-generally good thereafter	mild cracking	~40% cracked

^aThe pH of the drying solvent was maintained within this range by adding a solution made from 1 part conc. HNO_3 in 100 parts of 2EH containing a trace of Span 80.

2.5 - Plutonium Storage Facility (J. R. Parrott, R. G. Nicol, W. A. Shannon)

A facility for safely storing and handling plutonium is being built in Building 3019 to meet the needs for developmental work involving the sol-gel flowsheet for fast reactor fuels. This facility is located in the basement (room 501) adjacent to the Metals and Ceramics Division alpha laboratory. It will have a capacity of 100 kg of plutonium in a solid (fluoride) or a liquid (nitrate) form.

The vessel off-gas pipe line was joined to the Building 3019 vessel off-gas system. Installation of instrumentation and communication systems is in progress.

III. FUEL FABRICATION AND EVALUATION

A. L. Lotts, C. M. Cox, J. D. Sease, and
T. N. Washburn

The primary emphasis of fuel fabrication and evaluation studies related to the fuel cycle for the liquid-metal fast breeder reactor is on oxide fuels. The objective of our program is to obtain an economically optimized (U,Pu) O_2 fuel cycle for a liquid-metal fast breeder reactor by extending the performance capability and advancing the fabrication technology of oxide fuels. These fuels have the most advanced technology and greatest potential for reliable operation in first-generation LMFBR's. They have been tested in fast-flux environments but as yet have not been exposed under actual prototypic conditions. Currently, the burnup and heat rate are limited to about 50,000 Mwd/metric ton and 16 kw/ft, respectively, based on irradiation experiments with fuels that are not necessarily optimized for thermal, chemical, and mechanical performance.

The capability of oxide fuels can possibly be improved by adjusting structures or void distribution in the fuels. We emphasize irradiating fuels derived from the sol-gel process with thoroughly characterized structures and void distributions different from those of the oxide fuels irradiated heretofore. These include fuels fabricated by Sphere-Pac, vibratory compaction, extrusion, and pelletization. We compare the performance of these with the performance of reference fuels such as pellets derived from mechanically blended powders and coprecipitated material. The development of computer programs to assist in the analysis of test results and the development of a mathematical model to predict the performance of a fuel rod are integrated with the test program.

1. Fabrication Development

J. D. Sease

The purpose of our fabrication development work is to provide suitable fabrication processes for sol-gel-derived materials and to fabricate irradiation test specimens and capsules for a variety of irradiation tests.

1.1 Process Development (R. A. Bradley, W. L. Moore)

This work is currently concerned with the engineering-scale development of the Sphere-Pac process and the development of sol-gel pelletization techniques for the fabrication of irradiation test specimens.

1.1.1 Sphere-Pac. — Sphere-Pac is a technique for loading a fuel rod with graded microspheres. A complete description of laboratory development is contained in another document.¹ Our objective is to investigate the parameters that will allow the utilization of the Sphere-Pac process in the design of production facility. Work to date has indicated that the infiltration of the fine fraction into the coarse bed is the rate controlling process. During the month we investigated the effect of the size of the openings in the screen funnel on the filtration time of the fine fraction. In addition, we studied the infiltration rates of the fine in the core and perimeter of the coarse beds. The test consisted of loading three 0.375-in. ID pins with 8- and 14-g quantities of 510- to 600- μ thorium microspheres which had a normal distribution, and vibrating 5- to 45- μ thorium microspheres, which had a normal distribution, through the coarse beds. Each of the three pins had a screen with 88- μ , 149- μ , and 297- μ openings soldered to the bottom. All of the microspheres were stored in a desiccator when not in use. The pins were vibrated with a 60 Hz, low amplitude Syntron vibrator. The fines were loaded into the top of each of the three pins in the following manner:

1. Pouring the fines onto the top of the coarse bed and turning on the vibrator-unrestrained bed.
2. Pouring the fines onto the top of the coarse bed, setting the screen funnel on top of the fines (used as a follower rod), and turning on the vibrator-follower rod only.
3. Placing a screen funnel on the coarse bed, loading the fines onto the coarse bed and turning on the vibrator-screen funnel method.
4. Placing a screened tube (same as 3. above except the tube has a thin wall and, therefore, the fine has a greater area in which to enter the coarse bed) on top of the coarse bed and loading as in 3. above.

Two concentric cups were attached beneath the pins to collect the fine microspheres exiting from the 0.245-in. diam core of the coarse bed and from the perimeter of the bed. Table 1 gives the results of time for the fine microspheres to flow through the coarse bed and Table 2 gives the results of the quantity of fine microspheres collected from the core and perimeter of the pins. Two to four values were averaged to obtain the majority of the data points in Tables 1 and 2, while a few data points are the result of only one run; therefore, no standard deviation was calculated.

Analysis of the data showed no correlation between the four methods of loading the fines in terms of time for the fines to pass through the

¹F. G. Kitts, R. B. Fitts, and A. R. Olsen, "Sol-Gel Uranium-Plutonium Microsphere Preparation and Fabrication into Fuel Rods," pp. 195-210 in Intern. Symp. Plutonium Fuels Technol., Scottsdale, Ariz., 1967, Nucl. Met., Vol. 13, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1968.

coarse bed, nor did the loading methods affect the grams of fine microspheres per unit area collected from the center and the perimeter of the coarse bed. We found that more fines per unit area were collected from the center than from the perimeter of the coarse bed. There is a trend for the greatest quantity of fines per unit area to be collected in the center region for the pin with the 88- μ screen and to decrease to nearly equal quantities collected in the center and perimeter for the pin with the 297- μ screen. The time for the fines to pass through the coarse bed decreased with increased size of the screen supporting the coarse bed; therefore, we will investigate using larger screen sizes on the funnels for fine microsphere infiltration as a method to reduce fine loading time.

Table 1. Time (in seconds) for Fine Microspheres
to Pass Through Coarse Microsphere Beds

Loading Method	Coarse Bed Supporting Screen Size		
	88- μ Screen	149- μ Screen	297- μ Screen
Unrestricted Bed			
8 g Coarse Bed	17 $\pm$ 6	15 $\pm$ 2	11 $\pm$ 3
14 g Coarse Bed	21 $\pm$ 7	16 $\pm$ 2	14 $\pm$ 4
Follower Rod Only			
8 g Coarse Bed	14	14	10
14 g Coarse Bed	--	16	13
Screen Funnel			
8 g Coarse Bed	14	17 $\pm$ 3	13 $\pm$ 2
14 g Coarse Bed	21 $\pm$ 4	17 $\pm$ 2	15 $\pm$ 4
Screen Tube			
8 g Coarse Bed	14 $\pm$ 1	15 $\pm$ 1	13
14 g Coarse Bed	18	17 $\pm$ 2	12

Table 2. Grams of Fine Microspheres/Inch² Collected
From the Core and Perimeter of the Coarse Bed

Loading Method	Coarse Bed Supporting Screen Size					
	88- μ Screen		149- μ Screen		297- μ Screen	
	Fines Collected at:		Fines Collected at:		Fines Collected at:	
	Core	Perimeter	Core	Perimeter	Core	Perimeter
Unrestricted Bed						
8 g Coarse Bed	8.35 $\pm$ 0.35	6.40 $\pm$ 0.27	8.45 $\pm$ 1.10	6.33 $\pm$ 0.80	8.00 $\pm$ 0.35	6.70 $\pm$ 0.18
14 g Coarse Bed	8.66 $\pm$ 0.11	6.15 $\pm$ 0.06	9.01 $\pm$ 2.25	9.89 $\pm$ 1.22	7.82 $\pm$ 0.05	6.82 $\pm$ 0.04
Follower Rod Only						
8 g Coarse Bed	8.91	6.00	8.55	6.26	7.57	7.00
14 g Coarse Bed	----	----	8.36	6.41	6.76	7.60
Screen Funnel						
8 g Coarse Bed	9.40	5.90	8.38 $\pm$ 0.56	6.38 $\pm$ 0.41	7.29 $\pm$ 0.54	7.23 $\pm$ 0.41
14 g Coarse Bed	8.51 $\pm$ 0.76	6.27 $\pm$ 1.30	8.25 $\pm$ 1.30	6.49 $\pm$ 0.96	6.77 $\pm$ 0.88	7.57 $\pm$ 0.69
Screen Tube						
8 g Coarse Bed	7.94 $\pm$ 0.04	6.73 $\pm$ 0.04	8.06 $\pm$ 0.18	6.63 $\pm$ 0.13	7.56	7.00
14 g Coarse Bed	7.00	5.93	8.25 $\pm$ 1.16	6.49 $\pm$ 0.88	7.81	6.81

In determining the loading times in the short beds, we found the standard deviation to be higher than we first anticipated. This deviation is probably due to random packing in the short beds causing variation of effective open channels.

The fabrication of parts for an elutriation column has begun. This device will be used to separate desired fractions of fine microspheres for investigation of the effect of particle size distribution on Sphere-Pac loading times and densities.

1.1.2 Pelletization of Sol-Gel Urania-Plutonia. - During the past month our efforts were concentrated on making the annular pellets required for the ORR SG-3 capsule. The specifications for these pellets are:

OD	0.343 in.
ID	0.125 in.
Length	0.300 to 0.350 in.
Total fuel length	3 in.
Pellet density	$83.1 \pm 1.0\%$ T.D.
Smear density	$81.0 \pm 1.0\%$ T.D.
O/M	1.98 ± 0.01
Pu/(U,Pu)	0.20

We first attempted to make the pellets out of powder which had been calcined previously for Atomics International; however, the densities ranged from 84.8 to 89.5% T.D. for pellets pressed at 25,000 to 40,000 psi. Also, the shrinkage of this powder was excessive so the outside diameters of the pellets were too small.

We, therefore, calcined additional powder by heating it in argon to 520°C, holding 4 hr, and then cooling in CO₂. This differed from the calcination of the ETRAI powder in that argon was used instead of Ar-4% H₂. An experimental run was made to determine the relationship between forming pressure and sintered density. It was found that pellets pressed at 30,000 psi from this powder and sintered in Ar-4% H₂ at 1450°C for 10 hr had densities of about 83.5% T.D., outside diameters of 0.346 in., and inside diameters of 0.124 in. A total of 21 pellets was made in three sintering runs. The densities of these pellets ranged from 83.1 to 85.0% T.D. with an average of 84.0% T.D.

The O/M of the pellets in the three sintering runs was 2.003, 2.004, and 1.995; therefore, we heat treated them at 1300°C using Ta foil as a getter. The results of the O/M analysis on pellets from this heat treatment have not been received.

1.2 Capsule Fabrication (E. J. Manthos, M. K. Preston, R. B. Pratt)

Fabrication of the two instrumented TREAT capsules (TREAT I and II) has been completed and planning for the fabrication of the EBR-II, Series II fuel rods begun.

1.2.1 TREAT Capsule Fabrication. - Fabrication of the initial two instrumented TREAT capsules TR-I and TR-II is complete. After final assembly and leak testing, each capsule was heated to 435°C to test the heaters and 12 thermocouples. Heating and cooling curves were obtained for each capsule and these data will be used to calculate the heat capacity of each capsule. A preirradiated heating cycle to be used at the TREAT Reactor was also developed. As a final step, the resistance of each heater and thermocouple was measured and recorded; this information will be used to check out each capsule after it is installed in the TREAT.

Two 1/8-in. diam × 41-in. long stainless steel tubes were welded to the exterior of each capsule; these tubes will each contain an external flux monitor wire. The shipping container for the two capsules was modified to accommodate the 1/8-in. diam tubes. United States Department of Transportation approval to ship alkali metals and fissile material in the same container still has not been received.

All data sheets, certification papers for materials, inspection reports, and x rays are being compiled for each capsule. These data are now complete.

An inventory of all TREAT materials, both rough stock and machined hardware, is being compiled so as to facilitate purchase or fabrication of components for the TREAT capsules, TR-III and TR-IV. In addition, new designs for the heat sinks and heater can for TR-IV are being sketched for drafting in the near future.

All but two pictures have been taken of the assembly sequence and hardware for future reference and for inclusion in the assembly report.

1.2.2 EBR-II, Series II Unencapsulated Fuel Rods. - We are planning to irradiate a set of unencapsulated fuel rods in a 37-rod subassembly in the EBR-II Reactor. This subassembly will be jointly shared by the Babcock and Wilcox Company and ORNL. The objectives of this ORNL Series II, EBR-II irradiation tests are to establish the performance characteristics and limitations of (U,Pu)O₂ fuels fabricated by different processes in a fast-flux environment and to use these data, together with other complementary test data, to define fabricated fuel characteristics required for oxide fuels for advanced LMFBR applications. For the ORNL test rods, we will concentrate on sol-gel-derived pelletized and Sphere-Pac fuel for comparison with the B & W Vi-Pac and pellet fuel. In initial tests, we will irradiate 19 fuel rods. Fabrication form, fuel density, and oxygen-to-metal ratio will be varied in the 19 rods as shown in Table 3. The preliminary fuel rod design calls for 0.250-in. OD by 0.015-in. wall, type-316 stainless steel cladding. The cladding length will range from 40 to 60 in. long, depending upon the type of subassembly used for the irradiation test. The fuel column length will be 13.5 in. and the balance of the rod interior will contain depleted UO₂ blanket pellets, thorium oxide insulators, and an extensometer shielded by a nickel plug.

During the past month we have become familiar with the preliminary design for the fuel pins, as well as the requirements set forth in the EBR-II Experimenters' Manual. From this and other information, an arrow diagram has been prepared to show the interaction of various steps required for fabricating pins.

Table 3. ORNL, Series II, EBR-II Irradiation Tests
19 Allotted Positions
in the Proposed 37-rod Subassembly

Rod Number	Fuel Form	Smear Density (% T.D.)	O/M
19	Sphere-Pac	80	1.98
20	Sphere-Pac	80	1.98
21	Sphere-Pac	85	1.98
22	Sphere-Pac	85	1.98
23	Sphere-Pac	85	1.98
24	Sphere-Pac	85	1.98
25	Sphere-Pac	80	1.94
26	Sphere-Pac	80	1.94
27	Sphere-Pac	85	1.94
28	Sphere-Pac	85	1.94
29	Sphere-Pac	85	1.98
30	Sphere-Pac	85	1.98
31	Pellet	85	1.98
32	Pellet	85	1.98
33	Pellet	90	1.98
34	Pellet	90	1.98
35	Pellet	80	1.94
36	Pellet	80	1.94
37	Pellet	85	1.94

2. Fuel Evaluation

C. M. Cox, T. N. Washburn, and J. M. Leitnaker

The fuel evaluation work involves both out-of-reactor and in-reactor tests to characterize the fuels of interest and to determine performance limits of the fuels.

2.1 Characterization of Fuels (W. H. Pechin)

The development of sol-gel fuel fabrication requires characterization of the material to control the process and to determine which properties are important to irradiation behavior. Characterization requires determining both the chemical composition and the physical properties. Thermodynamic studies will contribute to the development of the process for the fuel and will aid in predicting fuel performance for both irradiation testing and model studies.

2.1.1 Analytical Chemistry. -- We are studying the analytical chemistry of $(U,Pu)O_2$ as it applies to the control of fuel fabrication processes and the qualification of the fuel for irradiation testing.

During this period we have continued our investigation of the release of sorbed gas from sintered sol-gel pellets.

The pellets remaining from the batch prepared for loading TREAT capsules I and II were utilized in an experiment to determine the correlation between gas release and other pellet properties. A secondary objective of the experiment was to determine the precision of the analyses for C, N, bulk density, and porosity. Six sintering runs numbered 78 through 84 were prepared for TREAT. Runs 78 through 82 were low density pellets (84% T.D.), while runs 83 and 84 were high density pellets. There were not enough pellets from the high density runs to get a full set of analyses. There were two pellets remaining from run 83 and none from 84. Of the low density runs, there were enough pellets except for run 82 which had only one pellet remaining.

From runs 78 through 81, seven pellets were broken in half. One-half pellet was submitted for each analysis to obtain five gas release, three carbon, three nitrogen, and three bulk density-porosity determinations for each run. Samples were submitted and analyzed in random order. The analytical results are listed in Table 4 and the precision of the analyses in Table 5.

The data were treated by an analysis of variance technique to determine which sintering runs had significantly different properties. The carbon content and bulk density did not vary significantly in runs 78 through 81. The nitrogen content of run 79 was significantly lower and the porosity of run 81 was significantly higher than the other runs.

It was found that either the bulk density or the porosity data has a positive bias since the two consistently combine to give a density greater than theoretical.

Table 4. Analytical Results for TREAT Pellets

Sintering Run	Carbon (ppm)	Nitrogen (ppm)	Bulk Density (g/cm ³)	Porosity (%)
78	85	40	9.14	18.17
79	71	19	9.23	17.91
80	74	54	9.04	19.46
81	77	47	8.60	23.10
82	66	--	----	----
83	43	--	----	----

95% confidence limits
 Carbon 28 ppm
 Nitrogen 21 ppm
 Bulk density 0.38 g/cm³
 Porosity 2.37%

Table 5. Precision of Several Routine Analyses
for Mixed Oxide Pellets

Analysis	Standard Deviation
Carbon	20 ppm
Nitrogen	15 ppm
Bulk Density	0.29 g/cm ³
Porosity	1.78%

The strongest effect on gas release was time. The gas release data from this series of analyses were combined with all previous gas release values for these sintering runs and plotted as a function of time since the final heat treatment. The data could be divided into three groups, all of which extrapolated back to an initial value of about $0.05 \text{ cm}^3/\text{g}$. The high density pellets of run 83 give a value of about $0.10 \text{ cm}^3/\text{g}$ after 60 days. The pellets from runs 78, 80, 81, and 82 give a value of $0.42 \text{ cm}^3/\text{g}$ after 60 days, while pellets from run 79 give a value as high as $0.80 \text{ cm}^3/\text{g}$ after 60 days. Although the nitrogen content for run 79 was significantly lower than the other runs, it is not felt that this is the explanation for the greater gas release from these pellets. A more likely explanation is that the oxygen-to-metal ratio of some of the pellets from run 79 was 1.97 compared to 1.98 to 1.99 for the other runs. While the greater open porosity of run 81 is significant when compared to the scatter in the data, it does not appear to have increased the gas release behavior significantly in this case.

In summary, the gas release values appear to be less than $0.10 \text{ cm}^3/\text{g}$ when the pellets are initially removed from the furnace, but this value increases with time. This behavior is probably caused by the adsorption of water from the atmosphere during storage and indicates the importance of proper storage and prompt loading of the fuel. The absolute minimization of gas release at values below $0.05 \text{ cm}^3/\text{g}$ may be dependent on controlling such factors as carbon and nitrogen content and fraction of open porosity. Because of the comparative lack of data on fresh pellets and the small or nonexistent variation of these factors between sintering runs so far, it is impossible to judge their effect.

2.1.2 Fission Product Interaction. - Interaction of alkali metals with UO_2 is of interest for two reasons. First, the coolant proposed for liquid metal fast breeder reactors is sodium. Pin holes in the clad may allow sodium to diffuse into the fuel pin, driven by the reaction of sodium with the fuel. Second, since cesium is a prominent fission product, the extent to which the cesium reacts with fuel, clad, and other fission products is important in interpreting results in in-reactor tests.

One convenient way of studying the stability of sodium uranates is by means of the reaction

Thermodynamics data exist for all of the reactants and products. Kubaschewski, Evans, and Alcock² tabulate heats of formation, ΔH°_{298} , and entropies, S°_{298} , of UO_2 , Na_2CO_3 , and CO_2 . Data for oxygen can be

²O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, Metallurgical Thermochemistry, 4th ed., Pergamon Press, New York, 1967.

obtained from Stull and Sinke.³ Rand and Kubaschewski⁴ list a value for the enthalpy of formation of Na_2UO_4 , and one can estimate its entropy by assuming it is the sum of the entropies of UO_3 and Na_2O . From these data and simple assumptions, we calculate that the enthalpy of Reaction (1) is -53.4 kcal and the entropy change is +16.1 eu, both at 298°K. Heat capacities as a function of temperature for the same materials can be obtained also. Thus, at 1000°K, we compute ΔG° for Reaction (1) to be -66,010 cal.

There are several ways to view this free energy change value. For example, if the CO_2 pressure were maintained at one atmosphere, the equilibrium oxygen pressure at 1000°K could be computed to be about 10^{-29} atm. Alternatively, since a CO/CO_2 ratio can be used to fix the oxygen potential, if one had one atmosphere of CO_2 , a pressure of CO of 10^4 atm would be observed at equilibrium.

Our conclusion was that heating UO_2 mixed with Na_2CO_3 in a CO/CO_2 mixture of 10:1 would produce Na_2UO_4 —or some other sodium uranate. Any higher pressure of CO_2 would increase the tendency for Reaction (1) to take place. However, the expected reaction did not take place. Samples heated at 800°C for 33 hr with intermediate cooling (for weight loss determinations and an x-ray sample) lost about the amount of weight which would be accounted for by the excess oxygen in the UO_2 used and some moisture in the Na_2CO_3 . The x-ray patterns showed only sharp lines of nearly stoichiometric UO_2 . (We have never been able to see the Na_2CO_3 in these samples.)

Heating the Na_2CO_3 - UO_2 mixture in a 1:1 CO/CO_2 mixture for 42 hr also did not produce any visible reaction, except that the oxygen content of the UO_2 was slightly higher ($\text{O}/\text{U} = 2.01$) as determined from the lattice parameters, $5.46966 \pm 0.00013\text{\AA}$.

However, heating a 1:1 mixture of UO_2 - Na_2CO_3 in a 100:1 CO_2/CO mixture at 900°C did produce reaction. This reaction was detected in two ways: (1) An x ray produced a new pattern and (2) a considerably larger weight change was observed, corresponding to additional loss of CO or CO_2 .

A number of experiments related to this new phase have been performed. Mixtures of 2:1 and 3:1 mole ratios of UO_2 - Na_2CO_3 were heated in 10:1 CO_2/CO mixtures to produce the new phase. Both the 1:1 and 2:1 mixtures have been single phase by x ray but the 3:1 mixture produces a two-phase pattern—a mixture of the new phase and UO_2 . We cannot decide as yet whether the new phase has a sizeable range of homogeneity.

³D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, American Chemical Society, Washington, D. C., 1956.

⁴M. H. Rand and O. Kubaschewski, The Thermochemical Properties of Uranium Compounds, Interscience Publishers, New York, 1963.

Perhaps the most significant piece of information is that on heating the reacted $\text{Na}_2\text{CO}_3\text{-UO}_2$ mixture at 900°C in 1:1 CO/CO_2 mixture, we obtain two products. One of the products is UO_2 and the other appears to be Na_2CO_3 with some Na_2O . (X-ray evidence is not yet available, but a water solution of the white material which collected on the sides of the crucible was strongly basic while Na_2CO_3 should be only slightly basic.) Thus, we appear to have approached equilibrium from two directions. The new compound formed appears to be a Na-U-O compound and not a carbonate compound, but this is not certain. A large batch is being prepared so that chemical, x-ray, and metallographic analyses can be made.

X-ray diffraction patterns of the new compound appear to show some resemblance to orthorhombic CaUO_3 , but indexing has not yet been accomplished.

2.1.3 Formation of Sodium Uranates (M. Allen, J. M. Leitnaker, AnnaBella Schaupp). — We have attempted to prepare pure samples of Na_2UO_4 and $\text{Na}_2\text{U}_2\text{O}_7$. The purpose is to provide background information so that the analogous mixed (U,Pu) compounds can be prepared for standards for the hot-cell electron microscope.

The procedure is to mix Na_2CO_3 and UO_2 in the proper proportions and heat in air or oxygen. So far, our samples have all been diphasic as determined by x ray. Metallographic techniques on pressed and sintered pellets are being attempted; but, thus far, have yielded uncertain results. We will not attempt to obtain chemical analyses until we have better information on obtaining single-phase material.

2.1.4 Chemical Effects of Nuclear Burnup on (U,Pu) O_2 Fuels (J. M. Leitnaker, K. E. Spear). — We have previously shown the difference in the calculated oxygen contents of the oxide fuel if the rare earths are dissolved, either as RE_2O_3 or as REO_2 at a variety of starting compositions. This oxygen content—or really oxygen potential—is important to know if one is to correctly interpret the results of compatibility experiments.

An experiment has been started to determine the oxygen content at specific oxygen potentials of solid solutions of rare earths and uranium. Because Eu_2O_3 was at hand and is a fission product, although not the most important one, and further, because it is one of the least likely to show oxidation, this compound was chosen as the initial one for study.

For this study, Eu_2O_3 and UO_2 were each equilibrated separately, using Pt buckets, in a 10:1 mixture of CO/CO_2 at 1200°C for 16 hr. An x-ray pattern of each material was taken, revealing the monoclinic form of Eu_2O_3 and the cubic form ($a_0 = 5.47075 \pm 0.00016\text{\AA}$) of UO_2 . These materials were then ground to pass 325 mesh-screen and mixed together by shaking 26.4651 g of the UO_2 with 3.1915 g of the Eu_2O_3 . From this mixture, a sample (27.0211 g) was heated in a 10:1 CO/CO_2 mixture for 16 hr. An increase of 0.1005 g was measured to eliminate any conceivable experimental error. If it were assumed that the weight change corresponded to the Eu specimen being oxidized from the +3 state to a higher

state, the Eu would be dissolved as $\text{EuO}_{1.88}$. This result seems to indicate that the oxygen potential in a fuel element will not rise as rapidly during burnup as feared. Further work needs to be done to establish, quantitatively, the effect of the rise. X-ray patterns of the solid solution reveal that true equilibrium has not been attained. Further efforts will be required to determine how to achieve this. We expect to investigate other rare earths as well.

2.1 Irradiation of Fuels (C. M. Cox, T. N. Washburn, E. L. Long, Jr., H. C. McCurdy)

The final evaluation of $(\text{U,Pu})\text{O}_2$ fuels will be based upon their irradiation performance. The irradiation testing program is concentrating on comparative tests of three fabrication forms: Sphere-Pac, pellets, and extrusions. The program includes thermal-flux irradiations that permit use of instrumented capsules and achievement of high burnup levels in relatively short times. These tests will provide supplemental information essential to the analysis of the fast-flux irradiation tests, in which the radial fission-rate distribution and cladding damage are more typical of anticipated LMFBR operating conditions. The test program also includes power transient tests to investigate fuel performance under abnormal operating conditions. The development of mathematical models to predict fuel behavior and of computer programs for analyzing fuel performance are integral parts of the irradiation test program.

2.2.1 Uninstrumented ETR Tests (A. R. Olsen, D. R. Cuneo). -- A series of tests was initiated in 1969 using uninstrumented capsules designed for irradiation in the X Basket facilities of the Engineering Test Reactor (ETR).

The status of the tests in this series is unchanged from that reported last month.⁵ Experiment 43-113 will be reinserted in the ETR during the Cycle 104 Reactor shutdown. We were unable to obtain, within a reasonable period of time, a neutron radiograph to check the NaK level in this capsule. However, the neutron radiographs made at the MTR after achieving a calculated burnup of 7.5% FIMA were of excellent quality and show no problems which might prevent the achievement of the full scheduled 10% FIMA burnup.

The dissolution studies on capsule 43-116 are reported in section 1. As yet, there is not sufficient analytical data available to calculate the burnup levels in the various rods.

⁵R. E. Adams, C. M. Cox, D. R. Cuneo, V. A. DeCarlo, R. B. Fitts, A. R. Olsen, C. F. Sanders, and K. R. Thoms, "Irradiation of Fuels," LMFBR Fuel Cycle Studies Progress Report No. 5, ORNL-TM-2671 (August 1969), pp. 89-91.

2.2 Instrumented ETR Tests (C. F. Sanders)

Four instrumented capsules will be inserted in the ETR on November 30, 1969 (ETR cycle No. 106). Two capsules (43-120 and 43-121), containing a 21-in.-long fuel column, with all of the plutonium in the coarse microspheres, will be irradiated to determine the performance of long fuel columns of sol-gel-derived Sphere-Pac. The other capsules (43-122 and 43-123) will each contain four 3-in.-long fuel pins with two pins containing pelletized fuels and two pins containing Sphere-Pac fuels. These will be operated at low heat rates to investigate the swelling of Sphere-Pac fuels under conditions of high fission-gas retention.

The detailed design is approximately 90% completed, and all of the hardware has been ordered. The delivery date for most of the hardware and fuel is scheduled for the last of September. Therefore, the assembly should be completed by the middle of October.

2.2.3 ORR Instrumented Tests (R. B. Fitts, D. R. Cuneo, V. A. DeCarlo, R. L. Senn). - The ORR instrumented irradiation tests are designed to study the thermal performance of experimental fuel rods. Temperatures of the cladding and fuel center and rates of heat generation in the fuel rod are continuously measured and recorded. These data will be used to evaluate the in-reactor thermal characteristics of various fuels and the effects of irradiation conditions upon the temperatures and rates of structural change within the operating fuels. The SG series of experiments, previously described,⁶ is studying sol-gel-derived (U,Pu)O₂ fuels.

Capsule SG-2 is presently undergoing postirradiation disassembly in preparation for detailed examination.

Capsule SG-3 is being fabricated. An analysis of the available flux level in the ORR poolside facilities has shown that this capsule should be operated in the O5 rather than the originally planned O3 poolside position. There is still some question about the adequacy of the maximum flux in this facility; but Reactor Operations has been requested to rearrange the ORR core fuel loading slightly to raise the flux level. The experiment is designed so that it can be moved to the higher flux P4 position, if necessary, for maximum power operation.

2.2.4 TREAT Reactor Tests (C. M. Cox, R. E. Adams, E. J. Manthos). - The Series I TREAT experiments will compare the transient behavior of sol-gel-derived Sphere-Pac and pelletized (U,Pu)O₂. The first two capsules, TR-I and TR-II, will be shipped to the TREAT Reactor as soon as DOT and TREAT approvals are received.

⁶Adams, op.cit., pp. 91-92.

The draft of the hazard analysis for the Series I TREAT experiments is being revised to consider the more severe power transients proposed for the maximum accident case.

The maximum accident assumes that clipping fails so that the transient is temperature limited. The resulting fission heat is three times the maximum design value. A maximum pressure in the inner capsule of 2800 psi was calculated at about 2.1 sec, which decreases to 1380 psi as heat flows to the outer capsule components; however, the adiabatic temperature of the inner capsule wall is about 825°C at 3.0 sec. Thus, the inner capsule could fail and release hot gases and sodium to the 2.3 liter void space within the pressure vessel. Sodium vapor would condense, and the pressure increase is estimated to be 20 psi, which gives a negligible stress increase for the 2.50 ID, 0.25-in. wall AISI-4130 steel pressure vessel at its adiabatic temperature of 374°C.

The heat generated by the maximum accident is sufficient to melt much of the aluminum heat sink. Should molten aluminum escape from the inner capsule, it would solidify upon contact with the cooler exterior capsule components, and no damage to the outer pressure vessel would be expected.

A rough draft of the TREAT Reactor Operating Manual for the first two irradiation capsules in the Series I experiments has been completed.

2.2.5 Fast-Flux Irradiation Tests (A. R. Olsen). — Although the thermal flux irradiation tests will provide information on many of the fuel performance characteristics of Sphere-Pac fuels, they do have different fission distributions from fast flux tests. The EBR-II tests are designed to approximate the conditions to be encountered in an operating LMFBR. The first five test rods of (U,Pu)O₂ Sphere-Pac fuel being irradiated in the EBR-II as ORNL Series I encapsulated tests have been exposed to 4710 Mwd of reactor operation as of July 31, 1969. This is equivalent to approximately 2.6% FIMA burnup for the peak linear heat rate rod. The currently scheduled peak exposure is 7500 Mwd of reactor operation.

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