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AQUEOUS PROCESSING OF LMFBR FUELS

PROGRESS REPORT

MAY 1969

NO. 3

Compiled by:

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

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ORNL-TM-2624

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

AQUEOUS PROCESSING OF LMFBR FUELS
PROGRESS REPORT
MAY 1969
NO. 3

Compiled by:

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JUNE 1969

OAK RIDGE NATIONAL LABORATORY
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Note: Previous issues of this report are identified as:

ORNL-TM-2552
ORNL-TM-2585

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

ABSTRACT

This report continues a series outlining progress in the development of aqueous methods for the reprocessing 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 PuO_2-UO_2 values, the containment of volatile fission products, and product purification for subsequent reconstitution into reactor fuel. 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 Annual Report.

HIGHLIGHTS

When samples of irradiated (20% PuC-80% UC) pellet remnants were oxidized at 750°C, conversion of the carbides to $(U, Pu)O_2$ was almost quantitative and 81 to 97% of the ^{85}Kr was released to the off-gas.

In studies of factors affecting release of iodine from nitric acid solutions, iodide ion was more effective than NO gas, sodium nitrite, or bisulfite in reducing non-volatile iodate to volatile free iodine.

Preliminary results were encouraging in using a spiral wire brush for transporting stainless steel hulls and spacer wires through a continuous screw-type leacher.

Adding 0.01 M Fe(II) to the 0.01 M HNO_3 solution used to co-strip plutonium and uranium from 15% TBP prevented plutonium retention by dibutylphosphoric acid impurity present in the solvent.

A digital computer code for predicting plutonium and uranium distribution in the Purex system is now operational.

Preliminary tests indicated that iodine can be removed from spent mercuric nitrate-nitric acid solutions by solvent extraction with organophosphorus esters or amines. This might permit re-use of these solutions for scrubbing iodine from off-gases. The extracted iodine, however, is difficult to strip from the solvent.

Catalytic oxidation of n-dodecane, using Hopcalite catalyst, at 500°C resulted in essentially complete conversion of the n-dodecane to CO_2 and H_2O. At 350°C, however, apparently only about 30% of the n-dodecane was completely destroyed with the balance being converted to unidentifiable low-boiling hydrocarbons.

TASK 1 - SHIPPING

(A. R. Irvine, B. B. Klima, R. S. Lowrie, C. H. Odom
D. C. Watkin, E. I. Wroblewski)

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.

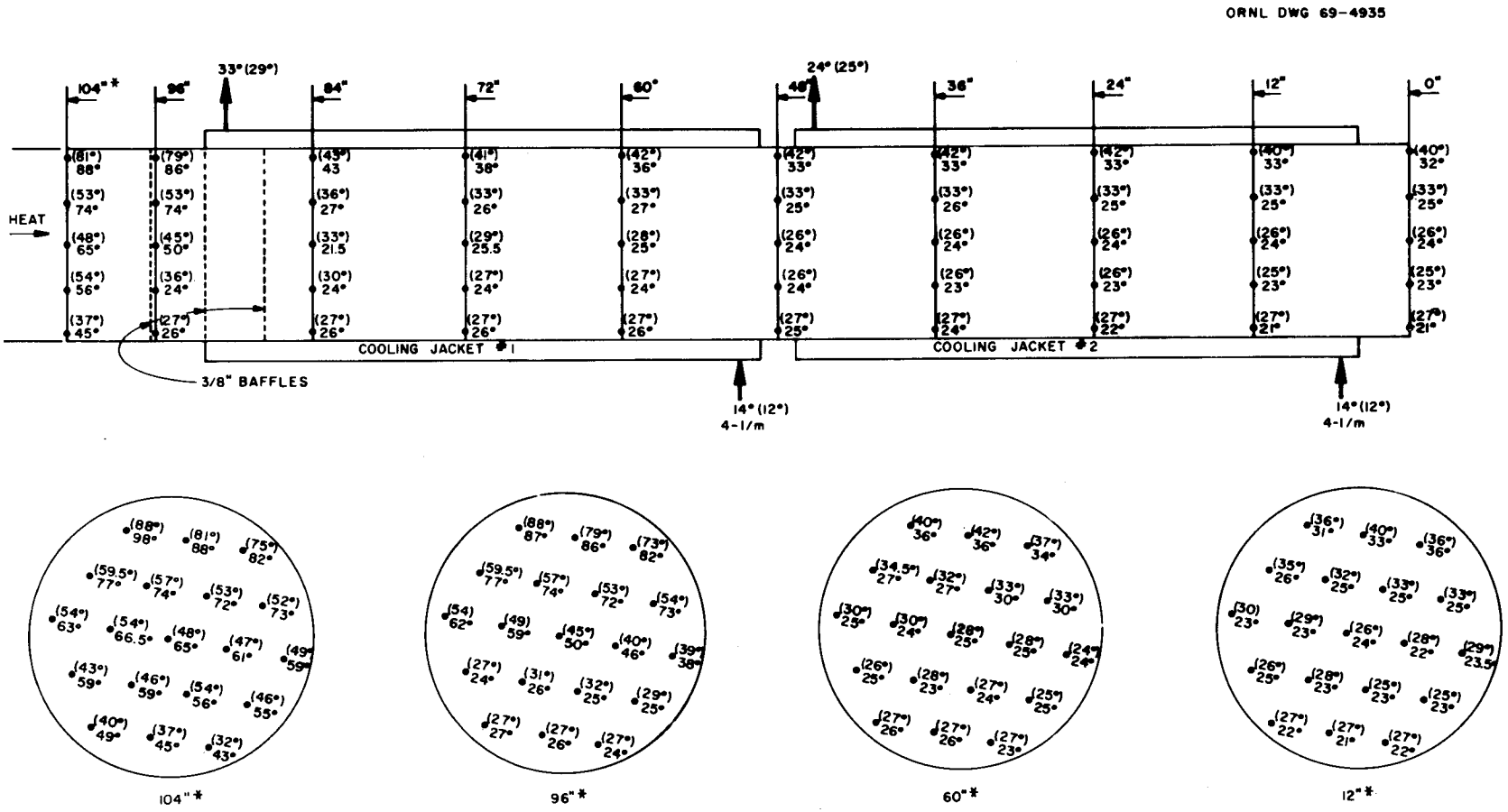
Reportable accomplishments include the following:

Task 1.2. - Heat Dissipation Tests

A. A reduced scale cask mockup was operated this month with mercury as the heat transport media. (A schematic drawing of this device can be found in ORNL-TM-2552.) The data for mercury, and similar data taken earlier for water, is displayed in Figs. 1-1 and 1-2. The scatter of data is sufficient to cause us to doubt its accuracy. To correct this situation, we will modify the equipment to improve temperature sensing capability and reduce unmeasured heat losses.

   The sharp break in temperature in the area of the three partial baffles near the heated end of the mockup appears to be out of proportion to the variation in flow resistance that would be expected. It is conjectured that the operative mechanism is dissipation of the heat transport fluid's kinetic energy at the point where the fluid is forced to change direction. We surmise that the major resistance to fluid (and heat) flow in this type of system is the inertia of the fluid. In any case, it can safely be concluded from these observations that fuel subassembly supports should be arranged to present minimal interference to fluid flow within the fuel cavity.

B. The components for test of heat transfer within an electrically heated mockup of an Atomics International Reference



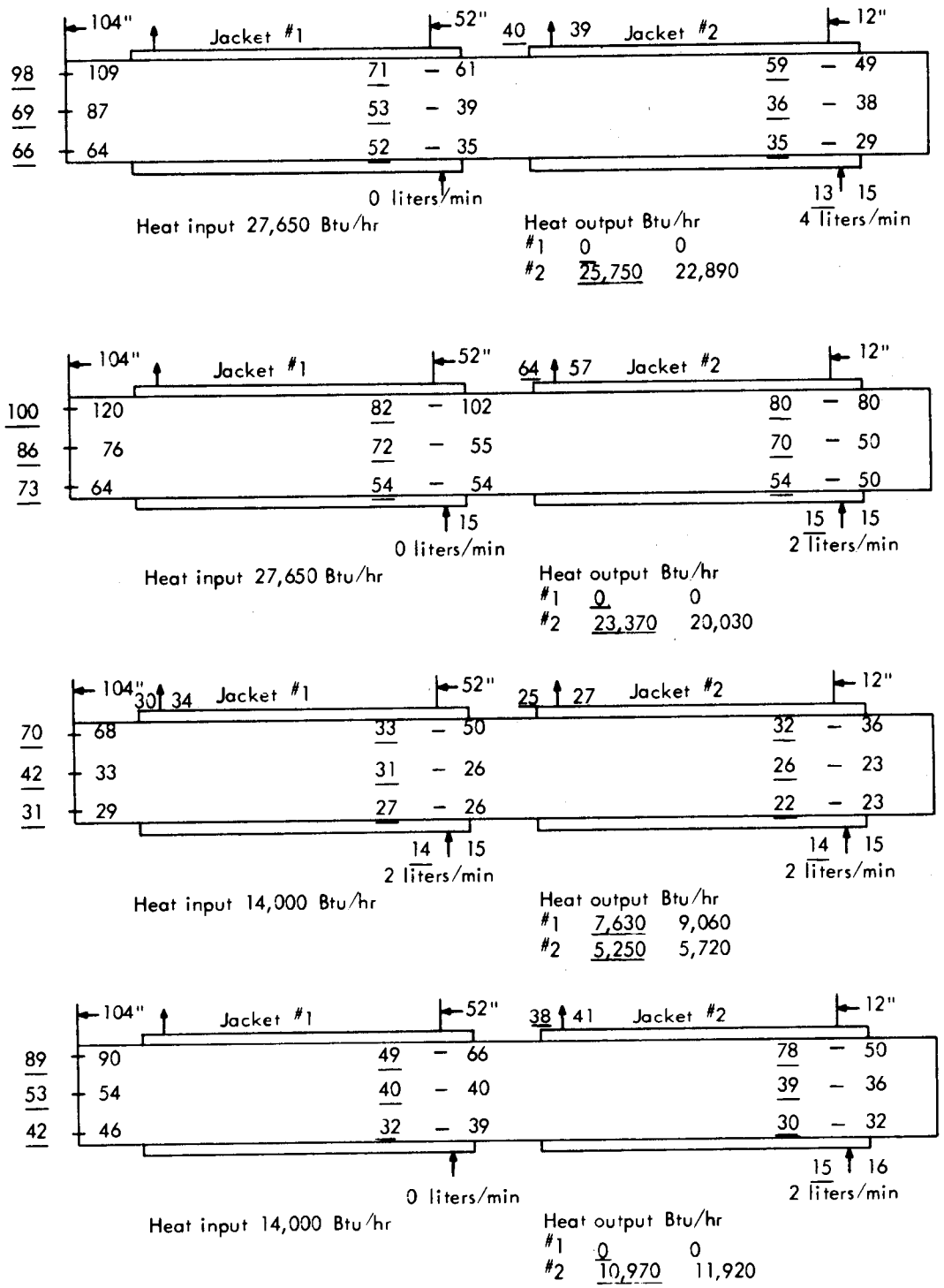
RUN # NCE-5-Hg
MERCURY AS HEAT TRANSFER MEDIA
HEAT IN - 27,660 Btu/hr
HEAT OUT - JACKET #1 - 18,100 Btu/hr AT 4 lpm H_2O
JACKET #2 - 9,530 Btu/hr AT 4 lpm H_2O

RUN # NCE-2-H_2O
WATER AS HEAT TRANSFER MEDIA
HEAT IN - 27,660 Btu/hr
HEAT OUT - JACKET #1 - 18,100 AT 4 lpm H_2O
HEAT JACKET #2 - 12,400 AT 4 lpm H_2O

NOTE
1 - TEMPERATURES ARE IN °C
2 - CONDITIONS WITH WATER FILL ARE IN PARENTHESES

Fig. 1-1. Cask Mockup Operating Data with Water and Mercury as Heat Transport Media.

ORNL DWG 69-4934



Note: Underlined H_2O; other mercury.

Fig. 1-2. Cask Mockup Operating Data with Water and Mercury as Heat Transport Media

Oxide Reactor fuel subassembly are being assembled into a working test device. Completion of the system is still expected in June.

C. The design of a full-scale, half length, 37-subassembly, sodium cooled, electrically-heated cask mockup is ~ 99% complete. Fabrication of the components is underway in ORNL shops. Essentially all the fabrication effort has been expended on the main test piece. The three shell pieces have been rolled and the seam welds made. The 5-in.-diam tubes have been cut to length and the welds dye penetrant tested and radiographed.

D. A "fish-tank" like device (see Fig. 1-3) is being operated by a second pair of MIT Practice School students. The first pair of students was P. Vayn and D. Swanson; the second pair is S. Bowers and T. Konishi. Their observations regarding the flow pattern and velocity profiles in the system are shown in Figs. 1-4 and 1-5, respectively. The flow pattern indicates a rather strong influence by inertia of the fluid.

E. A computer code is being devised that is intended to describe the transport of heat within a fluid-filled cavity. Although this code will finally have the capability for solution to three dimensional problems, the equations are initially arranged for two dimensions only. The equations take into account all known factors that affect heat and fluid flow. The code, prepared by Robin Texton and George P. Farris of the Computing Center, still has some defects which prevent its being operational.

Tasks 1.3 and 1.4 - Cask Integrity Studies and Tests

F. Additional tensile specimens are being prepared to determine a satisfactory method of connection of tensile members to a cask crash frame. The tensile members are intended for absorption of kinetic energy by stretching beyond their elastic limit. Other shop work is being delayed by lack of availability of craft time.

G. A test rig was designed for use in testing longer tensile specimens.

H. Work was started on design of cask-and-crash frame models to be used to prove the principal of the bird cage type energy absorber. These will be conservatively designed and will be drop tested in various attitudes.

I. A concept of a test device was prepared for the cask plug sealing system that was reported in the previous report (ORNL-TM-2585). One of the prime problems is that of providing a

ORNL DWG 69-4930

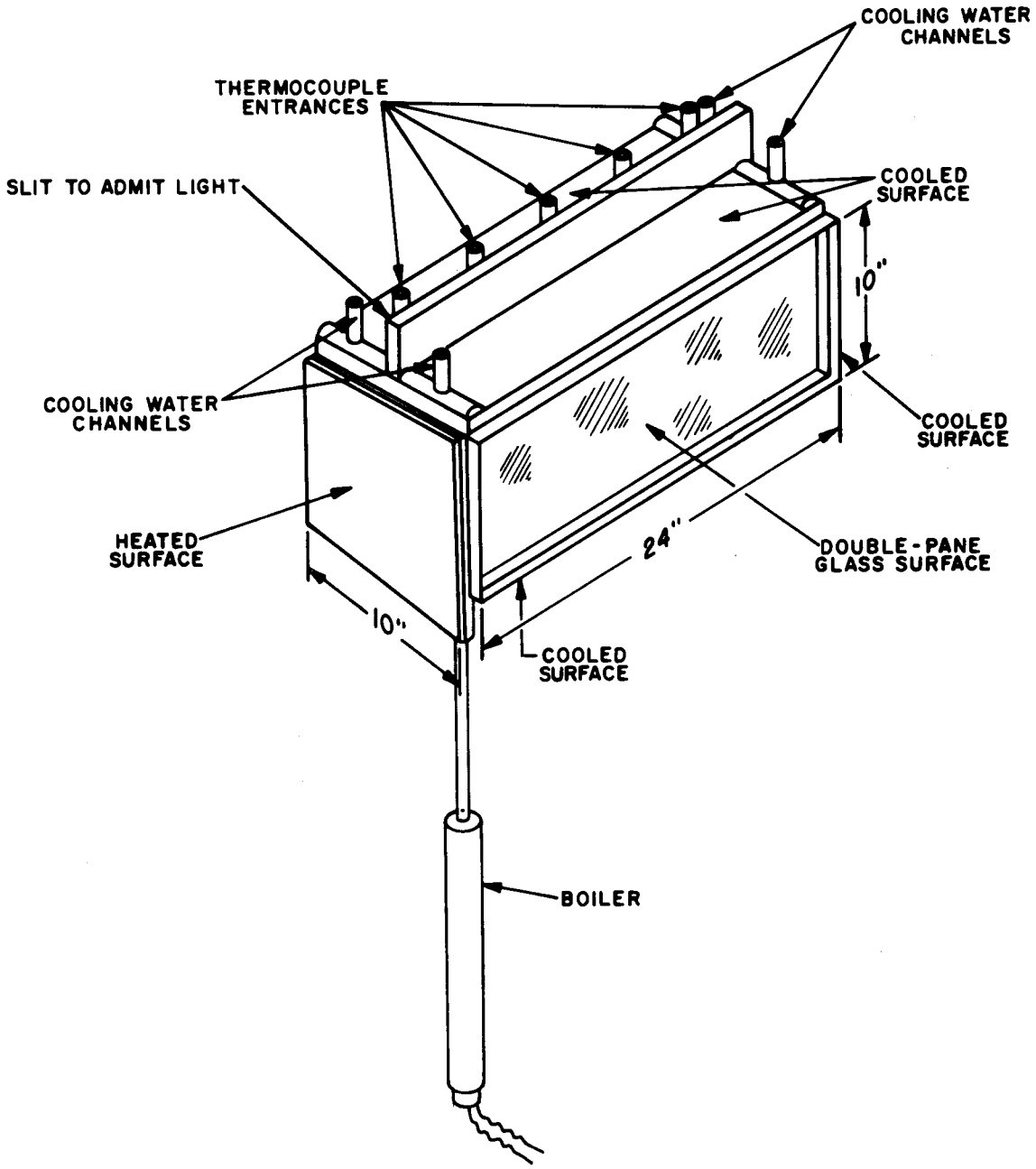


Fig. 1-3. Arrangement of System for Observation of Thermal Convection Flow Patterns.

ORNL DWG 69-4932

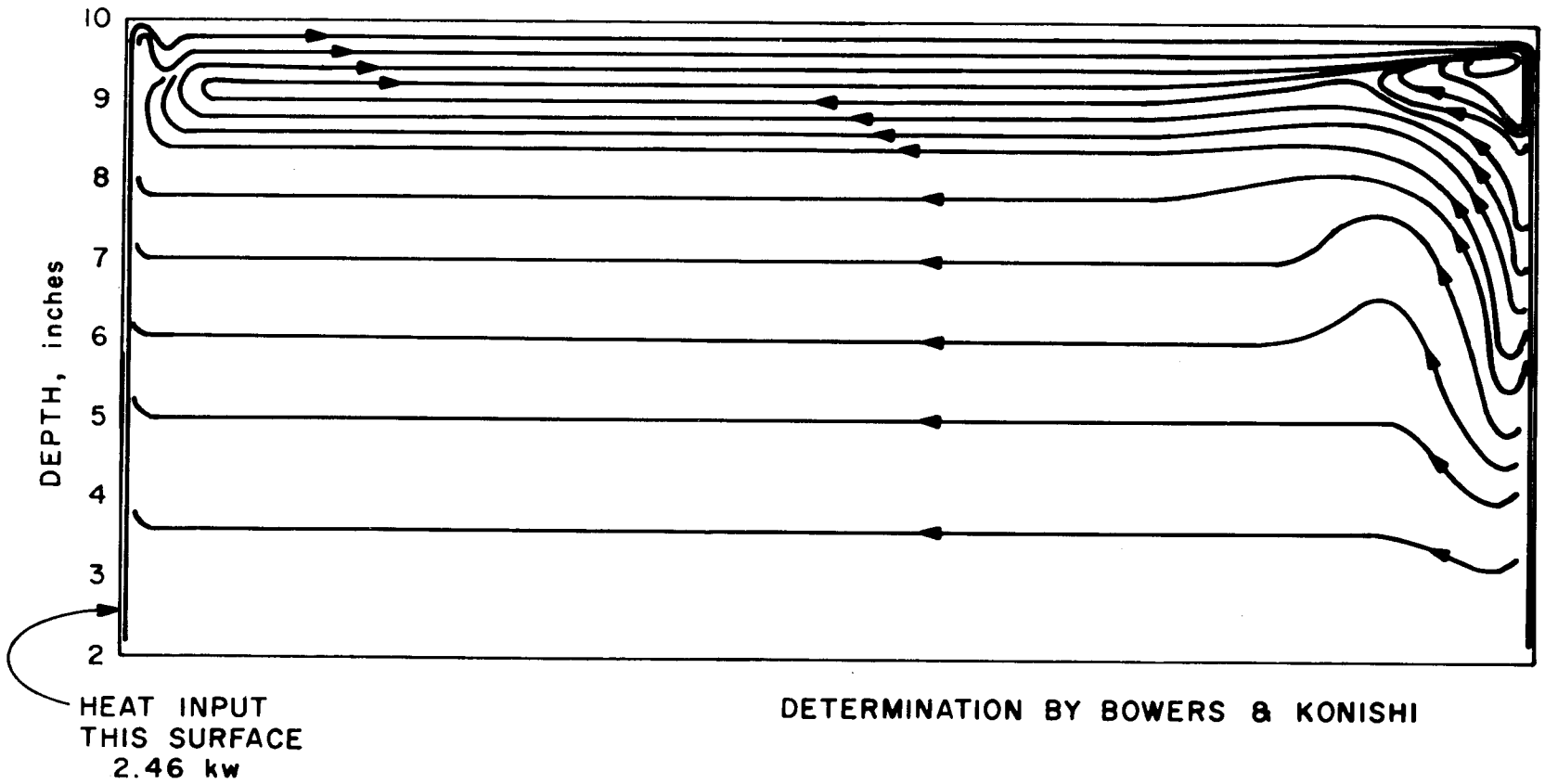


Fig. 1-4. Flow Pattern in Water-Filled Tank with one Vertical Surface Heated and Top, Bottom, and Opposite Vertical Surface Cooled.

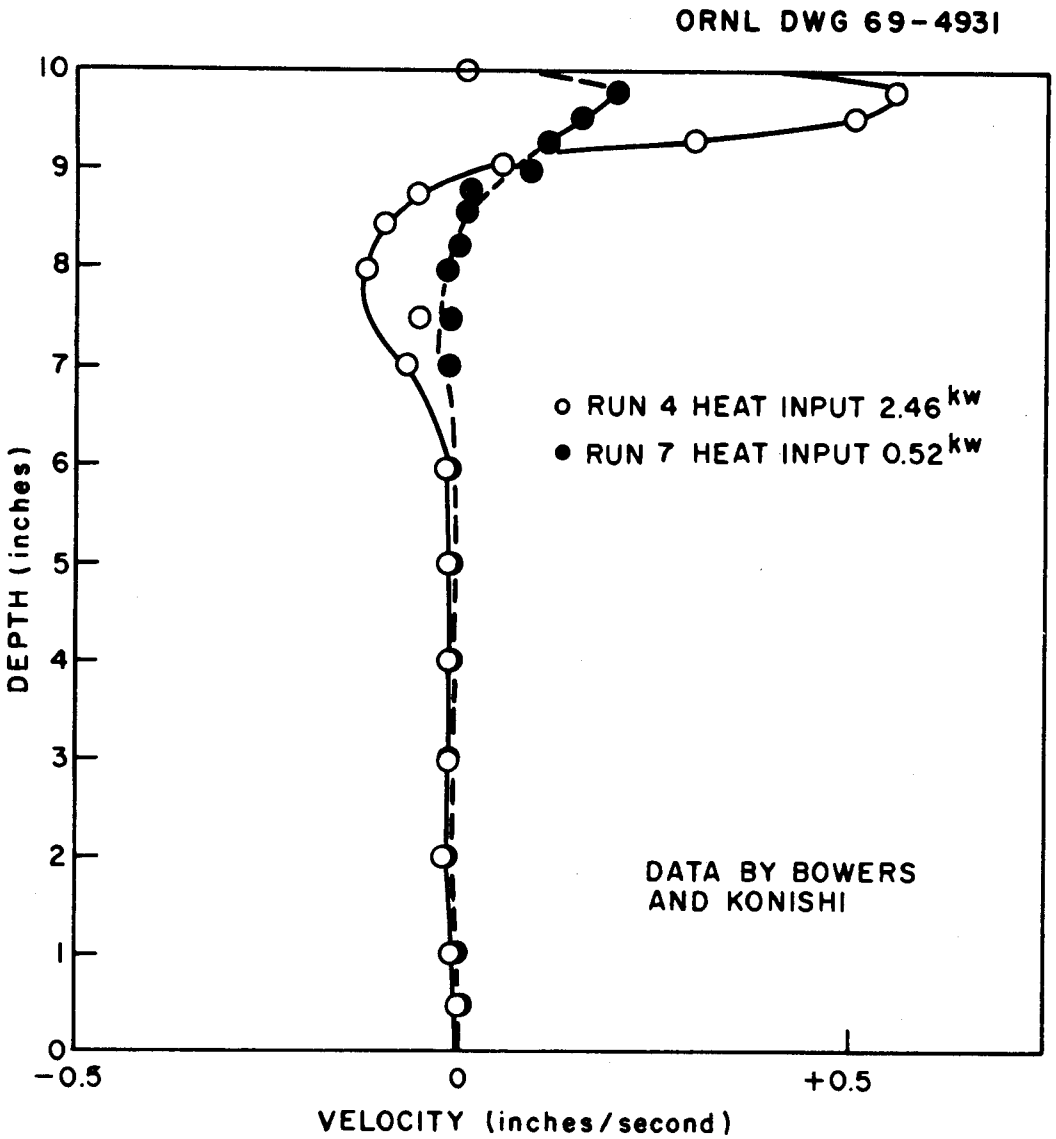


Fig. 1-5. Velocity Profile in Water-Filled Tank with one Vertical Surface Heated and Top, Bottom, and Opposite Vertical Surface Cooled.

leak checking system that will not compromise the integrity of the overall sealing system.

During the next report period the work will continue along the same general lines. Heat dissipation work will be limited generally to the small scale cask mockup and the mathematical representation of heat transport in a fluid filled cavity. Craft work will continue on the two other heat transfer models. Cask integrity work will deal principally with preparation of designs and concepts. Significant fabrication effort is expected to be held up for another sixty days.

TASK 2 - RECEIVING AND STORAGE

(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.

A logic diagram for this work was prepared.

TASK 3 — HEAD-END PROCESSING OF LMFBR FUELS
(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, a new computer code was developed to determine the safe handling time for any hexagonal arrayed LMFBR assembly without auxiliary cooling; a conceptual design of a dismantling unit was continued along with the design of fixtures for cropping and slitting tests; a new conceptual approach to single pin shearing was studied and fixtures were designed to obtain basic shearing data. The shearing force for 1/4- and 1/2-in. solid metal rods in a multipin shear unit was measured and design changes made in the hydraulic power supply to obtain higher shearing rates; fabrication and installation of an enlarged dry inert gas atmosphere box for sodium handling experiments was completed and leak testing begun; and the separation of molten stainless steel metal from urania measured at an inclination of 10° from the horizontal.

Reportable accomplishments include:

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

A computer code was developed to calculate the temperature-time history of fuel pins in a shrouded hexagonal assembly increasing in temperature as a result of heat produced by radioactive decay. The new code can be used to determine the safe handling time for an assembly without auxiliary cooling. For example, it could be used to find the time required for a fuel assembly with a given linear power to rise in temperature from, say, 300°F to 1275°F (the specified maximum allowable clad temperature). As only preliminary calculations are available, further calculations will be done in June and the results included in the June report.

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

The two cutting methods initially selected for cropping the ends of an assembly and removal of the shrouds are abrasive sawing and high speed steel slitting.[1] During this report period an investigation of units necessary to perform the basic operations was made so that the selected cutting methods can be evaluated. Also, a conceptual design of simple in-cell dismantling unit was continued. Abrasive sawing will be evaluated by modifying a 16 in. blade Ty-Sa-Man Saw in

Building 4505. Design changes on the saw are currently being made. The slitting tests can be performed on a standard milling machine in the ORNL shops. Appropriate fixtures and short sections of prototype fuel assemblies are being designed for fabrication.

The following activities will be continued during the next report period:

1. Design of the modifications necessary for basic abrasive saw tests.
2. Design of fixtures necessary to perform tests on:
   a. Fuel assembly cropping, and
   b. Fuel assembly slitting.
3. Continue the preliminary design of a proposed dismantling unit.

Task 3.3 — Shearing
(G. A. West, J. H. Evans, E. I. Wroblewski)

In this report period, a new approach to single pin shearing was studied. The preliminary design of a device for studying the parameters associated with single pin shearing was begun; and, changes in the present hydraulic and timing sequence on the ORNL assembly shear were studied as a hydraulic supply to a multipin unit operated at 100 cuts/min. Also, the shearing force required to shear 1/4 and 1/2 solid steel rods in the multipin shear was measured.

The following activities will be continued during the next report period:

1. Conceptual drawings of the Progressive Rotary Shear.
2. Fabrication drawings of a small experimental shear unit.
3. The effect of shortening the cylinder stroke of the multipin unit to reduce hydraulic oil requirements will be tried. Altering the hydraulic lines to supply fresh oil for each cycle, and a study of the hydraulic fluid temperature and heat transfer problems of the existing unit will be studied.

The new approach to single pin shearing is one in which the feeder requirements are simplified by using a Progressive Rotary Shear. In this concept, Fig. 3-1, an axially laminated cylinder, of a length greater than the longest fuel rod, is equipped with blades around about one-half the circumference of the cylinder. The axially spaced blades are located to the sheared length desired. Moving and stationary (grate-like) blades mesh such that as the cylinder rotates the staggered moving blades pass through the grate openings producing

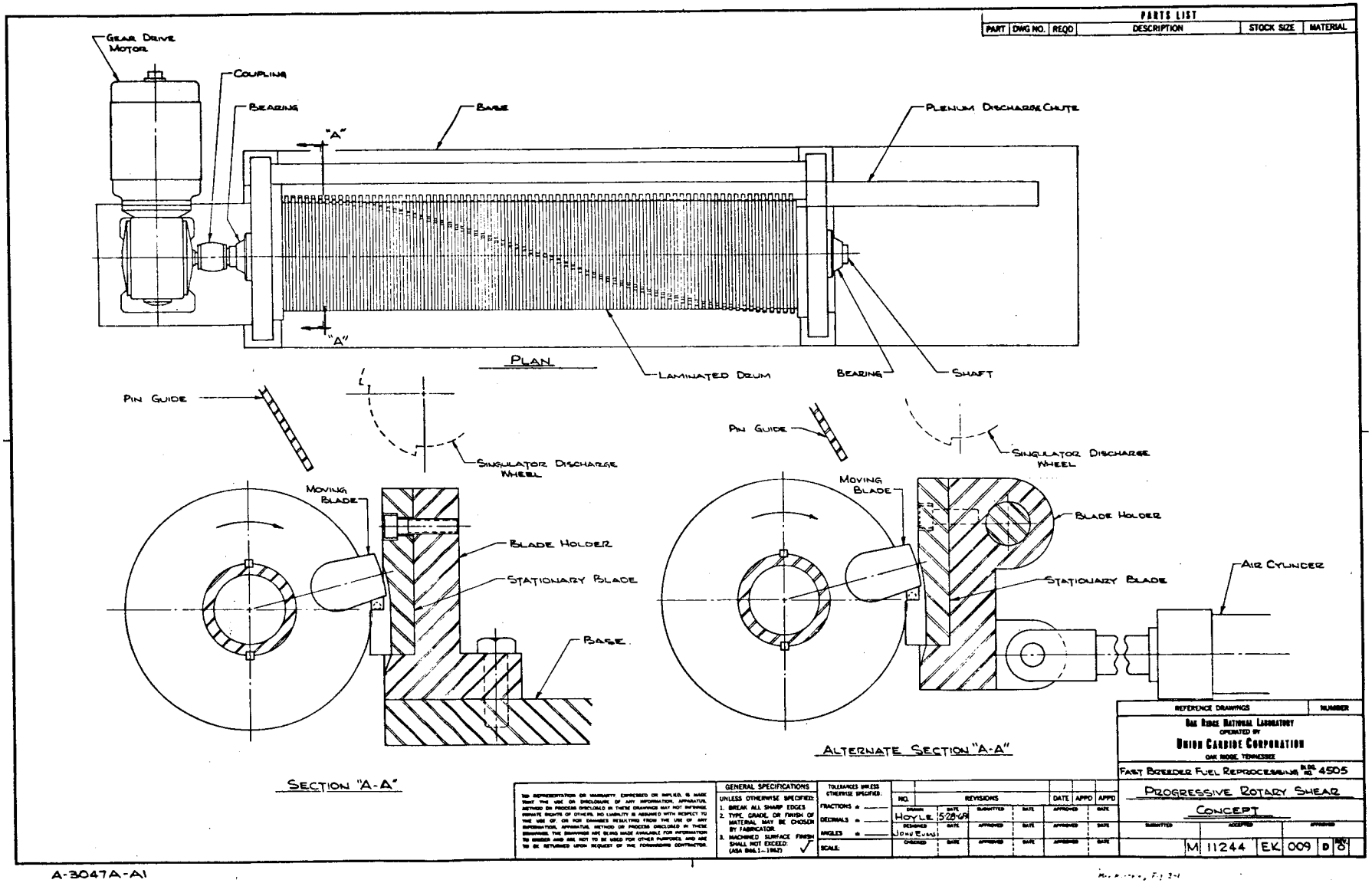


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Fig. 3-1. Progressive Rotary Shear Concept.

a shearing action. The feeding mechanism may be eliminated if the angular velocity of the cylinder is low enough to allow the fuel rod to fall in place by gravity directly from a singulator. At higher velocities, it may be necessary to move the stationary blade (grate) away from the rotating blades for pin loading. A design concept of this unit will be continued.

A device is also being designed to evaluate a single pin shearing operation as to, (1) blade velocity effects, (2) blade geometry, (3) blade clearance, (4) power requirements, (5) the effect of different fuel assembly materials, and (6) fuel rods and spacer wire characteristics.

The conceptual design of a multipin shearing process unit was continued. An existing experimental hydraulic shear unit (5-in.-diam x 2 in. stroke) and hydraulic system was used to determine shearing rates and forces required to shear 1/4-and 1/2-in. solid stainless steel rods.

The feeder and shear cycle was increased from 86 cuts/min to 150 cuts/min by increasing the clearance of the cylinder cushion. Prolonged cycling could not be tolerated because of the heat buildup of the hydraulic oil flowing through the 3/4 in. sch. 80 pipe and valves. The supply lines are to be increased to 1-1/2 in. sch. 80 pipe size and the valves replaced to decrease line friction.

The force required to shear a single 1/4- and 1/2-in. rods was 1 and 4 tons, respectively. A process capacity of 169 tons is conceivable with slight modifications of the existing system which will include a larger multipin shear cylinder (8- to 12-in.-diam) and hydraulic lines.

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

Fabrication and installation of an enlarged dry inert gas atmosphere glove box for sodium experiments was completed during this report period and leak testing was started. However, the design of the seal for the top viewing window, (located directly over the molten sodium vessel) will be changed to compensate for expansion and contraction due to fluctuating heat loads. Two prototype fuel test specimens were received from the shops, cleaned, and their surface conditions measured.

During the next report period leak checking of the glove box and concomitant instrument installation will be completed. Hopefully, a series of experiments to ascertain both the adherence of sodium to a prototype fuel assembly and its subsequent removal will again be started.

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

Melt-decladding is being considered as a backup process for the mechanical head-end. In this respect, it may be possible to convert the mechanical shearing (Task 3.3) and volatile fission gas removal operations (Task 4) into a single melt-decladding step. 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 to separate the molten cladding from the UO_2-PuO_2 pellets. During this report period, a few bench-scale experiments were made to measure the separation of molten metal from urania at 1550°C.

During the next month, the separation of molten metal from urania will be tried at temperature up to 1700°C using flat alumina boats with 0.25-in.-diam drain holes.

Reportable accomplishment follow:

The separating of molten stainless steel from uranium was measured in a few small-scale experiments. Three experiments were made in an induction furnace at 1550°C using urania pellets (0.270-in.-diam x 0.546 in. long, 10.5 grams/cc) enclosed in 6 in. lengths of 0.375 in. stainless steel tubing. The specimens were inserted in a 2.5-in.-diam cylindrical alumina crucible 18 in. long with a closed spherical end. In all of the experiments, the alumina crucible was inclined at an angle of 10 degrees with the horizontal. In the first test with only one stainless steel-urania sample present, 97 wt % of the stainless steel separated from the pellets and collected at the lower end of the crucible. In the second test four samples were placed side by side in the alumina tube, and 91 wt % of the stainless steel separated from the pellets. As the steel melted, the urania pellets rested against each other and tended to interfere with the flow of the molten metal. In the last test, ten specimens were wired together to form a pyramid and about 94 wt % of the stainless steel (total of 286 g) separated from the pellets and collected at the lower end of the crucible. Out of 90 urania pellets present in the latter test, one intact pellet was carried a distance of about 6 in. by the molten steel flowing to the bottom of the crucible. The amount of urania carried away by the molten metal cladding is being determined.

References

1. W. E. Unger, et al., Aqueous Processing of LMFBR Fuels, Progress Report, April 1969, No. 2, ORNL-TM-2585.

TASK 4 – VOLATILE FISSION PRODUCT REMOVAL
(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.

Most of this month was spent in preparing for a demonstration of the processing of short-cooled LMFBR oxide fuel specimens now being irradiated. Also, three oxidation tests were made with irradiated (U, Pu)C fuel.

Task 4.1 – Volatilization from Oxide Fuels
(J. H. Goode, V. C. A. Vaughen, O. L. Kirkland)

A series of tests of the removal of fission products from short-decayed fuel specimens is scheduled to begin about July 1, 1969. A NaK-cooled capsule containing four fuel rods of sol-gel 15% PuO_2--85% UO_2 (irradiated to about 20,000 Mwd/ton) will be discharged from the ETR about June 16, 1969, and shipped to ORNL about 10 days after discharge. We have been cold-testing a single-pin shear, a packed scrubber, and fission gas collection and sampling equipment to be used for the hot-cell experiments. At least three of the rods will be sheared, oxidized, dissolved, and processed through the first Purex cycle within 30 to 60 days after discharge. Laboratory work in preparation for this important experiment will continue this month.

<u>Analysis of Equipment Requirements and Processing Options</u> (S. D. Clinton)

During this report period, an order was placed to purchase an electrically-heated rotary kiln in which sheared LMFBR fuel at the rate of 5 kg per hr can be heated to 750°C in either an oxidizing or inert atmosphere. The procurement of this equipment will require about 16 weeks.

During the next report period a material balance for vented or sodium logged fuel will be made and possibilities for obtaining suitable UO_2--ThO_2 fuel as a stand-in for UO_2--PuO_2 will be investigated.

Task 4.2 – Conversion of Carbides and Nitrides with Oxygen
(J. H. Goode, V. C. A. Vaughen, O. L. Kirkland)

We subdivided unclad, fractured pellet (20% PuC--80% UC) remnants from United Nuclear Corporation's EBR-2 irradiation experiment UNC-80

(30,000 Mwd/metric ton) into several aliquots. Three oxidation tests were made with these fuel samples. In each case the sample, contained in a platinum bucket that was suspended in a stainless steel burner, was oxidized at 750°C in a stream of oxygen. The off-gases were passed through an aqueous scrubber and molecular sieve and charcoal adsorption traps to determine the amounts of fission products released. A LIRA continuous infrared CO_2 analysis instrument was used to monitor the combustion. The "ash" was dissolved in nitric acid and the release of fission products during dissolution was determined.

We have insufficient analytical data to completely describe the results, but some qualitative observations were made:

(1) Based on the weight gain of the fuel and the amount of CO_2 evolved in the first test, conversion of (U, Pu)C to the oxides was almost quantitative.

(2) In the second and third tests, little or no CO_2 was found in the off-gas. Apparently this was due to hydrolysis of the carbides by residual water or nitric acid in the burner that had not been completely removed following leaching of the burned specimen in the prior test.

(3) The amounts of ^{85}Kr released during the oxidation ranged from 81 to 97% for the three tests. The average ^{85}Kr concentration of the unclad fuel segments was 1.7 mc per gram of (U, Pu)C.

TASK 5 – DISSOLVING
(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 control 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 studies were begun of the factors affecting volatilization of iodine from nitric acid solutions. Of several chemical reductants studied for reducing non-volatile iodate to volatile free iodine, best results (98.8% volatilization) were obtained with an iodide salt.

Task 5.2 – Iodine Control
(G. I. Cathers, C. J. Shipman)

It would be attractive in processing short-decay fuel to volatilize essentially all of the iodine prior to solvent extraction. Early removal of the iodine in the process cycle would concentrate the iodine in a relatively small volume of gas, making attainment of high plant retention factors for iodine much easier. In addition, the production of volatile organic iodides would be minimized. We have initiated a study of the chemistry of iodine in nitric acid solutions to obtain a better understanding of the factors that affect iodine volatilization in the fuel dissolution and aqueous feed pretreatment steps.

Several effects that are important in determining the behavior of iodine in nitric acid solutions are summarized in the following list. These effects have been observed in various experimental tests but little quantitative information has been obtained on the equilibria involved or on the reaction kinetics.

1. Iodide is easily oxidized to volatile free (I_2) in nitric acid solution at concentrations down to less than 4 M. The literature indicates that nitrous acid, an impurity normally present to some degree in nitric acid, is more effective kinetically in the oxidation process than nitric acid.

2. Nitric acid at high molar concentrations is capable of oxidizing free iodine to iodate (or possible periodate). These species are not volatile. The effect is strongly dependent on acid concentration, being best observed at concentrations greater than 8 M.

3. Nitrous acid is capable of reducing iodate back to the free iodine state in nitric acid solution but this is an uncertain effect at best, being dependent on the nitric acid concentration, the nitrous acid concentration and the temperature. With respect to nitrous acid, some sort of equilibrium usually exists in nitric acid solution with NO, NO_2, N_2O_4, or other nitrogen oxide species loosely termed collectively as "nitrose gas." The effect of nitrous acid or of the various nitrogen oxides is strongly limited by their limited solubility in nitric acid solution, particularly at temperatures near the boiling point and when sparging gas is employed.

4. The iodate ionic species in nitric acid are not easily reduced to free iodine with nitrous acid, gaseous NO (mixed with air to

generate NO_2 and N_2O_4), or bisulfite. The iodide ion is perhaps the best reductant. A favorable factor limiting formation of iodate during dissolution of the fuel is that nitrous acid generated by reaction of HNO_3 with UO_2 acts as a holding reductant. The tendency toward iodate formation is greater if the solution is digested after the reaction with UO_2 is complete, particularly if the dissolver-condenser system is of a design that tends to trap volatilized iodine (i.e., the dissolver is connected to a reflux condenser).

5. The volatilization of iodine from nitric acid solution depends on the iodine being in the free iodine state, on the iodine partial pressure, and on the amount of gas sparging used for transpiration of the iodine. The free iodine partial pressure in nitric acid increases with temperature and is relatively high above the sublimation temperature of 82°C of solid iodine. However, there are no reliable data on partial pressure and activity coefficients of iodine in nitric acid fuel dissolver solutions or of the species that may be present.

6. The oxidizing or reducing power induced by radiation of the iodine-bearing solution may be an important factor affecting the iodine valence. Initial tests indicate that radiation can both induce the formation of iodate and promote its reduction to free iodine (see below).

Sparging Tests. — Results of a series of 10 tests on volatilizing iodine (initially present in the iodate form) from nitric acid solutions are presented in Table 5-1. Sodium nitrite, NO gas, sodium bisulfite, and potassium iodide were added to the heated solution to reduce the iodate to free iodine while sparging the solution. Most effective removal of iodine was obtained when iodide was added as reductant. In this test about 99.8% of the iodine was removed over a 3-hr period. Nitrite, gaseous NO, and bisulfite were less effective. The iodide ion, besides being an effective reductant, also has an isotopic dilution effect which is helpful. Changes in other variables such as the nitric acid concentration, the temperature, and the gas sparge rate did not appear to affect the results significantly.

Radiation Effects. — Preliminary irradiation tests with a ^{60}Co source showed that iodine, at a concentration of 2×10^{-4} M and less in 4 M HNO_3, is quickly decolorized, presumably due to iodate formation. The iodine apparently was not volatilized from the solution since no color was observed in a CCl_4 trap in the off-gas system. In contrast, however, irradiation of a 10^{-3} M iodate solution in 4 M HNO_3 resulted in free iodine being formed. We tentatively conclude that gamma irradiation of iodine--nitric acid solutions possibly results in an equilibrium being established between the different iodine species.

Study of the variables affecting iodine volatilization from nitric acid solutions will continue next month.

Table 5-1. Reduction of Iodate to Free Iodine in Nitric Acid Solutions
(Carrier iodide and ^{131}I tracer oxidized to iodate with hypochlorite initially)

Test	1	2	3	4	5	6	7	8	9	10
Conc. HNO_3 (M)	4	4	4	4	4	6	6	6	6	6
Conc. KIO_3 (M)	10^{-3}	10^{-4}	10^{-5}	10^{-4}	10^{-4}	10^{-3}	10^{-3}	10^{-3}	10^{-3}	10^{-3}
Reductant	NO	NO	NO	NO_2^-	NO_2^-	NO_2^-	NO_2^-	NO_2^-	HSO_3^-	I^-
Reductant addition rate (ΔM/hr)	a	a	a	b	c	0.04	0.08	0.12	0.04	0.04
Temp. (°C)	90	90	90	90	70	107	107	107	107	107
Air sparge rate (ml/min)	20	20	20	20	20	220	220	220	220	220
Iodine volatilized in consecutive 1-hr periods (% of amount present at start of each period)	41	68	40	28	48	17	37	38	39	72
	39	67	51	54	63	9	42	51	69	90
	42	65	58	65	--	9	45	73	59	92
	52	63	59	--	--	10	46	61	67	--
	--	--	--	--	--	10	--	50	65	--

[a] NO gas sparge rate was not determined but flow was sufficient to nearly saturate the solution.

[b] $NaNO_2$ concentration of 0.01 M at beginning of each of first two periods; the concentration at start of the third period was 0.05 M.

[c] $NaNO_2$ concentrations of 0.01 M and 0.05 M at beginning of first and second periods, respectively.

Task 5.4 – Equipment Concepts
(W. S. Groenier)

Studies of the feasibility of transporting sheared fuel via a spiral brush are continuing using the available rotary screw-type leacher prototype. Initial tests in which sheared stainless steel hulls and spacer wires were fed to the unit, were very encouraging. Material that was fed to a single flight was discharged as follows: 1st flight, 84%; 2nd flight, 5%; 3rd flight, 3%; 4th flight 1.4%; scattered throughout unit, ~ 6%. The stainless steel wire brush used was fabricated from 22-mil wire. A few flights were fitted with 8-mil wire brush which seemed to work better. More of the 8-mil brush is on order. We will equip the entire unit with this size of brush and retest.

Fabrication and materials costs for a stainless steel rotary dissolver[1] with an estimated capacity of 5 kg (U + Pu) per hr have been estimated at $16,000.

References

1. W. E. Unger, et al., Aqueous Processing of LMFBR Fuels, Progress Report, April, 1969, No. 2, ORNL-TM-2585.

TASK 6 – FEED PREPARATION
(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 work on this task was performed this month and none is planned for next month.

TASK 7 – SOLVENT EXTRACTION
(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 batch countercurrent tests showed that addition of a small amount of Fe(II) to the dilute nitric strip solution prevented plutonium retention by DBP impurity in the solvent. A test series was started to determine the plutonium concentrations that can be achieved in TBP without separation of a third phase. The digital computer code which should be useful for predicting the distribution of plutonium and uranium in a TBP countercurrent extraction system became operational. In solvent stability studies, additional data were obtained at 50 and 75°C for the decomposition of TBP in nitric acid solutions and progress was made in detecting and identifying TBP and its degradation products by liquid chromatographic techniques. Preliminary design of a pulsed-clone contactor with 0.2-in.-diam clones was completed and design of a stacked-clone contactor with 200 to 300 clones per stage was continued.

Task 7.1 — Flowsheet Development
(D. E. Horner, J. R. Collins)

The presence of small amounts of dibutylphosphoric acid (DBP) in the TBP solvent can cause retention of plutonium (and uranium) by the solvent when stripping with dilute nitric acid. This applies to the second cycle and also can apply to the first cycle if the plutonium and uranium are co-stripped with dilute acid rather than separated in a reductive partitioning step. Preliminary tests[1] indicated that addition of a small amount of a plutonium reductant (ferrous iron) to the dilute acid strip solution would ensure complete plutonium stripping in the presence of DBP but the test results were not conclusive. The beneficial effect of adding 0.01 M Fe^{2+} to the strip solution was recently demonstrated in batch countercurrent tests.

The organic feed for the tests was 15% TBP--n-dodecane--5 x 10^{-4} M DBP containing 4.5 g of Pu and 35 g of U per liter. In the first test with 0.01 M HNO_3 strip solution, 99.76% of the plutonium was stripped in seven stages at an organic/aqueous phase ratio of 1.7/1. The plutonium concentration in the organic phase was lowered to about 0.01 g/liter within the first 4 stages and then did not change, indicating that this amount of plutonium was retained by the DBP. In an identical test but using 0.01 M HNO_3--0.01 M $Fe(NO_3)_2$--0.03 M hydrazine strip solution, more than 99.97% of the plutonium was recovered (< 0.001 g Pu/liter of stripped solvent).

Third Phase Formation. — An important consideration for the Purex extraction step is the maximum plutonium concentration that can be obtained in the organic phase without separation of a third phase. Since the third phase contains a high plutonium concentration, this can be a criticality

hazard in equipment not geometrically-safe.

In previous batch tests with 15% TBP--n-dodecane in which a third phase formed, the maximum solvent plutonium concentration for no third phase formation was estimated to be roughly 26 g/liter. In recent tests the indicated maximum plutonium concentration was less than this. The addition of about 3% tridecanol to the organic phase increased the maximum plutonium concentration that could be reached without third phase formation to about 40 g/liter. An extensive test series was started this month to delineate conditions of third phase formation as a function of the plutonium and nitric acid concentration, the TBP concentration, and the temperature.

Computer Code for Purex System (W. S. Groenier)

The digital computer code (SEPHIS) is operational. Pulse column startup transients have been simulated for Purex first-cycle flowsheets employing a range of TBP concentrations (15-30%), aqueous feed Pu + U concentrations (70 or 200 g/liter), and U/Pu ratios in the aqueous feed of 5 or 9. These transient concentrations are potentially useful for making a criticality analysis of the solvent extraction process, but unfortunately are not exact because of the mass-transfer equilibrium equations used. New data and/or correlations are essential to the success of this work. The code also has application in the analysis of process upsets including accident situations.

Task 7.2 – Solvent Stability
(W. Davis, Jr., A. H. Kibbey)

Due to the decomposition of tributyl phosphate into dibutyl-, monobutyl-, and orthophosphoric acids in aqueous nitric acid solutions, zirconium butyl phosphates are precipitated when these solutions are aged and heated. We are studying the rate of precipitation in the aqueous phase (while maintaining a small TBP phase to ensure saturation of the aqueous phase with TBP) as a function of temperature, time, and HNO_3 and Zr^{4+} concentrations. Our most recent measurements (Table 7-2) at 50° and 75°C, at 1, 3, and 5 M HNO_3, and with 1 g of Zr^{4+} per liter, are in good agreement, both quantitatively and qualitatively, with those we reported previously.[2]

Quantitatively, the rate of precipitation is nearly a linear function of the HNO_3 concentration at 50°C and 1 g of Zr/liter. However, at 75°C there is only a small increase in decomposition rate as the acidity increases from 1 to 5 M HNO_3. Qualitatively, at 50°, a temperature not much above that at which a solvent extraction process might be operated, the precipitates may be characterized as follows: (1) in 1 M HNO_3 it is predominately peptized and passes through 0.45 μ Millipore paper; (2) in 3 M HNO_3 dispersed particles, readily filterable, are formed; (3) in 5 M HNO_3 all of the precipitate forms a single ball of solid except for that

Table 7-1. Beneficial Effect of Fe(II) in Preventing Plutonium Retention by DBP

Organic feed: 15% TBP--n-dodecane--5 x 10^{-4} M DBP containing 4.5 g of Pu and 35 g of U per liter

Strip solution: #1 - 0.01 M HNO_3
#2 - 0.01 M HNO_3--0.01 M $Fe(NO_3)_2$--0.03 M N_2H_4

Contact: Batch countercurrent at organic/aqueous phase ratio of 1.7/1.

Strip Solution	Stage No.	Analysis (g/liter) Organic Phase Pu	Organic Phase U	Aqueous Phase Pu	Aqueous Phase U	Aqueous Phase HNO_3 (M)
#1	1	0.64	28.8	6.7	56.5	0.32
	2	0.018	19.3	1.04	48.5	0.20
	3	-	8.50	0.075	33.3	0.12
	4	0.006	2.13	0.003	16.0	0.07
	5	0.010	0.24	0.001	4.00	0.03
	6	0.010	0.13	< 0.001	0.24	0.02
	7	0.010	0.07	< 0.001	0.03	0.01
#2	1	0.33	31.0	7.7	60.0	0.36
	2	< 0.001	23.0	1.00	51.8	0.19
	3	< 0.001	12.4	0.004	38.0	0.14
	4	< 0.001	4.8	< 0.001	19.4	0.09
	5	< 0.001	0.79	< 0.001	8.25	0.04
	6	< 0.001	0.18	< 0.001	0.81	0.01
	7	< 0.001	0.10	< 0.001	0.13	0.008

Table 7-2. Precipitation of Zirconium Butyl Phosphates from Aqueous Nitric Acid Solutions

Conditions: Zr^{4+} = 1 g/liter
Aqueous volume/undissolved TBP volume ≃ 300/1

Temp. (°C)	HNO_3 (M)	Reaction Time (hr)	Zr Butyl Phosphate ppt'n Rate (mg $liter^{-1}$ hr^{-1})
50	1	266	1.7
	3	266	6.2
	5	266	13
75	1	17.5	90
	3	17.5	107
	5	17.5	130

material which forms a ball-like coating on the teflon-cased magnetic stirrer.

During the past month we completed experiments on the decomposition at 35°C of TBP dissolved in 1 and 5 M HNO_3. The samples are now being prepared for methylation and subsequent gas chromatographic analysis. We have also set up two additional reaction vessels, and are currently rerunning the TBP decomposition experiments at 50°C in 1, 3, and 5 M HNO_3. The purpose of these runs is to supplement earlier data which were too meager to permit calculation of the HDBP and H_2MBP decomposition rate constants.

Chromatographic Studies of Solvent Degradation Products (J. G. Moore)

Liquid chromatography experiments using the Varian Aerograph Microadsorption Detector are in progress to determine the applicability of this instrument for the detection and identification of tributyl phosphate and its principal degradation product, dibutylphosphoric acid. Although minimum detectable quantities have not been determined, excellent responses were obtained in preliminary experiments using 1 λ aliquots

containing either 50 μg of TBP or 10 μg of DBP. In addition, the response curves under certain conditions were enough different that they might serve as a means of identification.

The detector, which is connected to the bottom of a liquid chromatograph column, has two identical 22-microliter chambers, each containing a glass-enclosed thermistor bead that senses the average temperature of the liquid as it flows through the detector. In these experiments, the upper chamber (which serves as the reference side) was packed with 105-115 μ Teflon Powder, a non-adsorbing material. The lower chamber was packed with 60-74 μ unfired Vycor glass powder, a highly adsorbing material. Any solute material in the mobile liquid passing through the detector can interact with this porous glass. When this occurs, a small amount of excess energy is given off to the surrounding environment, causing an increase in the temperature which is sensed by the thermistor. A temperature rise of only 6×10^{-5}°C can be detected by this instrument.

Initial experiments were made to determine if TBP or DBP could be detected using the Teflon-Unfired Vycor packings. The detector was connected to a capillary tube 6-in. long and 1 λ aliquots of n-dodecane solutions of TBP or DBP were injected into the system. Using n-dodecane as the carrier liquid, samples containing 50 μg of TBP or 10 μg of DBP were easily detected.

The shape and magnitude of the response curves for DBP and TBP were dependent on the solvent used as the mobile or carrier liquid. In an experiment using heptane as the carrier liquid, the responses were so completely different that the curves could serve as a means of identification (Fig. 7-1). In this experiment, 1 λ aliquots of n-dodecane were used that contained either 150 μg of TBP or 50 μg of DBP. The response was electronically attenuated by a factor of 8. Samples containing only n-dodecane produced essentially no response under these conditions.

Attempts will now be made to determine the minimum detectable quantities of each compound using a variety of solvents as the carrier phase. In addition, gas chromatographic studies will be started on the separation and detection of TBP and its degradation products.

Task 7.6 — Contactor Evaluation
(W. S. Groenier, W. M. Woods)

Stacked-clone contactor technology is being developed in the Chemical Engineering Research Studies Program. However, since various contacting devices are being evaluated in the LMFBR program, the information on stacked clones is also presented here.

A 9-clone per stage contactor was sent to the shop for modifications. The pump impellers will be shrouded and the casing diameter increased to reduce the intensity of shear on the liquid in the pumps. Apparently the

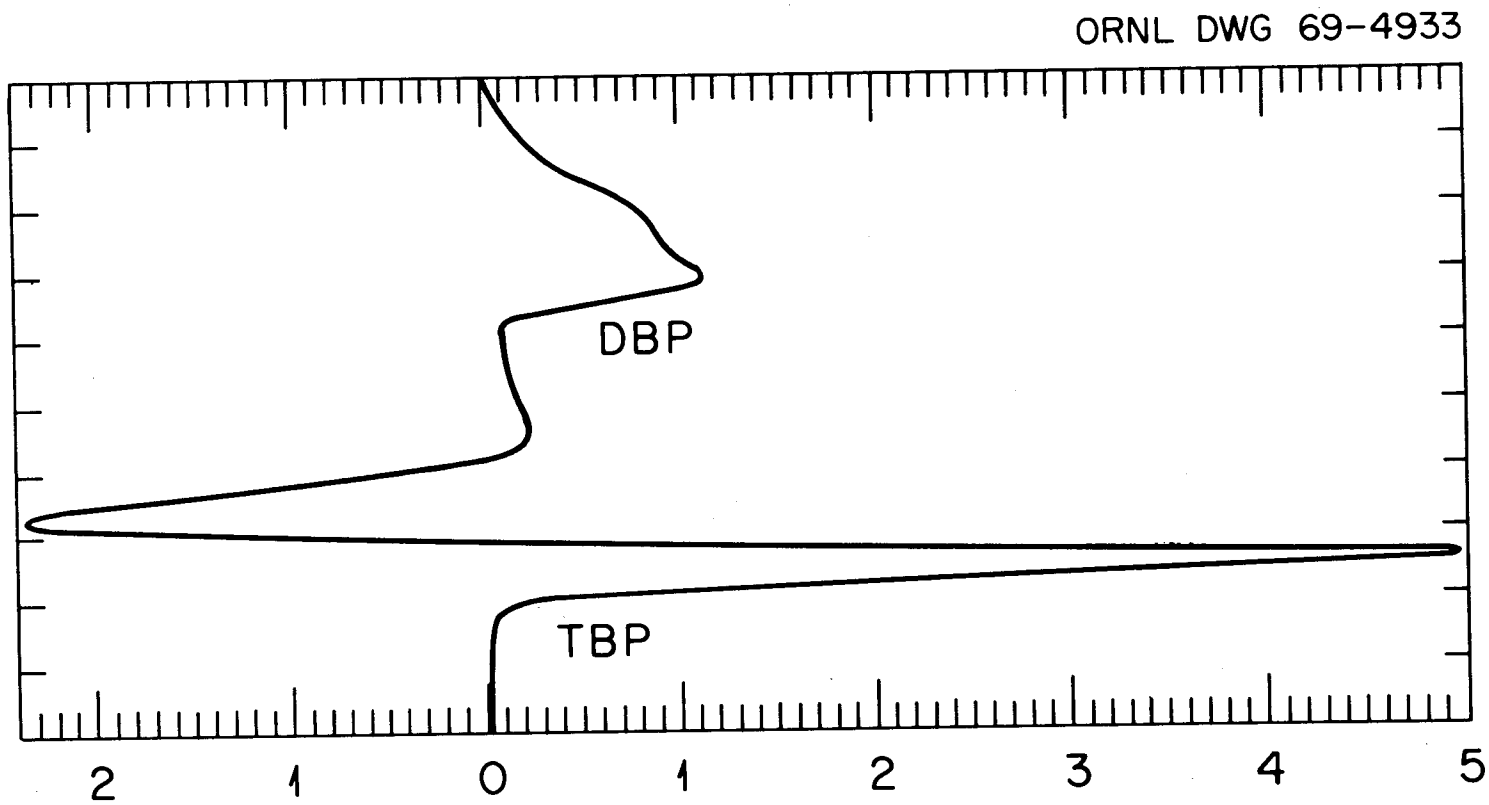

Fig. 7-1. Response of the Micro-Adsorption Detector to TBP and DBP Using Heptane as the Carrier Liquid.

high shear creates solvent droplets too fine to be coalesced in the clones and this reduces the capacity.

The pulsed-clone contactor, a model of which with 0.4-in.-diam clones and 10 clone-volumes in the cylinders was successfully tested previously, was redesigned with 0.2-in.-diam clones and 5 clone-volumes in the cylinders. Expected base frequency of the new design is 180 cycles per minute. The design is now being detailed for shop drawings.

A stacked-clone contactor with 200 to 300 clones per stage is being designed. Each clone will be 0.6 scale compared to the prototype model. The pumps will have a large-diameter low-speed impeller (about 16 in. and 800 rpm, respectively).

References

1. W. E. Unger, et al., Aqueous Processing of LMFBR Fuels, Progress Report, March 1969, No. 1, ORNL-TM-2552.

2. W. E. Unger, et al., Aqueous Processing of LMFBR Fuels, Progress Report, April 1969, No. 2, ORNL-TM-2585.

TASK 8 – PLUTONIUM ISOLATION
(D. J. Crouse)

The objective of Task 8 is to provide methods for separating plutonium from uranium and fission products in a form of adequate purity and concentration for delivery to the fuel refabrication system. The task includes evaluation of different methods of reducing plutonium when partitioning from uranium in the Purex process and evaluation of different processes, e.g., TBP extraction, amine extraction, ion exchange, for purification of the plutonium beyond the first cycle.

No work on this task was performed this month and none is planned for next month.

TASK 9 – WASTE TREATMENT AND STORAGE

Progress on this task is reported separately.

TASK 10 — OFF-GAS TREATMENT
(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. Logic 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, and (2) decomposition of organic solvent vapors and organic iodides by catalytic oxidation.

This month additional data were obtained for the rate of reaction of CH_3I with mercuric nitrate solutions and for the decomposition of organic solvents by catalytic oxidation. Preliminary tests indicated that solvent extraction of iodine from spent mercuric nitrate scrub solutions might be used to permit recycle of the solutions. In addition, it was demonstrated that passing an air stream containing organic vapors through a bed of iodized charcoal containing ^{131}I caused slow release of the ^{131}I to the gas stream.

Task 10.1 — Iodine

Reaction Rate of Methyl Iodide With Mercuric Nitrate Solutions (R. E. Adams, R. L. Bennett, Ruth Slusher)

The investigation of the reaction rate of CH_3I with mercuric nitrate--nitric acid solutions was extended to lower CH_3I and mercury concentrations. Previously reported results[2] were obtained with 10^{-4} M CH_3I in solution with 0.1 M $Hg(NO_3)_2$--0.1 M HNO_3. By utilizing electron capture detectors rather than hydrogen flame ionization detectors on the chromatograph, we were able to determine the rates for 10^{-6} M CH_3I with 0.005 M $Hg(NO_3)_2$--0.005 M HNO_3. The measurements are made by injecting the CH_3I solution into the reaction cell containing the mercuric nitrate solution; the cell is then sparged with a nitrogen stream and the CH_3I concentration in the effluent nitrogen followed by gas chromatographic sampling. The CH_3I concentration decreases as a result of the gas sparging and the reaction in the solution. For each set of conditions, determinations of CH_3I concentration versus time were made at five gas sparging rates ranging from 10 to 50 ml/min. Reaction rate constants were then obtained by plotting the reciprocal of the total observed rate constant against the total amount of CH_3I sparged from the solution (which is dependent on the flow rate) and extrapolating to zero amount of CH_3I sparged. To eliminate possible photochemical effects the reaction cells were blackened. The pseudo first order rate constant was about 0.44 min^{-1} and the CH_3I half-life was about

1.6 min in two tests at 30°C with CH_3I concentrations of 1.6×10^{-6} M and 7.9×10^{-6} M (Table 10-1). Other reaction parameters will be investigated this month.

Table 10-1. Rate of Reaction of Methyl Iodide with 0.005 M $Hg(NO_3)_2$--0.005 M HNO_3 Solution at 30°C

CH_3I Concentration (M)	Half-life of CH_3I	Pseudo First Order Rate Constant
1.6×10^{-6}	1.61 min	0.43 min^{-1}
7.9×10^{-6}	1.56 min	0.44 min^{-1}

Extraction and Stripping of the Mercury - Iodine Complex (J. M. Schmitt, F. G. Seeley)

If Hg^{2+}--HNO_3 solutions are used for scrubbing radioiodine from the processing plant off-gas, presumably the spent scrub solution could be stored and then recycled after most of the ^{131}I had decayed. However, ^{129}I, which has a long half-life and a low discharge limit, would accumulate in the solution. To obtain more efficient recycle of the scrub solution, some convenient method of removing iodine from the solution is needed.

As described previously,[3] the mercury-iodine complex is extracted with TBP but the extraction coefficients are low when excess mercury is present. As expected, the complex was extracted more strongly by diamylamylphosphonate (DAAP) and by trioctylphosphine oxide (TOPO) than by TBP (Table 10-2). Coefficients for extraction of iodine from 1 M HNO_3--0.1 M Hg^{2+}--0.01 M KI solution with 0.3 M solutions of DAAP and TOPO were 3.1 and 29.3, respectively. A 0.1 M Adogen 364 (tertiary amine) solution gave an extraction coefficient of 3.8. The mercury to iodine ratio in the solvent phase was 1/1 with all solvents except TOPO, in which case it was 2/1. Coefficients for extraction of mercury from 1 M HNO_3 (no I^- present) were 0.09 with Adogen 364 and about 0.01 with the TBP, DAAP, and TOPO solutions. These data indicate that the iodine could be extracted from the scrub solution with only small losses of mercury.

Stripping Tests. — Stripping iodine from the solvents with alkaline solutions was more difficult than had been expected. For example, contacting the TOPO and DAAP solvents with 1 M NaOH for 10 min at room temperature stripped only 3% and 43% of the iodine, respectively (Table 10-3). With the DAAP solvent, 78% was stripped with 1 M NaOH in 10 min

at 60°C. Of a variety of stripping agents tested, best results were obtained with $Na_2S_2O_3$ solutions. A 0.1 M $Na_2S_2O_3$ solution stripped 99.6% of the iodine from the DAAP solvent. In some stripping tests with $Na_2S_2O_3$ solutions, a black precipitate, presumably mercury sulfide, formed.

Table 10-2. Extraction of Mercury-Iodine Complex

Aqueous phase: 1 M HNO_3--0.1 M Hg--0.01 M KI
Phase ratio: 1/1

Solvent	Iodine Extraction Coefficient (E_a^o)
0.3 M TBP--n-dodecane	1.4
0.6 M TBP--ndodecane	2.8
0.3 M DAAP-n-dodecane	3.1
0.3 M TOPO--n-dodecane	29.3
0.1 M Adogen 364--diethylbenzene	3.8

Table 10-3. Stripping the Mercury-Iodine Complex from Various Solvents

Organic phase: Indicated extractant containing iodine that had been extracted from 1 M HNO_3--0.1 M Hg--0.01 M KI solution; organic extracts were washed with water to remove extracted nitric acid prior to stripping.

Phase ratio: 1/1

Contact time: 10 min at room temperature

Strip Solution	Iodine Stripped (%)			
	0.3 M TBP	0.3 M TOPO	0.3 M DAAP	0.1 M Adogen 364
1 M NaOH	35	3	43	8
1 M NaOH (60°)	-	-	78	-
0.2 M NaOH (60°)	-	-	58	-
0.1 M $Na_2S_2O_3$	91	8	99.6	4
0.05 M $Na_2S_2O_3$--0.5 M NaOH	-	-	-	69
0.1 M $Na_2S_2O_3$--0.1 M NaOH	-	-	87	-
0.1 M $Na_2S_2O_4$	-	-	98	8
0.5 M NH_4HCO_3	-	-	2	-
0.5 M $(NH_4)_2CO_3$--0.2 M EDTA	-	-	80	-
0.2 M NaOH--0.1 M HCHO	-	-	2	-
1 M Na_2CO_3	-	-	-	2
0.3 M Na_2CO_3--0.2 M EDTA--0.1 M Hg^{2+}	-	-	-	92

Effect of Organic Solvents on Retention of Iodine by Iodized Charcoal
(R. E. Adams, R. D. Ackley, Zell Combs)

Investigation of factors relating to the trapping of the various forms of radioiodine in off-gas systems was continued. The objective of this program is to develop information that will aid in the design of an extremely efficient iodine removal system for treating gaseous effluent from LMFBR fuel processing plants. A problem is created by the unavoidable introduction into the off-gas system of various organic vapors (from solvents used in the chemical processing) which can poison the iodized charcoal used for trapping organic iodides. One possible solution involves the use of Hopcalite oxidizing catalyst (Type 21215 from Mine Safety Applicances) to convert the organic vapors into CO_2 and H_2O, which are less damaging to the charcoal efficiency than the original vapors. Also, the Hopcalite converts methyl iodide into a form (similar in behavior to I_2) that is more readily trapped by charcoal than methyl iodide.

One question that arises is whether organic vapors in the gas stream would cause rapid release of iodine from iodized charcoal as a consequence of the catalytic oxidizer becoming temporarily inoperative. To investigate this potential situation, an apparatus containing two identical parallel systems was constructed. In each system, air containing ^{131}I-labeled methyl iodide at a concentration of ~17 mg/m^3 was passed through a Hopcalite bed (~350°C) and then through two, 1-in.-deep beds of iodized charcoal at ~70°C. The air velocity through the various beds was 40 x (T°K/298°K) fpm. Most of the ^{131}I (injected as CH_3I) penetrated the Hopcalite and was trapped by the first charcoal bed (in each leg) with more than 99.5% efficiency. To facilitate exposure to organic vapor, the first charcoal bed from each leg (denoted as Bed A and Bed B) was removed and installed in separate systems. Bed A was exposed to air (25°C, 65% RH) flowing at 40 fpm which had passed over diethylbenzene. Bed B was exposed in a similar manner except the air was passed over Amsco 125-82. In each case the air stream was estimated to be about 40% saturated with the organic vapors. Both solvents caused slow release of iodine from the bed:

Charcoal Bed	Organic	Cumulative Exposure (hr)	Cumulative ^{131}I Loss %
A	Diethylbenzene	4	0.02
		24	0.08
		48	0.14
B	Amsco 125-82	4	0.03
		24	0.15
		48	0.26

As an exploratory experiment, Bed A was further exposed for 24 hr to air containing vapor from ethanol denatured with methanol (SDA 3A-190); an additional loss of ^{131}I equal to 0.03% was noted. Bed B was similarly exposed to 2-ethyl-1-hexanol vapor; an additional loss of 0.07% occurred.

The final interpretation of these data must await the results from control tests; however, it appears that the sweeping of iodized charcoal with air containing organic vapors causes previously trapped ^{131}I to be released at a small but significant rate.

Catalytic Oxidation of Organic Vapors (M. R. Bennett, G. I. Cathers)

In continuing studies of the catalytic oxidation of n-dodecane over Hopcalite, efforts during the past month were directed toward determining the effect of temperature on the oxidation and whether or not intermediate organic products (incomplete combustion to CO_2 and H_2O) were formed that could later react with radioiodine in process off-gas streams to form organic iodides. In addition, since it is known that there is frequently a significant relationship between catalytic activity and surface area, the thermal stability of Hopcalite, as measured by surface area, was determined at temperatures up to 700°C.

The method employed for determining the formation of short-chain hydrocarbons during the combustion of n-dodecane over Hopcalite consisted of tests in which the amounts of CO_2 and H_2O produced were measured by sorption on traps of ascarite and drierite, respectively. Unoxidized n-dodecane and any short-chain hydrocarbons in the product stream were collected in a cold-trap at -140° to -170°C and subsequently analyzed by gas-chromatography after dissolution in an organic solvent. In a test at 500°C, use of the ascarite and drierite traps resulted in approximately a 100% material balance in terms of the amounts of CO_2 and H_2O produced. Also, no short-chain hydrocarbons or n-dodecane were found by gas chromatography, tending to confirm that destruction of the hydrocarbons was complete. In a test at 350°C, however, only about 30% of the theoretical amounts of CO_2 and H_2O were picked up on the traps and the corresponding cold-trap residue analysis indicated the presence of unidentifiable low-boiling hydrocarbons. Although the results of the test at 500°C showed essentially complete oxidation of the n-dodecane to CO_2 and H_2O, the sensitivity of the gas-chromatographic technique was not sufficient to conclude that no degraded hydrocarbon fraction was produced.

In studies of the thermal stability of Hopcalite, the temperature effect on catalyst surface area was clearly demonstrated in 1-hr tests in which samples of the material were heated in air to temperatures of 400, 500, 600, and 700°C. The surface area decreased from an initial value of about 132 m^2/g to the respective values of 123, 68, 17, and 11 m^2/g. The effect of time was shown in tests carried out over periods of 6 and 60 hr at temperatures of 400 and 600°C. In these tests, the surface area decreased to values of 104 and 15 m^2/g, respectively, in the 6-hr test, and to 94 and 12 m^2/g, respectively, in the 60-hr test.

Plans are being made to study Hopcalite oxidation efficiencies by infrared spectrophotometry. This should provide more reliable data on the production of CO_2 and H_2O as well as of intermediate oxidation products. If the infrared spectrophotometric technique is found applicable to study of the oxidation process, it should be useful for comparing Hopcalite with other possible catalysts.

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TASK 11 - RADIATION AND SHIELDING
(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).

Task 11.1 - Nuclear Data Compilation and Correlation
(E. D. Arnold and H. F. Soard)

Calculations were completed of the (n, γ), (n, p), (n, α), and (n, 2n) cross sections of several hundred fission products and cladding materials averaged over a typical LMFBR spectrum. These cross sections are being used to update the library of LMFBR nuclear data in the ORIGEN code.

Task 11.3 - Shield Attenuation Kerma
(E. D. Arnold and H. F. Soard)

Test calculations are being made with the ANISN code in the $S_{16}P_3$ mode using 27 energy groups for secondary photons in preparation for relatively precise calculations of the neutron dose rates that will result from neutron sources in the shipping and processing of LMFBR fuels. The initial studies with this program will be devoted to the determination of the external neutron dose rates that would result from the use of sodium-filled, steel-shielded shipping casks for LMFBR fuels. Simple hand calculations have shown that the projected quantities of ^{242}Cm and ^{244}Cm in spent LMFBR fuels may be sufficient to cause a significant neutron dose contribution.

TASK 12 - CRITICALITY
(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).

Task 12.2 - Calculation of Basic Parameters
(D. W. Magnuson)

Calculations were completed of the limiting critical concentrations of various mixtures of plutonium and uranium nitrate solutions and for mixtures of $Pu(NO_3)_4 \cdot 5H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$.[1] From these data it may be estimated that the limiting critical concentration of a solution that would result from dissolution of spent LMFBR core fuel containing 21% plutonium is about 12.8 g/l of total Pu or (more significantly) about 8.6 g/l of fissile plutonium. The estimated limiting critical fissile plutonium concentration is only slightly higher, about 9.0 g/l, for a solution that would result from dissolution of mixed core and axial blanket fuel containing about 10% plutonium. Based upon recent regulatory practices, it is recommended that LMFBR fuel reprocessing flowsheets that will exploit concentration control to avoid inadvertent criticality should be based on fissile plutonium concentrations no higher than 6.0 g/l (total plutonium ~9.0 g/l).

Calculations continued of the critical parameters of solutions of plutonium and fissile uranium in vessels packed with borosilicate glass raschig rings. Models were developed that predict adequately the results of critical experiments for such systems. These calculations will be completed and reported next month.

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