ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

REACTOR DEVELOPMENT PROGRAM
PROGRESS REPORT

August 1963

Albert V. Crewe, Laboratory Director

<u>Division</u>	<u>Director</u>
Chemical Engineering	R. C. Vogel
Idaho	M. Novick
Metallurgy	F. G. Foote
Reactor Engineering	L. J. Koch
Reactor Physics	R. Avery
Remote Control	R. C. Goertz

Report coordinated by
R. M. Adams and A. Glassner

Issued September 15, 1963

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FOREWORD

The Reactor Development Program Progress Report, issued monthly, is intended to be a means of reporting those items of significant technical progress which have occurred in both the specific reactor projects and the general engineering research and development programs. The report is organized in a way which, it is hoped, gives the clearest, most logical over-all view of progress. The budget classification is followed only in broad outline, and no attempt is made to report separately on each sub-activity number. Further, since the intent is to report only items of significant progress, not all activities are reported each month. In order to issue this report as soon as possible after the end of the month editorial work must necessarily be limited. Also, since this is an informal progress report, the results and data presented should be understood to be preliminary and subject to change unless otherwise stated.

The issuance of these reports is not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of ANL topical reports.

The last six reports issued
in this series are:

February 1963	ANL-6698
March 1963	ANL-6705
April 1963	ANL-6717
May 1963	ANL-6739
June 1963	ANL-6749
July 1963	ANL-6764

TABLE OF CONTENTS

	<u>Page</u>
I. Boiling Water Reactors	1
A. BORAX-V	1
1. Experiments	1
2. Water Chemistry	2
3. Maintenance and Modification	3
4. Design, Procurement, and Fabrication	4
5. Development and Testing	4
II. Liquid-metal-cooled Reactors	6
A. General Fast Reactor Physics	6
1. ZPR-III	6
B. General Fast Reactor Fuel Development	8
1. Fast Reactor Fuel Jacket Development	8
2. High-temperature Metal Fuels	9
3. Corrosion of Fuel-cladding Materials for Sodium-cooled Reactors	11
4. Tests of Tubing	12
C. EBR-I, Mark IV	13
D. EBR-II	13
1. Reactor Plant	13
2. Sodium Boiler Plant	15
3. Power Plant	15
4. Fuel Cycle Facility	16
5. Process Development	21
6. Training	25
E. FARET	25
1. Design Studies	25
2. Safety Analyses	26
3. Oxygen Meter	27
4. Fuel Development	28
5. In-pile Experiment	31
6. Shielding Analysis	31
III. General Reactor Technology	32
A. Theoretical and Applied Nuclear Physics	32
1. Doppler Effect Studies	32

TABLE OF CONTENTS

	<u>Page</u>
2. Analysis by Numerical Methods	33
3. AFSR	33
B. Reactor Fuels Development	34
1. Corrosion Studies	34
2. Ceramic Fuels	36
3. Particulate Metal Fuel Elements	37
4. Irradiation Studies	38
5. Extrusion Developments	39
6. Nondestructive Testing	40
C. Heat Engineering	41
1. Stainless Steel Loop Design	41
D. Chemical Separations	41
1. Chemistry of Liquid Metals	41
2. Uranium Oxide Reactions in Molten Halides	42
3. Plutonium Recovery Process	42
4. Head-end Treatments for Refractory Fuels	43
5. Fluidization and Volatility Separations Processes	43
6. General Chemistry and Chemical Engineering	46
E. Plutonium Recycle Program	47
IV. Advanced Systems Research and Development	49
A. Thermionic Energy-conversion Diode with a Film-boiling Liquid Metal	49
B. Magnetohydrodynamics	51
1. A Nuclear Magnetohydrodynamic System	51
2. MHD Power Generation	54
V. Nuclear Safety	55
A. Thermal Reactor Safety Studies	55
1. Metal Oxidation and Ignition Studies	55
2. Metal-Water Studies	56
B. Fast Reactor Safety Studies	56
VI. Publications	58

I. BOILING WATER REACTORS

A. BORAX-V

1. Experiments

Zero-power experiments on the central superheater core, CSH-1 were completed. The reactor was brought to operating temperature and pressure (489°F and 600 psig) by means of the electrical preheating system. Zero-power critical experiments permitted calibration of control rods, determination of the reactivity effects of flooding the superheater and of boric acid, and irradiations of flux wire. Preparations are being made for power operation.

To calibrate control rods, boric acid was added in increments after the reactor was raised to 489°F. For each increment, the critical control rod positions were determined, and differential control worths were obtained by measurement of the periods for various control rod movements. At 489°F, with superheater coolant channels drained and without boric acid, the control rod critical position was about 14 in. The available excess reactivity of 5.4%, compared with the 9.3% available excess reactivity at room temperature, gave a temperature defect of -3.9%. The loss in "safety effect" reactivity which would have occurred if the reactor were heated to operating temperature with no movement of control rods is estimated to be 4.9%.

The relative reactivity worths of the central control rod, intermediate rods, and outer bank of four T-shaped rods changed considerably as the temperature increased. At room temperature, with the boiler unborated, the central control rod was worth 74% and the outer rod bank was worth 134% of an intermediate rod, No. 2, at the same position. At operating conditions, the relative worths were 90% and 148%, respectively, indicating that the central rod and the outer bank gained in relative importance as the temperature increased.

At operating temperature, without boric acid, a determination was made of the differential reactivity worth of the central control rod as a function of its position relative to the remaining eight control rods above the remaining 8-rod bank, in the bank, and below the bank. The differential reactivity worth of the central control rod was determined as 0.0884%/in. when 3.5 in. above the 8-rod bank which was at 14.5 in; 0.152%/in. when in the 8-rod bank at 14.825 in.; and 0.181%/in. when 9.500 in. below the 8-rod bank at 16.60 in. The differential worth of the 8-rod bank varied from 1.06% $\Delta k/k$ /in. with the central rod withdrawn to 0.705% $\Delta k/k$ /in. with the central rod completely inserted. The position of the central control rod dictated the critical position and reactivity worth of the remaining rods.

Flooding of the superheater coolant channels at operating temperature without boric acid in the system produced a gain in available excess reactivity of 1.18% when all nine control rods were banked, and of 1.43% with the central rod fully withdrawn and the remaining eight rods banked. This contrasts with gains of 0.86% and 1.16% at room temperature reported previously.¹

With the boric acid concentration in the boiler and in the superheater moderator at 7.8 gm H_3BO_3 /gal H_2O at operating conditions and with the superheater channels flooded with pure water, the reactivity changes were +1.01% for the 9-rod bank and +1.05% for the eight rods banked and central rod fully withdrawn. Since there was a slight leakage from the boiler moderator to the superheater coolant channels, there was perhaps a small amount of boric acid in this region. Measured inleakage of moderator water into the superheated steam path is about 1.5 gal/hr with the superheater drained.

The reactivity effect of boric acid at operating temperature was 0.65% per gm H_3BO_3 /gal H_2O as compared with 0.76% per gm H_3BO_3 /gal H_2O at room temperature. In both cases the analyses were made with the samples at room temperature. The reactivity effect was linear within 4% at operating temperature and within 1% at room temperature. This deviation is within the limits of experimental accuracies.

Axial irradiations of flux wires were made at 489°F in six pressure thimbles located in boiler coolant channels, with the central control rod below and at the same height as the 8-control-rod bank. Boric acid concentration during the irradiations was 8.0 gm H_3BO_3 /gal H_2O , allowing the control rods to be almost completely withdrawn and thus simulating the rod positions at power operation. Data reduction and analysis of the results of these experiments is in progress.

2. Water Chemistry

During this period, the resistivity of reactor water varied between 2.8 megohms before the boric acid addition with the reactor at 500 psig and 470°F, to 0.40 megohm with 8.3 gm H_3BO_3 /gal H_2O in the reactor vessel at 600 psig and 489°F. The boric acid concentration in the reactor water before the reactor vessel was heated and brought to pressure was colorimetrically measured to be as low as 0.16 ppm.

pH varied from 6.5 before addition of boric acid to 5.5 with 8.3 gm H_3BO_3 /gal H_2O with the reactor at 600 psig and 489°F. The pH of condensed steam samples was slightly higher than that of the water.

After boric acid was removed by draining and flushing, reactor water was "cleaned" to a resistivity of 2.0 megohms/cm, a pH of 6.8, and a boric acid concentration of 3.6 ppm.

¹Reactor Development Program Progress Report, June, 1963, ANL-6749, p. 1.

The chloride concentration in the reactor water, monitored continuously throughout the addition of boric acid, remained below 0.1 ppm. Analyses of soluble iron varied from 0.01 to 0.13 ppm. The NO_3^- concentration was between 0.01 to 0.13 ppm for all tests. All samples of suspended solids were routinely gamma-scanned; there was no indication of fission product isotopes.

Checks on the "gross specific activity" of the reactor water revealed no detectable activity. The "gross specific activity" in the concentrated suspended solids filtered from the reactor water varied from 2,900 to 10,900 cpm/mg. The concentration of suspended solids varied from 0.03 to 0.26 ppm.

A study of boric acid carryover in the steam, with the reactor at ~600 psig and ~489°F and in a static condition, showed the carryover to be approximately 3% for all concentrations up to 8.0 gm H_3BO_3 /gal H_2O in the reactor water. The concentration of H_3BO_3 in the steam at various levels, determined by means of a steam-sampling probe in the steam dome of the reactor vessel, was not uniform. With the H_3BO_3 concentration in the reactor water at 8.0 gm/gal, the concentration varied from 70 to 80 ppm irregularly over the 4-ft steam dome height. This variation increased with a reduction in reactor pressure.

3. Maintenance and Modification

After completion of the zero-power experiments at 600 psig and 489°F, the reactor vessel head was removed and all the superheater fuel assemblies were transferred to storage. Leak-testing and seal-welding of the superheater fuel-insulating cans is in progress. Because of the radioactivity of the fuel removed from the reactor (2-3 r/hr on contact), the fuel assemblies were installed in a lead shield and the welding performed by a specially designed, remotely controlled TIG (tungsten inert gas) welding machine.

The water-cooled carbon ring-type seal on the 150-gpm auxiliary water circulating pump failed on two occasions. The first failure was at 600 psig and room-temperature conditions, and the second failure was at 600 psig and 489°F. In both cases the carbon ring was pitted and chipped, and the mating Stellite seal face was badly scored. The reason for these failures has not been determined.

The carbon ring seal was replaced with a water-cooled packing gland, with the packing made of aluminum foil-asbestos. The pump operated satisfactorily for the remainder of the experiments at operating conditions.

Revision of control-rod-seal cooling water control system to relocate the control valves and flow indicators from the subreactor room to the operating floor was started. Changes in temperature of feedwater

and of reactor temperature and pressure made it necessary to adjust seal water flow rates frequently to each of the nine control rod seals. Because of high activity levels, this could not be done during reactor operation. Relocation of this system will eliminate the need to shut the reactor down during these adjustments.

Installation of a third low-flow-rate superheater-flood valve to reduce the thermal stresses on the superheater fuel assemblies during flooding was started. The calculated flooding time through this valve is 10 min.

A new in-reactor-vessel saturated steam collector has been designed and fabricated. This collector, connected to the saturated steam exit pipe in the reactor vessel, raises the level of the steam outlet to a point near the top of the steam dome to prevent flooding the superheater via the pressure-equalizing valve and superheater flood-and-drain systems when reactor water is at normal levels.

Instrumented boiling fuel assembly I-1 passed a series of cycles in the autoclave at 600 psig and 489°F, with new flowmeter sensing coils installed. The remaining four sensing coils were autoclave-tested successfully and were ready for installation into boiling fuel assemblies I-2 and I-3. The flowmeters of assembly I-1 also were calibrated in the air-water test loop.

4. Design, Procurement, and Fabrication

The in-vessel, demister-type steam separator has been received at the reactor site and has been test-fitted on the inlet superheater fuel assemblies.

A new magnetic, drag disc-type downcomer flowmeter of improved design was under fabrication.

Design of the 12-thermocouple, subcooling temperature-measurement assembly, to measure entrance and exit boiler temperatures, was completed and fabrication has started.

Six samples of W-26% Re-sheathed, W/W-26% Re wire, ThO₂-insulated thermocouples, obtained from Pyro Electric Company, will be calibrated at temperatures to 5000°F. Preliminary results with two similar thermocouples from another manufacturer indicate satisfactory performance up to 5350°F.

5. Development and Testing

a. Boiling-fuel-rod Time Constant. The thermal time constant for the instrumented boiling fuel rod of BORAX V has been determined between 490 and 850°F. This $\frac{3}{8}$ -in.-dia fuel rod is made of 4.95-w/o enriched UO₂ pellets clad with 0.015 in. of Type 304 stainless steel and has a

tantalum-sheathed W/W-26% Re thermocouple spring loaded into a blind hole in the fuel. The average 63% time-constant values for three fuel rods are 8, 9.7, and 6.7 sec.

These data were obtained by heating the fuel rod to 850°F in a muffle furnace and then cooling in NaK maintained at 490°F. The response of the thermocouple located within the fuel was recorded by means of an oscillograph.

b. Advanced Superheater Fuel. A pneumatic-pressure-drop test was conducted on a mockup, advanced superheater fuel with a spherical-pellet configuration, consisting of a 24-in.-long array of 4008 $\frac{3}{8}$ -in.-dia plastic balls packed rhombohedrally inside a 3-in.-ID square tube and outside a $1\frac{1}{8}$ -in.-OD square tube. The mockup, constructed of $\frac{1}{2}$ -in. Plexiglas reinforced with steel bands, failed at a pressure of 50 psig, apparently due to stress concentrations at machine screw holes.

Limited data taken before failure indicate that the pressure drop across the test section was about 42 psi for a mass flow rate of 1660 lb/hr with an entrance pressure of 50 psig at 70°F. Because of the excessive pressure drop at such a low flow rate (flow rate per superheater fuel assembly equivalent to 20 Mwt reactor power is about 9,000 lb/hr), no further tests are planned for this configuration.

A new model made of aluminum and containing $\frac{1}{2}$ -in.-dia balls packed cubically inside a 3-in.-ID square tube and outside a 1-in.-OD square tube is being designed.

Inspection of 50 Type 406 stainless steel-UO₂ cermet superheater fuel plates received from a commercial supplier has been completed. All but three plates, rejected because of inadequate edge cladding, were accepted.

A vacuum-braze of simulated flattened-tip thermocouples with a Type 304 stainless steel sheath into slots in the edge of Type 406 samples was successfully made with Coast Metals-60 alloy powder. A similar braze with Prema-braze-128 wire resulted in porosity.

UO₂ spheres, $\frac{3}{8}$ in. in diameter, have been produced with a diametral tolerance of ± 0.0005 in. except for a narrow equatorial flat band, for development of the spherical-pellet concept of superheater fuel elements. The cold-forming electron beam and TIG welding of 0.010 in.-thick Incoloy-cladding hemispheres has been demonstrated successfully.

c. Tubing for BORAX-V. Approximately 15 m of Type 406 stainless steel (8.71-mm OD by 0.28-mm wall) tubing were tested with a dual-frequency eddy-current test system of 10 and 1750 kc. Five defective areas in which a localized reduction in the thickness of the tube wall greater than 10% were found. These areas were cut out and discarded.

II. LIQUID-METAL-COOLED REACTORS

A. General Fast Reactor Physics

1. ZPR-III

Experiments with Assembly 43 have been completed after several months. This assembly consisted of a central cylindrical core zone of about 162-liter volume but of composition corresponding to that of a 4000-liter uranium carbide core. Surrounding this was a filter zone consisting of depleted uranium and graphite, in turn surrounded by an annular driver zone whose fuel composition was somewhat more dense than that of the core. By this means the spectrum of a 4000-liter core could be achieved throughout a large fraction of the central region with a total inventory of fuel under 600 kg. The detailed compositions and dimensions are given in the Reactor Development Progress Report for April, 1963, ANL-6717, p. 6.

a. Central Reactivity Coefficients. A series of measurements of central reactivity coefficients resulted in the data of Table I. In each case, the reactivity value is reported with respect to a void of the same size as the sample. The two sizes of B_4C indicate the degree of self-shielding in this soft spectrum. The tantalum value of -15.9 lh/kg for a $2 \times 2 \times 2$ -in. sample is in addition to the value of -19.8 lh/kg for a $\frac{1}{4} \times 2 \times 2$ -in. sample

Table I. Central Reactivity Coefficients Relative to Void

<u>Material</u>	<u>Sample Size (in.)</u>	<u>Coefficient (lh/kg)</u>
B_4C	$\frac{1}{4} \times 2 \times 2$	-615 ± 15
B_4C	$\frac{1}{2} \times 2 \times 2$	-535 ± 15
Type 304 Stainless Steel	$2 \times 2 \times 2$	-2.6 ± 0.5
Depleted Uranium	$2 \times 2 \times 2$	-4.0 ± 0.2
Tungsten	$2 \times 2 \times 2$	-5.6 ± 0.3
Tantalum	$2 \times 2 \times 2$	-15.9 ± 0.5
Ph-I oxide	$2 \times 2 \times 2$	-18.5 ± 2.2
Ph-II oxide	$2 \times 2 \times 1.75$	-12.9 ± 2.4
Bismuth	$2 \times 2 \times 2$	-0.9 ± 0.4
Yttrium	$2 \times 2 \times 2$	-2.9 ± 0.9
Lead	$2 \times 2 \times 2$	-0.8 ± 0.3
Beryllium	$2 \times 2 \times 2$	$+2.4 \pm 2.1$
Carbon	$2 \times 2 \times 2$	-2.7 ± 2.5
Aluminum	$2 \times 2 \times 2$	-2.8 ± 1.4
Al_2O_3	$2 \times 2 \times 2$	-1.7 ± 1.4
Oxygen (by difference)	$2 \times 2 \times 2$	-0.4 ± 3.2

reported in Progress Report for July 1963, ANL-6764, p. 8. Reactivities have been corrected for stainless steel canning materials where necessary. The designations Ph-I oxide and Ph-II oxide refer to mixtures of oxides and salts of which the metallic components are a mockup for nuclear purposes of fission products.

b. Doppler Experiment in Softened Spectrum. In Reactor Development Program Progress Report for July, 1963, ANL-6764, p. 8, Doppler measurements for depleted uranium were reported in the spectrum of the 4000-liter carbide core, and in a spectrum from which the low-energy neutrons were attenuated with boron. To complete the series of Doppler studies, a measurement was made in a spectrum whose low-energy components were augmented by substituting some graphite for sodium. The filter composition was also altered by substituting graphite for U^{238} for the same objective. Compositions of the core and filter before and after the modification are given in Table II. In the immediate vicinity of the region modified for the Doppler experiment, the uranium was rearranged to minimize the Dancoff correction.

Table II. Atomic Density, (atoms/cc) $\times 10^{-24}$

	Original Assembly 43		Softened Assembly 43	
	Core	Filter	Core	Filter
U^{235}	0.001141	0.000045	0.001141	0.00003
U^{238}	0.007309	0.02169	0.007309	0.01447
Carbon	0.008326	0.02914	0.02498	0.0416
Sodium	0.01060	-	0.00636	-
Stainless Steel	0.01643	0.00770	0.01375	0.00770

A typical sample is shown schematically in Figure 1. Heating is supplied by passing electric current through the Hastelloy sheath which

Figure 1. Doppler Coefficient Sample.

surrounds the UO_2 . Heat is conducted into the sintered UO_2 through the helium-filled annulus and retarded from escaping outward by the evacuated shell. The 2-in. outer diameter is sufficiently small to permit the entire sample to be inserted in a ZPR-III matrix tube. Cooling air is drawn over the outside of the sample.

Two samples (2.2 kg each) of sintered UO_2 were inserted into the core. After recalibration of control rods, their difference in reactivity worth cold was measured. Each sample was heated to 823°K in turn and the difference in worth measured. A final measurement was made with one sample at 538°K . A check rerun with both samples cold was made between the first and second heated runs.

The preliminary result indicated that the total change in worth of the 2.2-kg sample due to heating from 303 to 823°K was 0.67 lh, and from 303 to 538°K was 0.35 lh. A calculation of the effect based on Greebler's² temperature-dependent cross section gave 0.67 lh change for the temperature interval 300 to 750°K . Although the two measured temperature intervals indicate a Doppler variation with the -0.6 power of the temperature, an exponent as low as -1 is well within the experimental uncertainty.

Experiments to evaluate small changes in position of the sample and of its associated hardware separately indicated that movement of the hardware alone was worth less than 0.02 lh/cm. X-ray examination of the hot samples indicated the extent of the U^{238} expansion, and this effect was also worth less than 0.02 lh. The reactor drift limited the accuracy of all measurements to about 0.03 lh.

At the conclusion of the experiment, x-ray examination showed that no permanent differences in configuration had occurred during the experiment.

This concluded the present series of Doppler measurements, and the reactor was disassembled.

B. General Fast Reactor Fuel Development

1. Fast Reactor Fuel Jacket Development

a. Breakdown of Refractory Alloys. Following unsuccessful breakdown attempts at 850°C (see July Progress Report, ANL-6764, p. 10) the Nb-9 w/o Ti-8 V, V-35 w/o Nb, and Nb-20 w/o V were recast.

²Greebler, Hutchins, and Sueoka, Calculation of Doppler Coefficient and Other Safety Parameters for a Large Fast Oxide Reactor, GEAP-3646 (1961).

Attempts to roll these alloys at 1150°C were equally futile. Either higher temperatures or other means of breakdown must be considered for these alloys.

b. Stainless Steel-clad Vanadium Cores. A metallographic evaluation of the extrusions of Type 304 stainless steel with a vanadium core and Type 304 stainless steel with a nickel-plated vanadium core (see July Progress Report, ANL-6764, p. 10) has shown a very tight bond at the vanadium-Type 304 stainless steel interface with no evidence of separation. Certain areas showed a discontinuous string of very fine particles, possibly oxides, along the interface. There was an excellent bond between the nickel and vanadium. The nickel plate was bonded to the stainless steel but localized areas of separation were evident. A fine-particle discontinuous network was visible in areas along the interface between the nickel and stainless steel.

A duplex billet of Type 304 stainless steel with a vanadium core was assembled in an inert atmosphere and extruded at a 4:1 reduction ratio at 1200°C. Ultrasonic and X-ray examinations indicated a sound bond between the stainless steel and the core. The duplex extrusion will be processed into small-diameter, thin-wall tubing of approximately 3.96 mm (0.156 in.) ID by 0.38 mm (15 mils) total wall thickness.

2. High-temperature Metal Fuels

a. Properties of Uranium-Plutonium-Fissium. As part of a program for studying U-Pu-Fs, tensile tests of uranium-10 w/o plutonium alloys at elevated temperatures have yielded very low elongations. Values given previously ranged from about 0.7 to 1.5% elongation at 550°C for the uranium-10 w/o plutonium alloy. Further tests were made by using various materials for crucibles in the injection-casting furnace to indicate what caused the brittleness.

High-purity uranium and plutonium were injection cast from a zirconia crucible rather than from yttria-coated graphite as previously. Reactor-grade uranium was injection cast in the same apparatus with both crucible materials. Tests were run at 550°C, that is, in the alpha range for both alloyed and unalloyed metals. Although strain rates varied from 0.06 in. (in.-min)⁻¹ to 10⁻⁷ in. (in.-min)⁻¹, the elongation to fracture remained constant.

Uranium specimens showed 47% elongation to fracture. Elongations of 6% were obtained in the high-purity uranium-plutonium alloy, a significant improvement over the impure castings tested previously. Since the elongation to fracture of this uranium-plutonium alloy does not approach the value of 47% shown by the uranium, these tests apparently indicate a greater effect of interstitials on plutonium-bearing alloys.

b. Compatibility of Plutonium-1.25 w/o Aluminum with Zircaloy-II.

The Mark IV loading of EBR-I consists of Pu-1.25 w/o Al fuel clad with Zircaloy-II. To study the solid interaction of this fuel-clad combination, a series of Pu-1.25 w/o Al vs Zircaloy-II diffusion couples were given various heat treatments. The couples were annealed at 500, 550, and 600°C for 7, 17, and 42 days, and at 650°C for 42 days.

Metallographic and microhardness investigations did not reveal any evidence of interdiffusion. The metallographic study did indicate good bonding present in all specimens.

To investigate further the possibility of diffusion penetration, electron beam microprobe analysis was performed at Mound Laboratory on the couple annealed at 600°C for 42 days. The analysis showed a penetration of about 10 μ (0.4 mil) into the Zircaloy-II. It is important to note that this significant amount of interdiffusion was not detected by ordinary metallographic and microhardness means.

The 10- μ penetration confirmed the good bonding and showed that diffusion penetration in this system is low at 600°C. At 500°C (the projected operating temperature at the diffusion interface) we should expect the penetration to be considerably less than that at 600°C.

c. Uranium-Molybdenum Alloys. Extrusion of U-14 w/o Mo was not successful at temperatures below 1000°C with an extrusion ratio of 5.3:1, as reported in the June Progress Report (ANL-6749, p. 16). The alloy has since been extruded at temperatures from 950 to 650°C and an extrusion ratio of 4.2:1. No cracks were detected in radiographs of the extruded product, but an irregularity in diameter was detected. This may be attributed to the difference in stiffness of the Zircaloy-II jacket and the core material. Attempts will be made to extrudeunjacketed alloy billets.

d. Uranium-Plutonium-Fizzium Alloy Pins. Table III indicates the quantities, lengths, and compositions of fuel pin specimens that have been produced and that are available for canning as EBR-II or MTR test specimens.

Table III. Fuel Pin Specimens

Nominal Composition, w/o	Melt Number	Length, cm	Quantity
Depleted U-20 Pu-10 Fz	R96, R97, R98	35.6	52
		32.0	31
		5.1	4
		5.1	24
7.7% Enriched U-15 Pu-10 Fz	R107	43.2	32
		7.6	25
		5.1	1
		5.1	24
Depleted U-15 Pu-10 Fz	R119	43.2	30
15.5% Enriched U-10 Pu-10 Fz	R115	43.2	44
		22.9	12

The tooling and techniques for welding end plugs in Nb-1 w/o Zr, vanadium, and Hastelloy tubes have been worked out. Some difficulty has been experienced in machining the tungsten lining from ends of the Hastelloy tubes. Diamond grinding points have been ordered for this operation. A sodium deoxidizing train (hot trap) and an extruder for making sodium wire have been installed and tested satisfactorily. A number of stainless steel control rods have been loaded, settled, closure welded, and radiographically inspected for sodium level. These operations have demonstrated that the required sodium level can be determined from volumetric density calculations.

Bonding the refractory metal jackets and specimens presents a problem. Preliminary tests have indicated that the 0.1 percent of impurities in the glovebox atmosphere may embrittle Nb-1 w/o Zr tubing bonded for 3 hr at 450°C. A vacuum-chambered bonder has been designed. This bonder will be evacuated and backfilled with welding-grade argon gas, but it will not be available for some months. In order to complete the specimens at an earlier date, tests are being run on bonding in helium-filled secondary containers using existing equipment.

3. Corrosion of Fuel-cladding Materials for Sodium-cooled Reactors

Microhardnesses of Nb-1 w/o Zr, Nb-5 w/o Mo, and Nb-39 w/o V-1 w/o Ti samples exposed to flowing sodium for 330 hr at 650°C (see July Progress Report, ANL-6764, p 10) were determined. The samples containing zirconium or molybdenum showed a constant hardness across their transverse sections. The hardness of the Nb-1 w/o Zr sample was harder by 100 DPH than a control, and the hardness of the Nb-5 w/o Mo sample was harder by 70 DPH than the control (indicating the pickup of oxygen between 50-100 ppm). The Nb-39 w/o V-1 w/o Ti sample showed a hardness gradient from 1000 DPH at the surface to 390 DPH at 300 μ from the surface.

A subsequent group of four specimens have been exposed to flowing sodium (0.15 m/sec) for 308 hr at 650°C. A sodium sample has been taken for oxygen analysis but to date has not been analyzed. Zirconium turnings were used as an oxygen getter during exposure of the test samples.

Three of the samples were given a vacuum-anneal stress-relief treatment for 2 hr according to Table IV. The ends of a fourth sample, a Nb-1 w/o Zr rod with a plasma-sprayed coating of Type 304 stainless steel, 127 μ thick, were exposed.

The corrosion results are also summarized in Table IV.

Table IV. Corrosion of Niobium Alloys in Flowing Sodium

Specimen, w/o	Annealing Temp, °C	Weight Loss,* mg/cm ²	Change in Thickness,* μ
Nb-5 Mo	800	11.41	81.3
Nb-2.37 Cr	700	54.6	127.0
Nb-39 V-1 Ti	600	17.72	22.8
Nb-1 Zr (Stainless steel coated)	-	-	no change

*Cleaned of sodium with alcohol and water; nonadherent oxide removed with soft brush.

The Nb-5 w/o Mo sample was severely split at the edges so as to increase the apparent thickness. The Nb-2.37 w/o Cr sample was severely split at the edges along the flow lines of the worked structure. A hardness traverse showed a gradient of 50 DPH from center to edge, with the center being softer at 250 DPH. The Nb-39 w/o V-1 w/o Ti sample showed the same hardness profile as the Nb-39 w/o V-1 w/o Ti sample discussed above with the exception that the disturbed surface layer was 200 μ thick.

The Type 304 stainless steel plasma-sprayed Nb-1 w/o Zr sample exhibited no dimensional change. The unprotected ends split apart, resulting in cracking of the clad at the ends. Away from the unprotected ends the mechanical bond between the rod and coating appeared the same before and after test.

4. Tests of Tubing

a. Electromagnetic Tests of Tubing. Electromagnetic tests on tubing being used or produced for general fast reactor fuel development and the results of these tests are summarized in Table V. These tests were all made with pulsed-field test equipment with mask-aperture assemblies appropriate to the tube size.

b. Radiographic Inspection. Approximately 25.6 m of Hastelloy X tubing of 4.21-mm ID x 0.23-mm wall were radiographically examined. The only defects noted were light inclusions, and these were prevalent in only a few tubes.

Radiographs were also made on 2 Nb-1 w/o Zr tubes plasma-coated with Type 304 stainless steel. The radiographs revealed some areas of relatively high transmission, but generally the coating appeared to be uniform. The areas of relatively high transmission indicate voids in the coating, or possibly in the tube wall. The condition of the tubing was not known prior to the application of the coating.

Table V. Electromagnetic Tests on Tubing for Fast Reactor Development

Material	Dimensions	Quantity	Results
Type 304 Stainless Steel	4.22 mm ID x 0.23 mm wall	44.8 m	91.5 cm scrapped for defects greater than 10%
Duplex tubing: Type 304 Stainless Steel on Nb-33 w/o Ta-1 w/o Zr	5.41-mm-OD outer tube; 0.38-mm-wall inner tube; 0.20-mm wall	52.1 cm	Poor bond. Pre- cipitation in grain boundaries of stainless steel
Duplex tubing Hastelloy X on Nb-33 w/o Ta-1 w/o Zr	Same as above	35.6 cm	Poor bond
Nb-1 w/o Zr	7.34-mm OD x 0.51-mm wall	40.7 cm	Defect free
Nb-1 w/o Zr	6.63-mm OD x 0.46-mm wall	0.3 m	Defect free
Nb-1 w/o Zr	5.97-mm OD x 0.38-mm wall	1 m	Numerous defects less than 20%
Nb-5 w/o Zr	6.07-mm OD x 0.51-mm wall	0.3 m	Defect free
Hastelloy X	4.22-mm ID x 0.23-mm wall	15 pieces, 173 cm long	5 tubes contained defects approximately 10%

C. EBR-I, Mark IV

Operation of the reactor continued during the month at design temperature and power with a total of 217 Mwh achieved on the Mark IV core by the end of the month.

Four capsules containing 1-in. wires of iron, nickel, titanium, and some lithium sulfate powder were irradiated in furtherance of a program to improve the accuracy of measurements of activation cross sections conducted by RED.

D. EBR-II

1. Reactor Plant

During the month of August it was possible to free the large rotating shield plug by raising the temperatures of the lowest freeze seals by approximately 15°F. Better distribution of the seal temperature for the molten condition has been attained by adjustment of existing equipment. However, the control system for the seal heater is not adequate for long-term operation. For example, the scanning switches and control and readout meters are unreliable. Components to improve reliability are on order.

Exchange of the initial filter subassembly was completed in the reactor. The primary sodium pump No. 2 was operated for approximately 32 hours at flow rates between 2300 and 330 gpm. When the pump was increased in speed from 600 to 645 rpm and operated for about 40 min, a marked change in vibration occurred and the pump was immediately shut down. After removal of the pump motor, measurements taken at the upper end of the impeller shaft indicated the shaft was bound as was pump No. 1 after a very brief period of operation.

Various alternatives for dealing with this second pump failure are being explored. Particular attention is being given to procedures to minimize the total time lost in operations which require cooling the system, erecting the removal equipment, pump removal, and reheating the system. Because the pump failure is so very similar to that of the first unit, there is good reason to believe that the required parts for replacement will be similar.

In view of these factors, consideration is being given to delaying pump removal until the wet critical experiments are completed. Pump removal and repair would then be effected concurrently with the replacement of pump No. 1 and the interconnection of the secondary system. All of these operations require cooling of the primary system and preclude performing essentially any other work.

Five filter subassemblies, which were previously specially cleaned and inspected prior to the 32-hr pump operation, were removed from the reactor and the sodium distilled off. Although the residue was similar to that previously found, the quantity was about one-quarter less. Most of the material is fine black powder, some of which is magnetic. Three non-magnetic metallic pieces were found (all about 0.010 in. in dia, two $\frac{1}{8}$ in. long, and one $\frac{3}{8}$ -in. long). This amount of particular contamination is considered well within the tolerable limit for system cleanliness. The residue is now undergoing chemical analysis.

The storage rack in the primary tank is being loaded with inner blanket subassemblies for replacement of the dummy subassemblies now located in the inner blanket region of the reactor.

During the above transfers from the Fuel Unloading Machine to the storage rack, troubles were experienced with the unloading machine gripper and with the storage rack packing gland. The gripper mechanism has been disconnected from the machine, and the sodium and sodium oxide cleaned. The gripper assembly now works properly and will be reinstalled in the unloading machine after cleanup and inspection of other parts that come into contact with sodium transferred by the gripper assembly.

The packing spacer in the packing gland was found to be galling the main storage basket support shaft. A new packing spacer is being installed and the material changed from stainless steel to aluminum bronze. The diametrical clearance between the shaft and the spacer has been increased from approximately 0.012 to 0.058 in.

The turbocompressor for the argon system of the fuel-unloading machine has been repaired and placed back in service.

2. Sodium Boiler Plant

Because of an unexpected and relatively high beta background originating from tritium in the secondary sodium system, the test for a water leak in the steam generator by means of a tritium tracer technique is not considered feasible. Preparations that had been made (see Progress Report for July 1963, ANL-6764, pp. 13-18) for this test were discontinued in favor of a helium mass spectrometer leak test.

To perform the helium leak test on the all-welded piping system the water side was pressurized with helium and a mass spectrometer used on the evacuated sodium side. Initial evacuation was achieved with the hogging ejector on the main condenser; later, a mechanical vacuum pump was used to further evacuate and dry the system. Helium was then added to a pressure of about 0.8 atm. Use of helium below atmospheric pressure assures no atmospheric contamination in the vicinity of the spectrometer.

Two helium leak tests, one of 24-hr and one of 48-hr duration, were conducted. Both were preceded by a 24-hr test to determine helium background. No leak appeared to exist so that sodium filling proceeded. On August 29 both systems were at 350°F and the sodium system was filled. After a brief period of circulation with the main, ac electromagnetic pump, the system was drained to the storage tank as planned. The temperature of the storage tank is currently being raised. The oxide content and plugging temperature will be determined prior to cold trapping. The amount of oxide picked up during this system fill will dictate subsequent operations. This first operation of the Secondary System was quite satisfactory.

3. Power Plant

Following the decision to conduct a helium leak test, the steam system was cooled from 350°F and 1000 psi by reducing the steam supply pressure to feedwater heater No. 4. The steam system was then drained, evacuated, and completely dried before the helium was added to the water side of the steam generator. The temporary piping which had been installed to feedwater heaters Nos. 3 and 4 for closed-loop circulation to accomplish the tritium leak test was removed and the system restored to normal.

Following completion of the helium leak test, the steam system was again brought up to the sodium filling temperature of 350°F by means of 175-lb steam in feedwater heater No. 2. The steam system was maintained at 350°F for the remainder of the period.

4. Fuel Cycle Facility

a. Argon and Air Cells. Argon gas has been introduced into the Argon Cell, however, only 80,000 standard cu ft of argon, instead of the planned 110,000 standard cu ft, were available for this purpose owing to difficulties encountered by the vendor. The air concentration in the cell was reduced to about 5 percent during the fill. Upon completion of the filling operation, the argon-purification system was started. After nine days of purification, the concentrations of impurities in the argon were as follows: about 4.3 percent nitrogen, less than 50 ppm oxygen, and less than 200 ppm water.

With an Argon Cell pressure at 2 in. of water below atmospheric, and with the purification system turned off, the rate of air inleakage into the Argon Cell was determined from the rate of increase of the oxygen concentration in the cell. The air inleakage rate is 0.012 scfm. An effort is being made to detect leaks so that this rate of inleakage might be reduced.

b. Cell Equipment. Corrective work on the Air Cell and the Argon Cell manipulators is nearly completed. The grips were modified and will now lift the design load of 750 lb. The solenoid-operated clutches for bridge and carriage drives were disassembled and reworked to eliminate their tendency to stick.

Brushes are being tested for the grip motors in order to obtain a brush with a long operating life under the very dry conditions of the Argon Cell. A resin-bonded, carbon-graphite brush containing molybdenum disulfide (Stackpole grade 660 brush) gave the best test results.

Ten glass cover plates ($\frac{1}{4}$ in. thick) have been installed to protect the innermost (A) slabs of the shielding windows of the Argon Cell against mechanical stress which might lead to an internal electrical discharge in the slab (see Progress Report for May 1963, ANL-6739, pp. 45 to 47). The composition of the glass cover plates is the same as that of the C slabs. The cover plates contain 1.8 percent cerium oxide and have a density of 2.7 g/cc. The cover plates along with the A slabs can be replaced remotely.

Installation and testing of various pieces of process equipment is being carried out. The core dismantler has been remotely installed in the Air Cell and its associated equipment installed on the service floor. Operational testing of the equipment is now under way.

Two tube clusters for temporary storage of spent and refabricated subassemblies in the Air Cell have been built. Each tube cluster will fit into any one of the ten 1-ft-diameter by 10-ft-deep storage pits. Each of the four tubes in a cluster can hold a single subassembly.

Results of preliminary tests of the heat-removal capability of the Argonne-built fuel-transfer coffin indicate that the cooling system will readily handle the heat load expected from a 2 percent burnup, 15-day cooled EBR-II core subassembly. The temperature of the center pin was maintained well below 600°F (the specified maximum temperature). Temperatures of the center pin were 300°F in air and 370°F in argon with a coolant flow rate of 20 scfm.

The periscope at Argon Cell Window No. 6 was installed and leak-tested. No leaks were found in the optical system and the gas seal.

Modifications of the method of removing and replacing the cable of the Argon Cell electromechanical manipulator were devised and successfully accomplished.

Installation of the Air Cell dismantler was completed. Trial runs indicated the necessity of some field modifications, which are underway. Work has continued on the second pin-processing machine and the welders.

The first melting of uranium (depleted) was accomplished satisfactorily in the melt-refining furnace system. A small amount of uranium was spilled outside the mold because of an improper pouring technique.

The square telescoping tubes of the electromechanical manipulator, which had exhibited some galling, have been modified by replacement of alternate steel sections with brass.

A roll pin sheared on one of the Air Cell operating manipulators, resulting in loss of bridge motion. This pin connects the driven half of a jaw clutch to the drive gear train. Because this part of the manipulator is not designed for remote maintenance without removing the entire manipulator, the roll pin was replaced by contact maintenance. Almost immediately following this incident, two manipulators in the Argon Cell failed similarly. The inaccessibility of the Argon Cell makes it difficult to ascertain if the type of failure is the same. Methods of determining the nature of failure are in progress, as are means of correcting this weakness in the bridge drive power train.

Trouble was encountered with one additional Argon Cell manipulator (No. 1) bridge drive. At first it was thought that the failure was of the same type encountered previously with the Argon Cell manipulator bridge drive units. However, removal of the motor from the cell showed that the pivot for the clutch was frozen in the open position. This was a result of amalgamation of the cadmium plating on the pivot from mercury splashed on this bridge drive motor when this manipulator was under the blister opening. The mercury was blown out of the blister seal during purging of the blister. The bridge drive motor from one of the other failed manipulators (No. 2) was placed in No. 1 manipulator and this (No. 1) manipulator restored to service. The carriage from No. 5 manipulator (out of service because replacement parts are not yet available) was removed to the service stand and No. 3 carriage placed on No. 5 bridge, restoring No. 5 manipulator to service. The failed bridge drive motor from No. 3 manipulator is being removed for diagnosis.

The Argonne-fabricated interbuilding coffin arrived and the electrical checkout was completed. The alignment of the coffin with the reactor fuel-unloading machine has been completed, and the alignment with the Air Cell floor plugs is in progress. The locating guides for the reactor fuel-unloading machine (located on the top of the coffin) interfere with the bottom of the 36-in.-diameter Air Cell plug. As yet this problem is unresolved.

Circuits have been installed for immersion thermocouples for both injection-casting furnaces. The heater assembly doors are being modified by providing Inconel sheet covers. The welders for the fuel elements are being modified to improve operability. Restrainer gas shoes, electrode holders, and pneumatic valving systems have been redesigned.

c. Beam Scale. The mechanical components of the beam scale, which has an accuracy of $\pm 0.01\%$, are shown in Figure 2. It consists of a 20-kg-capacity compound beam mechanism with a housed poise driven by a precision ball screw. Flexural pivots are used at each fulcrum and at all linkage points. This mechanism was manufactured to ANL specifications by the TriDyne Corporation.

The electrical circuitry for automatic servo balancing and digital (gram) readout was designed and constructed by the ANL Electronics Division. Movement of the beam away from the balance point was detected by means of a linear-variable differential transformer. The unbalanced signal of the transformer was amplified and converted to a pulsed power signal, fed into two parallel stepping motors. A radiation-resistant stepping motor mounted on the beam drives the poise screw to a new balance point. A synchronized stepping motor in the remote control station drives a digital counter calibrated in grams. Separate pulse signals can be fed into either motor for zeroing or tare compensation.

Figure 2. Beam Scale for Use in Retabrication of Irradiated Reactor Fuel.

An oil-filled damping device was provided originally. Although this worked reasonably well, the oil was not radiation resistant and the dash-pot mechanism could not be used. Although both magnetic and gas damping was tried, satisfactory results were achieved only by the use of a small, brass aneroid-type bellows with a compensating leak.

The beam scale was calibrated from 0 to 20 kg against Class S weights. The maximum error in any one reading was 3 g, with most of the readings within ± 1 g. Final recalibration of this equipment will be necessary in the Argon Cell because of the long lead lines required.

d. Bond-testing Machine. Pre-operational tests of the bond testing machine, shown in Figure 3, were completed. This machine indexes a 50-rod bonding magazine below a differential eddy-current encircling coil. The rods are inserted, one at a time, through the coil by a lift cylinder. The top of the rod is inserted in a chucking device which grips it.

Figure 3. Machine for Testing the Bonds in EBR-II Fuel Elements after Refabrication

The gripper is attached to a radiation-resistant, motor-driven chain elevator. This mechanism slowly pulls the rod through the coil and lowers it back into the magazine scanning it in both directions. Electric heaters in the magazine and in the elevator mechanism keep the sodium bond molten, so that the gas bubbles (rather than shrinkage cavities) may be detected.

The equipment was shipped to Idaho.

e. Fuel-element-assembly Machine. Component inspection of the fuel-element-assembly machine is being done in the vendor's shop. Assembly has not begun, since the main frame is still being worked upon. The ANL-developed controls and welding units were tested in Building 6 with Core-I production equipment. Thirty feet of mineral-insulated cable was used in the welding lines. Approximately 50 percent attenuation of the high-frequency voltage was found. This is somewhat higher than expected, and a reason for the voltage losses is being sought.

f. Injection-casting Equipment. Reliable determination of melt temperatures in the injection-casting furnace continues to cause some concern. A platinum-platinum-10% rhodium thermocouple is presently installed in the elevator pedestal. The tip of the thermocouple in a protecting tube is inserted in a hole in the bottom of the crucible. At the moment casting takes place, the pedestal is raised and the thermocouple contacts are broken. With repeated use, the contact resistance increases and the thermocouple signal becomes unreliable. Furthermore, this thermocouple does not give the temperature of the heat after casting, information necessary to determine the correct time for lowering the crucible when casting gamma-radioactive fuel.

Wiring is being installed for a secondary dipping thermocouple which can be inserted through the center of the mold pallet. This thermocouple must drop into the crucible as the charge melts and must be lifted

with the rising crucible. The protective tube must resist corrosion by the fissium alloy at approximately 1375°C. Because of the motions, ceramic protective tubes do not appear practical. Platinum-platinum-10% rhodium thermocouples in tungsten-coated tantalum sheaths have been ordered for the application.

g. Pin Processing and Inspection. Modification of the shear-station feeding tray was required to prevent jamming by a warped, short, or malformed fuel pin.

The amplifier provided with the data-processing equipment to read out pin diameter was found to provide a marginal signal when used at maximum gain. The vendor of this equipment has agreed to provide an amplifier of higher gain.

h. Welding Machine. Sealed master-slave manipulators were not available at the time the requirements for the restrainer loading and welding operations were set up. For this reason the welders were originally designed with mechanical devices for feeding and inserting the restrainer plugs in the top of the fuel tubes. During Core-I production, it was found that the fit between the plug and restrainer must be quite good in order to reduce the number of reject welds. This, in turn, imposed a difficult requirement on the restrainer loader section of the welding machine

The operation can be more easily accomplished by the newly installed sealed master-slave manipulators. A settling machine was, therefore, moved to the Window-2 station where the following operations are performed: (a) load fuel tubes into the welder magazine, (b) load fuel pins into the fuel tubes, (c) transfer magazine to the settler, melt the sodium, and settle the fuel pins into the tube, and (d) insert restrainers into the fuel tubes and the molten sodium. Operations (a), (b), and (d) are accomplished by master slave manipulators with suitable guide fixtures.

5. Process Development

a. Melt-refining Process Technology The evaluation of tungsten as a container material for uranium at 1200°C was continued. It was previously reported (see Progress Report for July 1963, ANL-6764, p. 20) that a 1-in.-diameter by 1-in.-high crucible made from swaged tungsten rod suffered only minor corrosion while containing uranium at 1200°C for 50 hr, and that a second crucible fabricated by slip casting and then sintering failed in 30 min in a uranium-holding test at the same temperature. Further examination of the data revealed that the uranium solution was rapidly saturated with tungsten in the first test. A series of experiments was therefore performed with swaged tungsten under conditions that made saturation of uranium with tungsten impossible. In these tests, which were

conducted at 900 and 1200°C, extensive corrosion of the tungsten by uranium occurred rapidly. Tantalum was also severely corroded by uranium at 1200°C. It is concluded that neither tungsten nor tantalum are suitable container materials for molten uranium.

b. Skull Reclamation Process. The skull reclamation process will be used for the recovery and purification of the fissionable material that remains in the melt-refining crucible after a melt-refining operation. A series of small-scale (100 g of uranium) process demonstration runs is being made to optimize process conditions and to resolve process problems.

In one recently completed run, a modified flowsheet (see Figure 4) was used in which all steps except the final step of evaporation of magnesium and zinc and the melting of the uranium product were performed in a single tungsten crucible. In this flowsheet, the uranium cake that is formed upon the decomposition of the intermetallic compound is redissolved in zinc-12 w/o magnesium to allow transfer of the uranium to another crucible (probably a small beryllia crucible) for evaporation and melting.

Figure 4. Flowsheet for Skull Reclamation Process

The flowsheet in Figure 4, which was utilized previously for three runs in the pilot-plant-scale skull-reclamation processing equipment (see Progress Reports, June and July 1963; ANL-6749, p. 19; ANL-6764, p. 21), is being considered as an alternative to the flowsheet in which two crucibles are utilized for the steps preceding the evaporation of magnesium and zinc (see Chemical Engineering Division Summary Report, July, August, and September 1962, ANL-6596, p. 46).

The small-scale run was successful except for a phase transfer. Following precipitation of the intermetallic compound, only 70 percent, instead of the usual 85 percent, of the supernatant zinc was removed. Since the phase separations may be related to the scale of the experiment, further study will be done in pilot-plant equipment. In the present run, the supernatant from the intermetallic compound precipitation step contained 3.8 w/o of the uranium in the charge, which was in considerable excess of the solubility of uranium in zinc at 525°C. Apparently, some of the uranium-zinc intermetallic compound remained in the supernatant.

There was evidence that zinc chloride volatilized rapidly during these runs; one-third of the zinc chloride initially present in the salt phase was absent after one-half hour of processing, although very little uranium was present in the salt phase at that time. Loss of zinc chloride may be minimized by the use of a different salt composition, by dissolving the fuel pins in zinc before the metal phase is contacted with the salt phase, or by dissolving the clad pins directly in a salt phase to which zinc chloride is added slowly. It was concluded that leaching of uranium from clad fuel pins is feasible. Future work will be concerned with the development of specific methods for the removal of fuel from particular cladding materials.

The removals of cerium, ruthenium, and molybdenum in this run were good. The amount of zirconium removed from the process stream in the zinc supernatant from the intermetallic compound precipitation step was less than had been anticipated. Only 70 percent of the supernatant was transferred. The amount of zirconium which remained in the process stream, therefore, was greater than the amount which would have remained if the usual 85 percent transfer of the supernatant had been achieved. Nevertheless, the zirconium content was reduced from 2.7 g in the charge to 0.25 g in the product uranium.

Two additional large-scale (2.5 kg skull oxide) skull-reclamation runs were made in the pilot-plant-processing equipment, with all process steps being carried out in a tungsten crucible. Data from these runs are now being evaluated.

A study has been made to determine whether the noble-metal-extraction step of the skull-reclamation process can be adapted to the removal of uranium from various cladding materials. Uranium-5 w/o fissium

pin segments (1 to 1.5 in. long and about $\frac{1}{8}$ in. in diameter) used in this investigation were clad in one of the following: Type 304 stainless steel, tungsten-coated Type 304 stainless steel, tungsten-coated Hastelloy X, or niobium-1 percent zirconium alloy. The pins were contacted at 750°C for 4 hr with mixtures of zinc and salt (47.5 m/o calcium chloride-47.5 m/o magnesium chloride-5 m/o magnesium fluoride, with zinc chloride added in proportion to the amount of uranium in the charge). The uranium is dissolved in the zinc phase, oxidized to uranium trichloride by zinc chloride, and extracted into the flux phase as the chloride. As was indicated in a previous report (see Progress Report for July 1963, ANL-6764, p. 22), 65 to 90 percent of the uranium was dissolved and then extracted into the halide flux phase in runs with the various pin claddings. The uranium retained in the metal phase was distributed in the following manner:

	Uranium Retained in Metal Phase (percent of uranium charged)	
	Undissolved	Dissolved
Pins clad with tungsten-coated Hastelloy X	0.6	15.1
Pins clad with tungsten-coated stainless steel	24.2	0.192
Pins clad with niobium-1% zirconium	34.7	0.11

The rate-determining step of the process appears to be the dissolution of the fuel pin segments in the zinc. It is believed, therefore, that with dissolution times longer than 4 hr, complete dissolution (and transfer of uranium to the salt phase) can be achieved.

c. Sodium Coolant Chemistry. An activation method that depends on the $O^{16}(n,p)N^{16}$ reaction is being explored for the determination of 10 to 100 ppm oxygen in sodium metal. Preliminary experiments in which oxygen-containing standards were irradiated have established that for a 30-sec irradiation (93.7 percent saturation), about 225 counts are observed per milligram of oxygen originally present. Samples of impurities often found in sodium, such as magnesium, aluminum, phosphorus, silicon, cobalt, potassium, nickel, manganese, and iron, were also irradiated; examination of their spectra indicated that their presence would not interfere with the analysis of oxygen.

d. Removal of Nitrogen from Argon. Future process requirements may make it necessary to remove nitrogen from the Argon Cell atmosphere. In anticipation of this possible need, a study is being undertaken of the removal of nitrogen from argon by gettering the nitrogen with titanium sponge, chosen because of its high efficiency and low cost per mole of nitrogen-removal capacity.

The present study is concerned with the kinetics of the titanium-nitrogen reaction. In the initial test, a gas mixture of 1000 ppm nitrogen in argon was passed through eight contiguous titanium beds which were packed alternately with particles of titanium sponge having average diameters of 0.072 and 0.148 in. The weights of the individual beds varied between 9 and 12.5 g. The temperature of the beds was maintained at 900°C for 95 hr while the gas mixture was passed through the beds at a flow rate of 840 liters/hr. The percentage of titanium converted to titanium nitride was about 54 percent. The overall rate of reaction appeared to be independent of particle size and the position of the individual beds in the series of eight beds.

6. Training

Training activities for August involved preparation of supervisory personnel for wet critical operation and continuation of the reactor technology, plant orientation, and personnel protection and plant safety areas of training for new technicians

Shift supervisors completed 120 hr of classroom and field group sessions specific to wet critical operation. Material reviewed included reactor physics, reactor design, reactor operation and control, administrative procedures, primary coolant system, shutdown coolers, thimble cooling, shield cooling, argon system, sodium purification, radiation monitoring, major electrical systems, nuclear instrumentation, startup and shutdown circuitry, and building isolation. A similar program of preparation for wet critical for reactor operations foremen was initiated and is three-fourths complete.

Shift supervisors participated in a three-day oral proficiency review conducted by appropriate EBR-II Project and Idaho Division Staff personnel.

Seventeen new technicians completed 88 hr of reactor technology classwork emphasizing the fundamentals of nuclear engineering. Plant orientation for these technicians continued.

E. FARET

1. Design Studies

As noted in Progress Report for July, 1963, ANL-6764, p. 23, a preliminary agreement between the Laboratory and the Bechtel Corporation for Architect-Engineering services for the FARET facility was reached in June 1963, and limited effort on Title I work was initiated on June 17, 1963. After approval by the Commission, the contract was formalized on July 30, 1963, and Bechtel's effort was accelerated significantly. Meetings between Bechtel and Laboratory personnel have been held on a nearly weekly basis, and the functional, operational, and design requirements of the facility

have been reviewed exhaustively. The architect is reviewing the design described in the Preliminary Feasibility and Cost Study Report in order to establish suitability and adequacy. In addition, work is being performed in certain areas of the design which were recognized at an early date as requiring more extensive review and study. Typical of the areas being studied are: (1) containment considerations; (2) materials selection and allowable stresses; (3) piping layout for the primary system; (4) cell, cavity, and vault cooling system; (5) reactor vessel design; (6) site considerations; (7) cost and schedule estimates; and (8) analysis of system performance.

The Laboratory has undertaken to prepare a Critical Path Analysis of the FARET design and construction effort. The diagrams have been completed, the computer program has been established and checked, and a hand calculation has been made. The diagrams and information upon which these diagrams were developed will be given to the Bechtel Corporation for their use in establishing a Critical Path Analysis for the Title I effort.

2. Safety Analyses

Safety analyses are in progress and initial results have been obtained. Work is progressing in the following areas:

1. evaluation of the consequences of a sodium-air reaction within the containment structure;
2. evaluation of the containment structure to resist the release of a significant quantity of nuclear energy;
3. study of release of nuclear energy from typical FARET experimental cores;
4. determination of hypothetical activity release to the atmosphere;
5. analysis of performance of primary system.

The Laboratory's evaluation of the effects of a sudden release of nuclear energy upon the containment structure does not confirm that the structural design described in the Preliminary Feasibility and Cost Study Report is completely satisfactory. Design specifications for the cell, cavity, and vault should be increased from the present pressure limits of 30 psig and 2 psig, respectively. In addition, the use of a separate energy-absorption structure within the cavity is being studied.

A mathematical model of the reactor and associated heat transfer systems is being developed under contract by Electronics Associates, Inc. for the purpose of analyzing by analog computer the performance of the system.

3. Oxygen Meter

An electrochemical cell (see Figure 5) with one electrode of sodium saturated with Na_2O , one of sodium unsaturated with Na_2O , and a solid oxide electrolyte through which current is transported by O^{2-} , is being constructed to measure the oxygen content of sodium continuously. The voltage of the cell changes with the oxygen content of the system.

Figure 5. Oxygen Meter Cell

To date, the limiting operating temperature of this type of cell is about 650°F , which is below the FARET operating design conditions of 1200°F . Above 650°F , the electrolyte (zirconia) is attacked by the sodium. The use of a fused thoria electrolyte is expected to overcome this limitation. The stability of the reference electrode (sodium saturated with Na_2O) over extended operating periods will be observed. A unique advantage of this method is the accuracy of monitoring which should increase with decreasing concentrations of the impurity, as expressed by the equation

$$\Delta G = -RT \log_e \frac{C_0}{C} \quad ,$$

where

C_0 = the oxygen concentration in the saturated or reference electrode

C = the oxygen concentration in the unsaturated electrode (system sodium)

ΔG = free energy

R = gas constant

T = absolute temperature.

The free energy, which is reflected by the output voltage of the cell, should increase with decreasing oxide content in the system sodium.

4. Fuel Development

The proposed FARET design³ provides for an annulus, 0.65 mm wide, separating the fuel from the can. The existence of this annulus is contingent on a study of the Doppler effect, and the ceramic fuel must remain in shape and position within certain confident limits.

Under steady-state conditions and uniform heating across the section of the pin, the maximum heat fluxes allowed for the proposed ceramics materials to be used are shown in Table VI.^{4,5}

The temperatures were selected on the basis of a maximum temperature drop of 500°C through the annulus gap, and also of lower (200°C) and upper (600°C) coolant temperatures. For the ratios length/ID and OD/ID used in the design of the fuel, the shape factor on the thermal fracture of cylinders seems to change little (within $\pm 20\%$ approximation) according to Smalley et al.⁶

Samples of UO_2 cylinders for bench testing were fabricated with and without fins by extrusion. Two percent Methocel 4000 was used as binder, and a 1:3 (by volume) solution of glycerine water as a lubricant. The rods, which were 40-45% of green density, were dried overnight without bending and were found to have enough green strength to be cut and lightly machined. These samples were sintered in hydrogen at 1650-1700°C to a density 90-95% of theoretical.

³Interim Report: FARET Experimental Program, ANL-6708 (April 1963)

⁴J. C. Carter, Temperature and Stress Distribution in Spheres, Rods, Tubes and Plates in Which the Heat Source Is within the Boundaries of the Solids, ANL-4690 (Sept 1951).

⁵J. A. L. Robertson, $\int kd\theta$ in Fuel Irradiations, AECL-807 (April 1959)

⁶A. K. Smalley et al., The Thermal Fracture of Ceramic Cylinders, BMI-1102 (June 1956).

Table VI. Estimated Maximum Permissible Fuel Heat Fluxes for FARET Design

	UO ₂ (1)	UC(2)	UN(2)	US(3)
Estimated Sintering Density, percent of Theoretical	95	90	80	90
Temperature Operation, 800°C				
q_v , w/cm ³	5.6 ⁽¹⁾	47	80	
q_l , w/cm	33 ⁽¹⁾	205	440	
ΔT , °C	72	70	90	
Temperature Operation, 1000°C				
q_v , w/cm ³	27			5.0
q_l , w/cm	115			28
ΔT , °C	40			80
Temperature Operation, 1200°C				
q_v , w/cm ³	3.8 ⁽¹⁾ deforms		55	
q_l , w/cm	21 ⁽¹⁾		310	
ΔT , °C	72		65	

q_v = Volume heat generation; q_l = Linear heat flux; ΔT = Maximum temperature drop along the radius

- (1) Values of mechanical and physical properties from Uranium Dioxide: Properties and Nuclear Applications, edited by J. Belle, Naval Reactors, Division of Reactor Development, USAEC. The thermal conductivity value at 800°C, the one used for FARET calculations, is the most optimistic one. A more conservative value reduces the linear heat flux by a third. The fracture stress, $\sigma_t - \sigma_2 = 0.92 \text{ kg/cm}^2$ (13,000 psi) is 50 to 100% higher than the values obtained on samples broken under bending stress at ANL.
- (2) Values from K. M. Taylor and C. H. McMurtry, Synthesis and Fabrication of Refractory Uranium Compounds, Contract No AT-(40-1)-2558, The Carborundum Company, ORO-400 (Feb 1961).
- (3) P. D. Shalek, Preparation and Properties of Uranium and Thorium Monosulfides, J. Amer. Cer. Soc. 46 (4) 155-161 (1963), plus some assumptions about the Young modulus value and the variation of the thermal conductivity with temperature.

All the samples tested fractured at estimated heat fluxes between 12 and 24 w/cm. Taking into account observations (see footnote No. 1 of Table VI) and the little knowledge available on thermal failure of brittle materials, it is estimated that about 10 w/cm could be considered the maximum thermal flux for UO₂. The same criteria should be applied to the remaining data in Table VI.

Special fuel elements are being developed for use in the FARET reactor to permit the measurement of the magnitude of the Doppler effect. The test fuel elements must be designed to separate the effect of thermal expansion of fuel on reactivity. This will be achieved by special design features which have been previously described (see Progress Report for December 1962, ANL-6672, p. 22). Basically, this can be accomplished by controlling the thermal conductivity between the fuel and coolant independently of reactor power. In the design the fuel is cut into pellets and separated from each other and the clad by means of spacers. The gas pressure or composition in the gaps is then varied to adjust the fuel temperature at constant reactor power.

An initial program goal is to obtain a 500°C temperature variation in the test zone fuel, with constant reactor power. Calculations and preliminary experiments showed this could be accomplished by varying the pressure of helium in a 0.025-in. gap between fuel pellets and clad, with an average coolant temperature of about 300°C. The corresponding maximum linear heat generation in any fuel element is 30 w/cm and the total reactor power is 7 Mwt.

An analysis (see Progress Report for July 1963, ANL-6764, p. 26) indicated that UO_2 pellets when heated electrically to a linear heat flux of 14.5 w/cm would crack. Identical stresses are caused by a maximum reactor heat flux of 23 w/cm. A subsequent test of four pellets run at 12-w/cm heat input also produced extensive cracking. At least for the extruded and sintered uranium dioxide specimens, the test work as well as additional calculations show that thermal fluxes will have to be reduced to values of the order of 10 w/cm in the reactor, or to approximately 6-7 w/cm in the bench test, if cracking of the pellets is to be avoided.

The corresponding calculated variations of fuel temperature possible for this condition are shown in Table VII. The table shows a maximum temperature variation of 325°C compared with the initial goal of 500°C can only be achieved.

Table VII. Calculated Effects of Gap Gas
Changes on Average Fuel Pellet
Surface Temperatures (0.025-in.
Gap, 2.2-Mwt Reactor Power,
and 300°C Average Coolant
Temperature)

Gap Gas	Fuel Pellet Surface Temperature (°C)
Helium	345
Argon	515
Vacuum (10 μ)	670

5. In-pile Experiment

An apparatus has been designed to test sample fuel pellets and fuel-pellet-support devices in the thimble No. VT-27 of the CP-5 reactor. The apparatus consists of an instrumented test capsule which is positioned within a transducer for measuring heat transfer. The test capsule can be changed without removing the transducer.

Initially, the test capsule will be loaded with samples of natural or enriched uranium. At a later date, plutonium samples will be irradiated. Detailed drawings are in process for final review, and a cost estimate will be completed shortly. The equipment necessary for the control and operation of the loop is being assembled. This work is approximately 20% completed.

6. Shielding Analysis

Eighteen-group cross-section sets were used to calculate the neutron leakage at the outside of the radial reflector for small, medium, and zoned cores. The medium core gave the highest leakage flux.

In addition, source strengths and energy distributions to be used in designing shipping casks for irradiated FARET fuel subassemblies were determined.

III. GENERAL REACTOR TECHNOLOGY

A. Theoretical and Applied Nuclear Physics

1. Doppler Effect Studies

In previously reported calculations of the Doppler effect of fissile materials, the interference interaction of resonances of fertile material in the mixture has been assumed to be negligible over a statistical average of many resonances in the unresolved region. The validity of this assumption becomes rather questionable in the intermediate region as pointed out earlier by Codd and Collins.⁷

In our recent studies a simplified method has been developed to determine the interference effect of levels in the unresolved region. Two conclusions have been reached: (1) the interference effect is washed out only at high energy, and (2) the effect becomes considerable in the intermediate energy region, say between 0.5 and 10 kev.

Calculations have been made for a system of Pu^{239} and U^{238} with enrichment ratio of 1:5. At neutron energies of 0.61 and 2.25 kev, the Doppler effect of Pu^{239} between 300 and 600°K is reduced by approximately 55 and 80%, respectively, by the interference effect, which seems to indicate that the positive contribution to the overall Doppler coefficient from Pu^{239} in the presence of considerable U^{235} is likely to be very small.

Detailed studies not involving statistical averaging were made for a typical pair of resonances at 1 kev. The effects of interference between U^{238} and Pu^{239} resonance levels were determined for a variety of parameters and energies by use of the code 1559/RE,⁸ now designated B559/RP. For average values at 1 kev, the Doppler shift in Pu^{239} in U^{238} - Pu^{239} mixtures of 7:1 was -1.33 times the shift in Pu^{239} with no interference. Significantly, the interference may markedly reduce the low-energy Doppler shift. A predominant effect is interference scattering in the U^{238} resonance.

The code B559/RP is being revised to use a library tape. Thereby the running time for each problem will be reduced by perhaps an order of magnitude, since it is cross-section computations which take nearly all the time.

⁷J. Codd and P. J. Collins, Symposium on Advance in Reactor Theory, Karlsruhe, 23/24 April 1963.

⁸C. N. Kelber, 1559/RE: A Code to Compute Resonance Integrals in Mixtures, ANL-6709 (May 1963).

2. Analysis by Numerical Methods

One of the more convenient methods for numerical integration of systems of first-order ordinary differential equations is the Runge-Kutta technique. Programs previously available for this method did not provide any indication of the truncation error. It was thus a difficult task to determine the step size to be used to achieve a specified accuracy, and it was highly inconvenient to vary the step-size during the course of a given trajectory. A variant of the Runge-Kutta method due to R. H. Merson⁹ provides such an estimate at the cost of one extra evaluation of the derivatives per step.

The Kutta-Merson procedure has been programmed for the LGP-30 computer in both the ACT-III and SCALP (Algol) languages. Tests of the programs indicated that the specified accuracy was indeed attained, and that the step-size adjustment can save appreciable computing time when the solutions are badly behaved in only a small section of the range. The ACT version of the program is being submitted to the LGP-30 User's Organization, and the Algol version of the program will be published in the Communications of the Association for Computing Machinery.

3. AFSR

Experimental work continued on the development of a solid-state detector for use as a fast neutron spectrometer. Difficulties have been encountered because of the high background in the core of AFSR. The counter assembly has been rebuilt to permit easy removal of the Li^6 -containing foil. This will allow independent in-core measurements of the background. The relative gamma flux is being measured by means of a miniature Geiger tube at various positions in the core to help estimate the background contribution from the high gamma radiation.

The prompt neutron lifetime of the reactor was remeasured by the Rossi-alpha technique. Proportional counters filled with He^3 at 10 atm were used so as to provide an increase in sensitivity of more than an order of magnitude over those previously used. Since results of the experiment were not in agreement with previous results, the measurement is to be repeated shortly.

The central reactivity coefficient of boron-10 was measured as -21.9 lh/g . Additional runs were made to check performance of ion chambers for BORAX-V experiments.

⁹R. H. Merson, "An Operational Method for the Study of Integration Processes," Proceedings of a Symposium on Data Processing, Weapons Research Establishment, Salisbury, South Australia (1957).

B. Reactor Fuels Development

1. Corrosion Studies

a. Zirconium Alloys for Superheated Steam. Steam-resistant zirconium alloys are being corrosion tested in 650°C flowing steam (61 m/sec) containing additions of oxygen and hydrogen, as described in earlier reports. Exposure up to 48 days showed no effect of these gas additions to the steam. It was shown previously that these materials are rather insensitive to the flow rate (up to 92 m/sec) in both a 650°C deoxygenated system and oxygenated systems. Corrosion rates, however, have been relatively high in these 650°C, 42.4-kg/cm² steam tests - from 5 to 7 mdd (3 to 4.2 mils/yr) penetration - after 20 days. Film cracking occurred at sharp edges early in the test and on broad faces after about 40 days.

Detailed studies of corroded samples by means of microhardness tests and metallography are continuing. There is evidence that diffusion of oxygen into underlying metal is appreciable at 650°C in these materials (although the deeper metal remains relatively ductile). The need for additional efforts to reduce the oxygen-diffusion rate through alloying is indicated.

Other corrosion tests of binary alloys, as-cast materials, and heat-treated materials are in progress. Investigation of electrical phenomena at corroding surfaces is being continued.

b. Ferrous Alloys in Superheated Steam. Samples of BORAX-V fuel plates have been cycled a week at a time between superheated steam at 650°C and a pressure of 42 kg/cm², and distilled water at room temperature. It had been noted in other tests that Type 304 samples rusted badly in oxygenated room-temperature water after a high-temperature steam exposure. There was concern lest perforation of the BORAX-V fuel plates should occur during the periods of inactivity when the fuel surfaces might be wet.

Although there has been metal attack at rust spots during the cycle test, there has been no deep or serious pitting. Fairly large quantities of the scale formed at high temperatures have come off in the room-temperature water. This might be a problem in the reactor.

The dynamic test of Types 304 and 406 stainless steels (see July Progress Report, ANL-6764, p. 41) has gone about 55 days and is scheduled to continue for an additional four months.

A new "autoclave within an autoclave" test facility is being constructed to permit steam testing at higher temperatures (~800°C) and higher pressures.

c. Miscellaneous Materials in Water and Steam

(i) TD Nickel. Corrosion tests comparing TD nickel with unalloyed nickel are being concluded, and a summary of the results is being prepared. In brief, the corrosion resistance in 360°C water and in 650°C, superheated steam appeared to be more dependent on stock purity, and perhaps metallurgical history, than on the presence or absence of dispersed thoria. In water TD nickel bar stock developed small surface blemishes which were not observed on unalloyed bar stock. In steam TD nickel sheet material was superior to one stock of "A" nickel, and similar to another stock of the same (nominal) "A" nickel material and to foil samples of higher purity, Ni 270. On the more resistant materials chemically polished surfaces displayed relatively low weight gains in steam.

(ii) Pure Metals. Nickel and chromium, used frequently in alloys for high-temperature service, are being evaluated as unalloyed materials in oxygenated steam corrosion tests at 650°C and 42.4 kg/cm² (600 psi). After 17 days electropolished chromium had formed a thin, dull, green film and had lost weight slightly. Chemically polished Inco Ni 270 formed a light interference film in the first 10 days of exposure and gained weight slightly. The test is continuing.

d. Protection of Refractory Metals in Liquid Alkali Metals Containing Oxygen. Current densities in the range from 0.3 to 1.0 amp/cm², employed for the protection of zirconium samples, gave considerable oxidation inhibition. Similar results were obtained with niobium, although some uncertainty resulted from the poor condition of the as-received material.

With sensitive equipment initial resistances of the cell were high and subsequently decreased as a critical potential setting was exceeded. Two possibilities have been considered for this occurrence: a) there is a potential bias at which an oxide film on the metal surface is forcibly detached, and b) sufficiently high voltages cause an oxidation reaction reversal that results in a more conductive liquid-solid interface behavior.

Experimental efforts to test these possibilities are concentrated at the initial stages of formation of the oxide film, when resistance changes are rather pronounced. A mechanically activated system has been developed which, when coupled with a fast X-Y recorder, enables recording of the cell resistance at a fraction of a minute past zero time. Long-range determinations are also being attempted to determine the effect of potential bias on the continuity of the oxide film.

2. Ceramic Fuels

a. Urania Burnable Poisons. Uranium oxide compacts, which were formed at a pressure of 3.36 metric tons per square centimeter and sintered at 1700°C for 4 hr in a hydrogen atmosphere, were subjected to the corrosive effects of oxygenated distilled water at 360°C for times from 15 to 138 hr. The weight losses of the samples were appreciable. The right cylindrical shape of the compact was destroyed and the surface was covered with a readily removed green powder ($\text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ by X-ray analysis). The hemihydrate is the stable form of uranium trioxide.¹⁰

Compacts of UO_2 -3 w/o Eu_2O_3 and UO_2 -3 w/o Sm_2O_3 were similarly prepared and tested. These retained their cylindrical shape. A slight green corrosion product, which was tightly adherent to the surface, was evident. X-ray diffraction lines of the corrosion product broken from the surface corresponded to patterns of U_3O_8 and Eu_2O_3 for the europia-containing compact and of U_3O_8 and Sm_2O_3 for the samaria-containing compact. There was no evidence of a hydrated product on the rare-earth-containing compacts.

Compacts of gadolinia and urania were pressed at 3.36 metric tons per square centimeter and sintered at 1700°C for 4 hr in hydrogen and in argon atmospheres. The samples were crushed to a fine powder for X-ray analysis. A face-centered cubic solid solution of gadolinia in urania exists to at least 60 w/o Gd_2O_3 . Lattice constants vary, following Vegard's Law, from 5.4635 a.u. for UO_2 -5 w/o Gd_2O_3 to 5.4080 a.u. for UO_2 -40 w/o Gd_2O_3 for argon-sintered compacts. There is a discontinuity above 40 w/o Gd_2O_3 , and the lattice constants (up to 60 w/o Gd_2O_3) vary only slightly from 5.4048 a.u. In this range, there is X-ray evidence of material other than the fluorite-type solid solution. This phase has not yet been identified. As the gadolinia content increases, the complexity of the X-ray diffraction pattern increases. The analyses of the remaining argon-sintered samples is continuing as is the analyses of the hydrogen-sintered samples.

b. (U,Th,Pu)-P Systems. As part of a program for the characterization of compounds in the (U,Th,Pu)-P systems, studies on the synthesis of UP by the reaction of uranium with phosphine gas have been completed. Reaction temperatures during synthesis were varied from 280 to 720°C. Changing the P/U ratios of the starting materials from 0.82 to 1.30 does not significantly affect homogeneity of the final material. Best overall results were obtained when the reaction was carried out at 385°C with a P/U ratio slightly greater than one. Material had to be calcined in vacuum at 1200°C or above to homogenize it and drive off the excess phosphorus. The very fine calcined powder was stoichiometric and had an average

¹⁰J. K. Dawson, E. Wait, K. Alcock, and D. R. Chilton, Some Aspects of the System Uranium Trioxide-Water, J. Chem. Soc., 1956 3531-3540.

oxygen content of 0.24%, corresponding to a UO_2 content of about 2% in agreement with insoluble-residue data. The density of the UP powder as determined by liquid displacement was 9.75 g/cc, which is 95% of the theoretical value. This indicates that 5% of its volume consisted of pores that were inaccessible to CCl_4 . The UP powder is not hygroscopic and can be stored in air at room temperature.

UP slowly loses its phosphorus upon heating in vacuum at elevated temperatures. Loss was first noticeable at 1600°C; after 2 hr at this temperature the composition was $\text{UP}_{0.99}$. After 2 hr at 1800°C the composition was $\text{UP}_{0.97}$.

The system UP-US has been looked at in order to determine the effect of replacing part of the phosphorus with sulfur. X-ray diffraction and metallographic investigations show complete solid solution between the end members. A plot of the lattice constants versus composition shows a consistent positive deviation from a straight line (i.e., deviation from Vegard's Law). Studies of the UP-US system are of a limited nature. Further work on the phase relationships as well as the properties of the various compositions in the system will determine whether or not these studies should be continued as a separate program.

3. Particulate Metal Fuel Elements

a. Preparation of Metal Powder. A centrifugal casting machine has been adapted for the atomizing of metal powders. The existing furnace shell, induction heating coil, rotor chamber, rotor, and drive were used. A special collector tray and conical baffle mounted on the rotor table were added. This baffle is so designed that the powder is thrown radially by centrifugal force while the argon gas reverses direction and escapes through annular slots in the top of the collector. The metal is melted in a graphite or tantalum-lined graphite crucible. A nozzle projects from the bottom of the crucible and delivers molten metal through a series of small openings. Compressed argon gas is blown across this opening to atomize the metal. The compressed argon gas is circulated by a pair of canned 125-psi compressors.

A series of nine metal-atomizing melts have been made. Seven involved copper and aluminum bronze and two uranium-10 w/o plutonium-10 w/o fissium alloy. Nozzle configuration, orifice size, metal temperature, and the relative positions of the metal and gas nozzles were found to be most critical. Because of the extremely short distance between the nozzle and the collector, only the very fine powder did not coalesce in the collector. Therefore, most of the powders collected were less than 200 mesh. The heavier particles stuck together, tending to form irregularly shaped, spongy masses. Further work is being done to remedy this.

The -200 mesh aluminum powders have been examined at 100X. Approximately 75 percent of the particles were spherical or semi-spherical in shape. Twenty percent were elongated or teardrop in shape and the balance elongated or flattened shapes. Efforts are continuing to increase the yield of unfused powder.

b. Vibratory Compaction Studies. An accelerometer has been procured and installed on the Ling vibratory driver. All units appear to operate satisfactorily. An experiment to determine the optimum conditions for the vibratory compaction to maximum density of various sizes of steel spheres is under way.

In the initial phase, the compaction of a single screen fraction in tubes of varying diameter is being studied. Ratios of tube diameter to particle diameter of 3 to 100 have been investigated. A second phase is concerned with the compaction of two-size component mixtures to maximum density.

4. Irradiation Studies

A possible approach toward decreasing or eliminating the cost of reactor control rods is to use a rod whose economic worth at the end of its life is greater than its original cost. Cobalt-base control rods may meet this criterion because of the production of valuable cobalt-60 during their use. To evaluate their potential, five capsules containing sintered pellets of 30 w/o dysprosium oxide dispersed in cobalt have been irradiated.

The initial two capsules in this series, ANL-51-1 and ANL-51-2, have been returned for evaluation after irradiation to integrated effective thermal-neutron fluxes of 3.3×10^{20} nvt and 4.4×10^{20} nvt, respectively, at temperatures of approximately 300°C. Measurements indicated that the pellets were dimensionally stable and that no changes had occurred. Metallographic examinations of representative pellets indicated that no reaction had occurred between the Dy_2O_3 particles and the cobalt matrix.

The results of postirradiation compression tests conducted at room temperature are tabulated in Table VIII and compared with unirradiated values. The ultimate compressive strength and percent decrease in length have decreased with increasing neutron exposure for all the specimens except Specimen 51-2-5. The reason for the anomalous behavior of this specimen is unknown.

One pellet from each capsule was analyzed for production of cobalt-60. The specific activities of pellets from ANL-51-1 and ANL-51-2 were found to be 13.8 and 18.3 c/gm, respectively. The values of the cobalt-60 in ANL-51-1 and ANL-51-2 were \$190 and \$260, respectively, compared with a cost of about \$1 for the cobalt and dysprosium oxide present.

Table VIII. Comparison of Room-temperature Pre- and Postirradiation Compressive Strength of Co-30 w/o Dy₂O₃ Pellets

Specimen	Integrated Effective Thermal Neutron Flux, nvt x 10 ⁻²⁰	Ultimate Compressive Strength, kg/cm ²	% Total Decrease in Length at Fracture
Unirradiated	-	7520 to 7878	19.4
51-1-1	3.3	6100	7.6
51-1-2	3.3	5300	16.2
51-1-3	3.3	5000	13.8
51-1-4	3.3	5580	16.9
51-1-7	3.3	5270	13.8
51-1-8	3.3	5600	16.4
51-2-1	4.4	4700	10.4
51-2-2	4.4	4470	14.4
51-2-3	4.4	4590	12.0
51-2-5	4.4	8020	17.6

5. Extrusion Developments

a. Refractory Tubes. Two Nb-1 w/o Zr tubes, 3.96 mm ID by 0.38 mm wall, with a plasma-sprayed coating of Type 304 stainless, have been made available to the Engineering Corrosion and Irradiation Groups for evaluation. This method of duplexing appropriate tubing materials appears worthy of consideration. Preliminary results on compatibility with sodium are encouraging. Further effort will await irradiation test results.

Early results from fabricability tests on Climax Molybdenum's low carbon content (<0.006%) pure molybdenum appear very promising. Indications are that lowering the carbon content from the usual 0.01 to 0.04% lowers the ductile-to-brittle transition temperature. This change in properties should greatly simplify fabrication methods and at the same time produce a much more ductile, high-impact-strength material.

b. Thorium-20 w/o U Irradiation Test Specimens. The additional billet stock mentioned in the June Progress Report (ANL-6749, p. 32) has been prepared. Four 2.49-cm (0.980-in.) diameter, copper-jacketed billets of the Th-20 w/o U (fully enriched) alloy have been extruded at a 25.5:1 reduction ratio through a 0.503-cm (0.198-in.) diameter die at 500°C.

The copper jackets were removed by pickling, and the 147-cm (58-in.) to 155-cm (61-in.) rods are being centerless ground to the 3.66-mm (0.144-in.) diameter finished size. The sized rods will then be sectioned into 5.08-cm (2-in.) and 33-cm (13-in.) irradiation-test specimens.

6. Nondestructive Testing

a. Experimental Fast Reactor Components

(i) Niobium Rod Jacketed with Type 304 Stainless Steel. One piece of niobium rod jacketed with Type 304 stainless steel (nominally 8.5 mm in OD) was inspected for bond quality by an ultrasonic through-transmission technique at a frequency of 5 Mc. Both transmit and receive transducers were collimated to a 3.2-mm diameter. A 1.6-mm-dia x 1.27-cm-long drill hole in one end of the rod served as the reference standard. The relative signal amplitude of the first transmitted pulse varied from 2-5 units. A transverse section in one of the two unit areas revealed a nonbond approximately 0.16 cm in diameter.

(ii) Vanadium Rods. A pulse-echo shear-wave technique was utilized in the inspection of two pieces of vanadium rod stock for transverse cracking. At a frequency of 1 Mc, many defect indications were noted in both rods. These indications were compared with the response from a known crack in a 1.21-cm-OD rod.

A vanadium rod jacketed with Type 304 stainless steel was evaluated for bond quality by an ultrasonic pulse-echo technique. The test was conducted at a frequency of $2\frac{1}{4}$ Mc with a circular focused transducer. A 1.6-mm dia x 1.27-cm-long drill hole in one end served as the reference standard. Fairly uniform bonding was achieved in this sample.

b. Neutron Imaging. Film processing and the interpretation of the results of the neutron radiographic study of postirradiation annealing have been completed.

From a radiographic point of view this first attempt to employ neutron radiography for a time-lapse study was reasonably successful, and no major changes in radiographic technique are contemplated for future trials. From a radiation safety point of view, the man-power arrangement for the first run also appears to warrant no major change. Reports of personnel film badge examination for all the people involved in the extended radiographic test indicated that no one was subjected to unusual radiation levels. These reports included finger, wrist, and total exposure for all the people who handled the transfer radiographic screens.

In other studies during this period neutron radiographic inspections of an irradiated reactor fuel capsule and of an unirradiated fuel assembly were completed.

c. Correlation of Heat Transfer Properties and Bond Quality. The flash method¹¹ originally developed to measure thermal diffusivity is being

¹¹Parker, W. J., Jenkins, R. J., Bolter, C. B., Abbott, G. L., Flash Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity, J. Appl. Phys., 32 1697 (1961).

utilized to determine the heat transfer properties of small bonded samples. The front surface specimens are uniformly irradiated by a very short pulse ($>500 \mu\text{sec}$) of radiant energy provided by the flash tube. The temperature history of the back surface is continuously monitored by feeding the output of the back surface thermocouples into a differential amplifying system and then into an oscilloscope. This oscilloscope trace can then be photographed. The triggering time-delay and the power supply are completed; the amplifying circuits for the thermocouples are being constructed. Measurements with this system will later be correlated with the sound transmission properties over the same areas.

C. Heat Engineering

1. Stainless Steel Loop Design

An experimental apparatus has been assembled for obtaining radiation shape factors from a coil to its surroundings. This apparatus consists of a point light source located in the center of a frosted glass hemisphere. A scale model of the coil is placed inside the hemisphere; the shadow of the coil upon the hemisphere is photographed from a large distance above. The unshaded portion of the hemisphere divided by the total area of the hemisphere shown in the photograph is the shape factor of the coil to its surroundings.

Measurements will be made to estimate radiation heat transfer rates from a coil condenser for use in a liquid metal loop.

D. Chemical Separations

1. Chemistry of Liquid Metals

a. Technetium-zinc System. Studies of the technetium-zinc system were continued. Measurements made by means of the recording effusion balance indicated that the most technetium-rich intermetallic phase in this system has the composition $\text{Tc}_2\text{Zn}_{11}$. This phase decomposes into technetium and zinc when heated. A provisional value of the free energy of formation of $\text{Tc}_2\text{Zn}_{11}$ from solid technetium and liquid zinc is $-3.42 \text{ kcal/g-atom}$ at 500°C . The density of $\text{Tc}_2\text{Zn}_{11}$ has been found to be 7.4 g/cc at 25°C .

b. Mass Transfer in Flowing Liquid Cadmium. A study has been made by E. D. Traylor of Ohio State University to obtain information concerning the dissolution of uranium in flowing liquid cadmium. The rate of mass transfer from a uranium sphere to cadmium flowing around the sphere was investigated as a function of the velocity of the flowing cadmium, the temperature of the system, and the degree of saturation of the

solvent. When the mass transfer factor J_d (a dimensionless factor which is related to the mass transfer coefficient, velocity of the liquid at the sphere, and the effect of physical properties of the system on the mass transfer from the sphere) was plotted against the Reynolds number, the curves obtained for the uranium-cadmium system had the same general shape as those obtained by Steele and Geankoplis¹² in studies of spheres of phenolic and carboxylic compounds in water. However, a hump which occurs in the region of a Reynolds number of 10^5 is considerably more pronounced in the U-Cd system than in systems of organic compounds in water. The hump is attributed to turbulence at the surface of the uranium sphere. The rate of mass transfer was found to be strongly affected by previous metallurgical treatments. Heat-treated uranium spheres yielded J_d values which were 2 to 5 times higher than those obtained with spheres which had not been subjected to heat treatment.

2. Uranium Oxide Reactions in Molten Halides

Further measurements have been made of the equilibrium constant for the thermal decomposition of uranyl chloride in molten salt solution. The value of the equilibrium constant

$$k = [\text{UO}_2\text{Cl}]^2 [\text{PCl}_2(\text{atm})] / [\text{UO}_2\text{Cl}_2]^2$$

at 650°C in lithium chloride-potassium chloride eutectic was found to be $(1.2 \pm 0.6) \times 10^{-6}$ atm. The present value is smaller than the preliminary value reported previously (see Progress Report for April 1963, ANL-6717, p. 53).

3. Plutonium Recovery Process

Cadmium-zinc-magnesium alloys are being considered for possible use as process media for plutonium-bearing reactor fuels. The solubility of uranium in the cadmium-rich portion of the system is being investigated. In this region of composition, the uranium solubility increases with increasing zinc concentrations and a retrograde solubility is observed from 466 to 630°C. Metallographic examinations showed the presence of the following solid phases: alpha uranium, UCd_{11} , and U_2Zn_{17} .

The reduction of plutonium dioxide to the metal by zinc-5 w/o magnesium alloy in the presence of a molten halide flux was demonstrated on a 30-g scale. The reduction was carried out at 800°C for 2 hr. The addition of magnesium prior to final retorting aided in the consolidation of the metallic plutonium product. The product contained lower concentrations of most metallic impurities than did the plutonium dioxide used as the starting material.

¹²Steele, L. R., and Geankoplis, C. J., A.I.Ch.E. Journal, 5, 178 (1959).

4. Head-end Treatments for Refractory Fuels

Various head-end procedures for converting uranium monocarbide fuels into a form suitable for liquid metal processing are being investigated. Addition of sodium nitrate to uranium monocarbide in a sodium chloride-potassium chloride mixture at 800°C in air atmosphere appears to produce complete conversion of the carbide to sodium diuranate. The sodium diuranate product can be reduced by zinc-magnesium alloy to produce metallic uranium in liquid metal solution.

5. Fluidization and Volatility Separations Processes

a. Fluoride Separations. The investigation of the alpha decomposition of gaseous plutonium hexafluoride was continued. In recent studies, the effect of various amounts of plutonium tetrafluoride on the decomposition of plutonium hexafluoride was evaluated. Prefluorinated nickel spheres (about 125 cc in volume) containing from 0 to 349.2 mg of plutonium tetrafluoride were filled with 100 mm Hg of plutonium hexafluoride and held at about 25°C for 75 days. The results clearly indicated that no increase in the alpha-induced decomposition occurred as a result of the added amounts of plutonium tetrafluoride.

b. Fluid-bed Fluorinations of U_3O_8 - PuO_2 Mixtures. Scouting experiments directed toward the establishment of optimum conditions for the fluorination of mixtures of U_3O_8 and plutonium dioxide in a $1\frac{1}{2}$ -in.-diameter fluid-bed reactor were continued. Two runs were carried out in which the fluidized alumina beds from previous fluorination runs (see Progress Report for July 1963, ANL-6764, pp. 51 and 52) were subjected to 10 hr of additional fluorination to determine what effect the extension of the fluorination period would have on the removal of residual plutonium from the alumina.

In the runs described previously (ANL-6764, p. 52), the fluorination was carried out in two steps. The first step was a fluorination-feeding period (one hour) during which the feed material (a mixture of U_3O_8 , plutonium dioxide, and alumina) was continuously transported into a fluidized bed of alumina at 500°C and simultaneously reacted with 20 v/o fluorine in nitrogen. The second fluorination step was carried out for a period of 5 hr at a bed temperature of either 500 or 550°C, with recycled 100 percent fluorine.

Two of the alumina beds from the previous runs (one bed from each type of run) were fluorinated for an additional 10 hr. The same bed temperature (500 or 550°C) used during the 5-hr fluorination period was used during the additional 10-hr fluorination period. Extending the fluorination period from 5 to 15 hr resulted in only a slight decrease in the residual plutonium content of the alumina in the fluorination test at 500°C.

In the fluorination carried out at 550°C, however, a marked reduction occurred in the amount of plutonium retained by the alumina; the residual plutonium content decreased from 0.022 to 0.011 w/o.

Tests are being planned in which a bed temperature of 450°C will be used for the feeding-fluorination step. The choice of 450°C for the first fluorination step is based on the excellent removals of plutonium and uranium from alumina that were achieved when this temperature was used in the first step of earlier fluorination experiments with oxidized uranium dioxide-plutonium dioxide solid solutions in a static system (see Progress Report for August 1962, ANL-6610, p. 55).

c. Separation of Uranium Oxide Fuel from Cladding by Fluid Bed Oxidation. Work was continued on the development of a method for the removal of uranium dioxide pellets from stainless steel cladding by oxidation of uranium dioxide to U_3O_8 in a fluid-bed reactor. The pellets break into pieces because the two oxides have different densities. The U_3O_8 fines that are formed in the reaction are transported from the oxidation zone of the fluid-bed reactor into the fluorination zone by the oxidizing gas stream.

Two additional engineering-scale runs were made in which internal vibration of the fluidized-packed bed was used (see Progress Report, for July 1963, ANL-6764, p. 54). Internal vibration of the fluidized-packed bed aids in loosening residues of uranous oxide which may have become lodged in the cladding during the oxidation reaction.

The fuel charge consisted of 1-in.-long by $\frac{1}{2}$ -in.-diameter stainless steel tubes, each tube containing two uranium dioxide pellets. The ends of the tubes were open to simulate sheared fuel elements. In each run, 1500 g of fused alumina (-40 +170 mesh) was used as the inert fluid-bed material. In the first run, 60 fuel segments were used; the height (static) of the fluidized-packed bed was about 9 in. and the total bed height (static) was about 22 in. In the second run, 40 fuel segments were used; the height of the fluidized-packed bed was 6 in. and the total bed height was 15 in. Both runs were carried out in a 2-in.-ID reactor.

Gas pulsing of the fluidizing gas was used in each run. The pulse duration was 0.5 sec with a pulse frequency of 2 pulses/min at a gas manifold pressure of 30 psig. Air was used as the fluidizing gas. The temperature of the bed was increased from room temperature to 450°C over a period of 4.5 to 5 hr, after which the bed was held at 450°C for 3 hr.

In the first run, only 77 percent of the uranium dioxide was separated from the cladding. In the second run, 93 percent of the uranium dioxide was removed. These results indicate that the mechanical vibration provided was not vigorous enough for the deeper bed of the first run.

It is believed that complete removal of uranium dioxide from the cladding by oxidation can be achieved by increasing the intensity of the vibration.

d. Separation of Uranium from Zirconium Alloy Fuels. Development of a chlorination-fluorination scheme for reprocessing highly enriched uranium-zirconium fuels was continued. In the present scheme, the fuel is first reacted with hydrogen chloride in a fluidized bed of inert solids. The zirconium is thereby converted to the tetrachloride and the uranium is converted to the trichloride. Since the hydrochlorination reaction is performed at temperatures above the sublimation point of zirconium tetrachloride (331°C , 1 atm), a separation of the zirconium tetrachloride from the solid uranium trichloride is achieved. The uranium trichloride is then fluorinated to the volatile uranium hexafluoride and is thus removed from the inert solids of the fluidized bed.

The objective of the present study was to determine the effect on the process of the use of moist hydrogen chloride in the hydrochlorination step. This study is pertinent to the establishment of criteria for the proposed use of recycled hydrogen chloride.

The charge in the present run consisted of two 148-g fuel sub-assemblies; each subassembly consisted of three plates uranium-Zircaloy-2 alloy clad with Zircaloy, uranium being present to the extent of 2.1 w/o. Each plate was 5 in. long. The reaction bed contained 320 g of fused alumina (Type 38 Alundum, Norton Company); the packed-bed filter contained 320 g of -14 +20 mesh alumina. The alumina in the packed-bed filter had been used in two previous runs and contained 0.007 w/o uranium.

The following reaction sequence was employed in the run: hydrochlorination, hydrofluorination, and fluorination. The hydrochlorination step with moist hydrogen chloride (1100 ppm water) was performed at an average rate of 28 g of alloy per hour while maintaining the temperature of the fluid bed at about 380°C . The hydrofluorination was conducted at a fluid bed temperature of 350°C over a period of 2 hr. This was followed by a fluorination period during which the temperature of the bed was gradually increased from 250 to 500°C while feeding 10 v/o fluorine-nitrogen mixture.

The uranium recovered was 99.1 percent of the initial uranium charge (6.3 g). The uranium retained by the alumina was 0.8 w/o. An additional loss of uranium (0.03 percent of that initially charged) occurred through the packed-bed filter during hydrochlorination. The average concentration of uranium retained by the alumina in the fluid and filter beds at the end of the run was 0.008 w/o.

The use of moist hydrogen chloride (with 1100 ppm water) resulted in an increase in the quantity of zirconium retained by the alumina in the fluid bed. The content of residual zirconium in the fluid bed was 2.0 w/o, an elevenfold increase over the zirconium retention (0.18 w/o obtained in previous runs in which the moisture content of the hydrogen chloride was 35 ppm). However, both the hydrochlorination rate and the hydrogen chloride utilization efficiency were unaffected by the increase in moisture content of the hydrogen chloride.

The results of this study suggest that recycled hydrogen chloride can be used in the hydrochlorination step after the bulk of the water vapor has been condensed out of the gas phase, and that the application of stringent methods to achieve high removals of water vapor will not be necessary.

6. General Chemistry and Chemical Engineering

a. Preparation of Uranium Monocarbide. Four preparations of uranium monocarbide on a 500-g scale have been made. The method involved the precipitation of uranium monocarbide by the addition of carbon to uranium dissolved in zinc-14 to 18 percent magnesium solution. The precipitated carbide was recovered by removing the supernatant and re-torting the remainder of the mixture. The carbon content of the carbide products was about 5.4 w/o (the theoretical carbon content is 4.8 w/o).

Efforts are being made to reduce the carbon content of the products to near the theoretical value. Work is also being done in an effort to reduce the oxygen content of the product. The lowest oxygen concentration obtained thus far has been 0.39 w/o. The main source of oxygen appears to be the oxygen that is sorbed on the activated carbon used as a reactant. To eliminate this problem, other types of carbon which have less tendency to sorb oxygen are being tested and improved desorption techniques are being developed.

b. Preparation of Uranium Monosulfide. Preparation of uranium monosulfide on a 300-g scale is continuing. Hydrided-dehydrided uranium powder is treated with hydrogen sulfide and the sulfide product is homogenized by heating to about 1900°C. Analyses of one batch of material indicated that the homogenization step reduced the oxygen content of the uranium monosulfide from 0.3 to 0.09 w/o.

c. Gas-phase Reaction for the Production of Plutonium Compounds. Glovebox PF-21 has been made available for the production of plutonium compounds by gas-phase reactions. Independent glovebox atmosphere system and pressure controls are being installed, so that the general helium system will not be contaminated with gases to be used. The necessary electrical services to the glovebox for the operation of furnaces and process equipment has been installed, and the components required to provide a high-purity inert atmosphere have been ordered.

A mockup of a reaction chamber has been made and tested in a 24-in.-long, 4-in.-diameter split-tube furnace. Mild steel components were used as substitutes for the very expensive refractory materials required in the gas-phase reaction chambers. Tests are now under way to determine temperature profiles and conditions required to achieve satisfactory sparging rates and ease of control of the gas-metal reactions.

d. Analysis for Plutonium Hexafluoride. An analytical method for the determination of plutonium hexafluoride was studied. The method depends upon the selective reduction of plutonium hexafluoride to the tetrafluoride with sulfur tetrafluoride. The uranium hexafluoride, excess sulfur tetrafluoride, and the sulfur hexafluoride formed during the reaction are volatilized out of the reaction vessel. The plutonium tetrafluoride is then dissolved in an acidic aqueous solution and the plutonium content measured by radiochemical analysis or by an amperometric titration.

The study showed that the plutonium hexafluoride in a 0.5 w/o plutonium hexafluoride-uranium hexafluoride mixture (a concentration similar to that expected in the laboratory studies of the fluid-bed fluorination of U_3O_8 -plutonium dioxide mixtures) can be reduced quantitatively by intermittently shaking the hexafluoride mixture with an 11.5 mole excess of sulfur tetrafluoride with respect to plutonium hexafluoride for one hour at 85°C. A mole ratio of sulfur tetrafluoride to plutonium hexafluoride of 1.90 may be used if the reaction time is extended to 22 hr.

e. Solubility of Rare Gases in Alkali Metals. The interaction of nonmetallic atoms with metals offers an opportunity to study the electronic structure of metals. Because of the simplicity of their electronic structures, the interactions of rare gases with alkali metals will be studied by measuring their solubilities. The solubilities and their temperature coefficients will provide data for the calculation of thermodynamic quantities.

In the initial study, the determination of the solubility of argon in liquid sodium was attempted. Tests made at 200°C and at argon pressures up to 10 atm have indicated that the solubility of argon in sodium is less than 10^{-9} atom fraction, the limit of detection by the mass spectrometric method.

Experiments with krypton-85 are being planned. It is expected that the use of this radioactive isotope will allow measurement of solubilities as small as 10^{-15} atom fraction of krypton in sodium.

E. Plutonium Recycle Program

The use of cross sections appropriate to the spectrum of the central, 1.5 percent plutonium regions results in a slight alteration in the amount of poison in the shim zone. Each element will now contain approximately 41 g of europium and 7.5 g of samarium (atoms europium/atoms uranium = 0.0024; atoms samarium/atoms uranium = 0.00045). The

corresponding numbers were previously 34 g of europium and 6.2 g of samarium (obtained using cross sections appropriate to a 2.5 percent plutonium region).

Cross sections appropriate to the spectrum of the plutonium region at a burnup of 6000 Mwd/tonne have also been obtained and used to generate cross-section correction factors (CSCFACS) which are used in CYCLE 2 to effect a linear change in cross sections with burnup. The use of CSCFACS resulted in a maximum reactivity swing of 1.8% Δk during a burnup step of 6000 Mwd/tonne compared with a 2.5% Δk swing when using the cross sections appropriate to zero burnup. The principal reason for this improved behavior with respect to long-term reactivity is the much reduced value of σ_a^{40} at higher burnups resulting from increased self-shielding of the Pu^{240} resonance as the concentration of Pu^{240} increases.

The buildup of Sm^{149} in the various reactor zones has been calculated as a function of burnup in order to determine reactivity (both cold and operating) accurately as a function of burnup. The positive reactivity effect of burnout of Sm^{149} in the shim zone fuel is very nearly compensated by the buildup of Sm^{149} in all zones and other reactivity-reducing effects out to 2000 Mwd/tonne, after which the reactivity of the system steadily decreases. Up to 2000 Mwd/tonne the negative and positive effects are so nearly balanced that at operating conditions the reactivity peak (which occurs at 1000 Mwd/tonne) amounts to only 0.05% Δk , whereas with the reactor in the cold condition the reactivity peak at 1600 Mwd/tonne is 0.2% Δk higher than the reactivity at zero burnup.

Calculations have been made which confirm additional reactivity will be required in the driver zone to perform cold critical experiments when burnups are greater than 3000 Mwd/tonne.

Hydrodynamic calculations to correlate regional power and voids for both zero burnup and at 6000 Mwd/tonne exposures are underway using RZ and PDQ calculations in conjunction with the CHOPPED code.

IV. ADVANCED SYSTEMS RESEARCH AND DEVELOPMENT

A. Thermionic Energy-conversion Diode with a Film-boiling Liquid Metal

A film-boiling liquid metal diode has now been operated with cesium instead of potassium. The same type of data was obtained that was reported in ANL-6739 (Progress Report for May 1963, pp. 53-54) and in ANL-6705 (Progress Report for March, 1963, p. 56) for potassium.

The thermocouple which measured the collector temperature was recalibrated against the boiling point of cesium by means of the published relationship between the vapor pressure and the liquid temperature.¹³ The cesium calibration curve is shown in Figure 6 together with that for potassium. The disagreement in calibrations, when translated into vapor pressure differences, averages to about 20%. This is the accuracy given by Honig for the vapor pressure data.

Figure 6. Calibration of Collector Thermocouple by Boiling Point Determinations with Cesium. (Previous Calibration with Potassium Shown as Dashed Line.)

Figures 7a, b, and c shows the maximum submersion of the emitter into the liquid metal pool for which a satisfactory vapor film was possible. The effect of collector and pool saturation temperature is shown for three different emitter temperatures. The data are qualitatively very similar to those for potassium, but the maximum submersion is greater

¹³R. E. Honig, Vapor Pressure Data for the More Common Elements, RCA Review, 18, 195-204 (1957).

and the subcooling range which is permitted for stable film boiling in this geometry is much greater. Also, with cesium an instability was observed at very shallow submersion for almost every datum point. For deeper submersion the instability was suppressed. This effect was not present with potassium.

(a)

(b)

(c)

Figures 7a, b, and c
Effect of Emitter, Collector, and Saturation Temperatures on Maximum Submersion of Emitter in Cesium Pool. (Numbers Given Are in cm.)

A current-voltage characteristic for the film boiling cesium diode appears in Figure 8. The observed current is of the same order as for a cesium vapor diode with solid electrodes at the same temperature and pressure.¹⁴ Thus, the initial assumption that liquid and solid electron collectors would appear the same electrically is confirmed.

¹⁴Proceedings of the Third Government-Industry Thermionic Round-table Discussion, AD-270905, Vol. 1, Section 1, p. 13 (January, 1962).

Figure 8. Cesium Diode Current-Voltage Curve for Emitter Temperature 2000°K, Collector Temperature 550°K, Saturation Temperature 635°K, Cesium Pressure 7.74 Torr.

down a high-velocity liquid boundary between the outside containment walls and the spinning liquid sodium rotor, thus reducing the shear force (friction loss).

Centrifugal action forces the uncondensed vapor and excess liquid through openings on the inside containing wall of the torus.

The physical arrangement of eight pairs of magnets in a ring permits a range of voltage from 75 to 600 v dc. However, there is some question as to the feasibility of operating at 600 v. Seventy-five volts is considered optimum.

The purpose in arranging the generator rotor and magnets as shown in Figure 9 is to reduce the variation in temperature difference between the driving vapor and the liquid rotor, the variations in pressure, and the acceleration of the rotating mass of liquid sodium in the torus.

The greater the number of magnet pairs around the torus, the less are the variation in these quantities and the greater the efficiency of energy transfer. The use of eight magnet pairs is a reasonable compromise between weight and performance.

B. Magnetohydrodynamics

1. A Nuclear Magnetohydrodynamic System

A conceptual design of a boiling sodium fast reactor coupled with a liquid metal magnetohydrodynamic (MHD) generator having an output of 1 Mwe and a specific power of 4.9 kg/kwe has been analyzed. The generator consists of liquid sodium spinning in a torus around which eight magnets are equally spaced. Jets of sodium vapor tangent to the mean circumference of the torus keep the liquid sodium spinning through the magnetic fields at constant velocity.

Ahead of each vapor jet is a jet of flashing sodium. The vapor from the flashing sodium adds some kinetic energy to the torus, but the main purpose of flashing is to lay

Figure 9. A Nuclear Magnetohydrodynamic Power Plant

The temperature of the liquid in the generator has been optimized for the system.

The radiator weight and volume vary as the fourth power of the surface temperature. There is a good reason to make the cycle rejection temperature high, but a high reject temperature is incompatible with high cycle efficiency. In addition, the electrical resistivity rises sharply with temperature; therefore, the generator is more efficient at lower liquid temperatures. Low temperatures also permit the use of lower system (reactor) pressure, resulting in lighter components. High temperatures also increase the size and weight of the magnet as well as of the bus-bar-cooling system.

The choice of liquid velocity is also subject to compromise. Voltage is directly proportional to fluid velocity, but the hydraulic losses roughly increase as the square of velocity.

A mounting frame of structural I-beams supports was used to mount all of the components. The entire power plant package in its folded condition was 216 cm in diameter by 331 cm high. In operation, the wings of the radiator would be extended so that the distance from wing tip to wing tip is 924 cm. The overall design parameters are noted in Table IX.

Table IX. System Characteristics

Power output, Mwe	1.0
Voltage (dc), v	75-100
System efficiency (full power), %	$6\frac{1}{4}$
Pressure, atm	
In reactor	5
In generator	1
Liquid temperature entering reactor, °C	870
Vapor temperature leaving generator, °C	893
Power plant size, cm	
Length	331
Diameter (radiator closed)	216
Uranium	
Mass, kg	785
Enrichment, %	29.8
Core lifetime, yr	1
Total weight - reactor and generator, kg/kwe	4.9

2. MHD Power Generation

a. MHD Vapor Condenser. The first stage of an analytical study of an electromagnetically controlled metal vapor condenser (see Progress Report for May 1963, ANL-6739, p. 59) has been completed. It is proposed that an electromagnetic field be utilized to pump condensed vapor off of a condenser surface, thus increasing heat transfer rates and eliminating the necessity of gravity. A simplified mathematical model of the transport phenomena was devised and numerical solutions were obtained for a wide range of physical parameters. It was shown that condensation heat transfer rates for sodium and mercury could be increased by factors of 5.4 and 2.5, respectively, under readily attainable laboratory conditions.

From these promising results, it appears that an experimental program is in order to verify the assumptions used in the model and to demonstrate the feasibility of this technique.

b. MHD Duct Flow. A comprehensive analytical study of the effects of heat transfer and electrical conductivity of a finite channel wall upon the efficiency of an MHD power generator has been undertaken. Several idealized situations have been analyzed and a numerical program is being devised.

V. NUCLEAR SAFETY

A. Thermal Reactor Safety Studies

1. Metal Oxidation and Ignition Studies

a. Oxidation of Plutonium and Plutonium-Aluminum Alloy. Studies of the oxidation of plutonium are being extended to a higher temperature range in order to interpret the results of ignition studies of plutonium and its alloys (see Progress Report for June 1963, ANL-6749, pp. 56 and 57). Previous oxidation studies of plutonium were limited to a maximum temperature of 480°C, because excessive self-heating occurred above this temperature. To overcome the difficulty of self-heating, two small stainless steel plates were clamped on 5-mm cubes of plutonium. The stainless steel plates served as heat sinks and thereby inhibited self-heating. Isothermal oxidation runs at temperatures up to 550°C have now been completed.

It has been previously reported (see Progress Report for March 1963, ANL-6705, p. 63) that the oxidation of plutonium followed a parabolic-linear rate law up to temperatures of 300°C, with activation energies of 32 kcal/mole for the parabolic portion of the rate curve and of 16 kcal/mole for the linear portion. Above 300°C, a change in kinetics of the reaction appears to take place, which results in a minimum in the rate of reaction at about 420°C. In the current experiments, it was found that the activation energy (32 kcal/mole) for the initial parabolic oxidation process above 420°C (high-temperature regime) was the same as the activation energy for the parabolic portion of the rate curve at temperatures below 300°C (low-temperature regime). The activation energy for the linear oxidation process in the high-temperature regime, however, was found to be higher (29 kcal/mole) than that for the linear portion of the curve in the low-temperature regime (16 kcal/mole).

Isothermal oxidation studies were also performed with 5-mm cubes of plutonium-2 a/o aluminum alloy, chosen because previous ignition studies (see Progress Reports, ANL-6739, p. 61 and ANL-6764, p. 65) indicated that the presence of aluminum might lead to the formation of a more protective oxide coating than that which is formed in the oxidation of pure plutonium. In general, the results of the oxidation experiments, which were conducted over the range from 240 to 490°C, verified that the oxide layer formed on the aluminum-plutonium alloy was more protective than the oxide layer formed on pure plutonium. The protective effect was more pronounced at the lower temperatures in the range studied.

b. Aluminum-U₃O₈ Reaction. Studies of the aluminum-U₃O₈ thermite reaction were continued. Cold-pressed compacts containing 30, 45, 60, 75, and 90 w/o U₃O₈ were subjected to two modes of heating. In one series of experiments, the samples were heated uniformly at 25°C/min to 1300°C. In another series, the samples were heated rapidly, so that the

temperature of the samples reached 1300°C in 3 to 4 min. Although some self-heating of the samples occurred in both series, the maximum self-heating recorded was 400°C. Greatest self-heating occurred with samples containing 60 and 75 w/o U_3O_8 .

2. Metal-Water Studies

a. Vapor-phase Burning of Aluminum in Liquid Water. A brief study was made of the vapor phase burning of aluminum in liquid water. Samples of aluminum ranging in weight from 150 to 1000 mg were levitated, heated, and ignited in air. The specimens were then dropped into water at room temperature. The times of consumption of the specimens were noted as a function of specimen size. A plot of the initial diameter of the aluminum pellets versus the times of consumption of the pellets was linear, and indicated that the pellet diameters decreased at the rate of 0.16 mm/sec, which corresponds to a consumption rate of 1.0 g aluminum/(sq cm)(min).

b. Metal-Water Studies in TREAT. Preparations are underway for several series of experiments in TREAT. In the first series, four 89.35 w/o zirconium-10.65 w/o uranium (fully enriched) specimens will be subjected to vigorous neutron bursts while submerged in water. The alloy specimens are in the form of plates and have been drilled to accept an imbedded thermocouple. Two experiments will be conducted in room-temperature water and two in heated water. Transient-temperature measurements should provide accurate information concerning the differences in the heat transfer processes occurring during heating. The information is needed to interpret differences that have been noted between the overall reaction which occurs in room temperature and that which occurs in heated water (see Progress Report for May 1963, ANL-6739, p. 62).

The development of apparatus to view specimen meltdown and metal-water reaction in TREAT by means of motion pictures is continuing. Transparent capsules are being modified to enable them to withstand increased pressures. Specimens of Zircaloy-clad and stainless steel-clad uranium dioxide-core fuel pins have been sent to MTR for irradiation as a part of the program of studies with pre-irradiated specimens.

B. Fast Reactor Safety Studies

A description of the objectives of in-pile oxidation studies is given in ANL-6705, Progress Report for March 1963. Interest centers on the particle-size distribution occurring when reactor fuels are heated in flowing air in a reactor environment. Samples 1 through 6 of this series were irradiated from March through June, and Samples 7 and 8 were irradiated this past month. In this connection, it should be noted that Table X, Column 5, of the June Report, ANL-6749, p. 59, inadvertently gives the dimension for crucible area in square inches when it should be shown as percent of total residue. This is correctly shown in Table X below for samples irradiated this month.

Table X. Summary of In-pile Oxidation Experiment for August 1963

Samples		Reactor Integrated Power (Mw-sec)	Peak Sample Temp Re- corded (°C)	Residue in Crucible Area (%)	Final Sample Distribution, % on Screen				
No.	Composition				74 μ	43 μ	25 μ	5 μ	1 μ
7	100% Uranium (5% enriched)	261	1500	91.4	6.88	0.86	0.61	0.2	0.003
8	95% U-5% Fs (20% enriched)	230	2980	96.2	2.10	0.7	0.71	0.21	0.11

Sample 7 was pure uranium and was appreciably oxidized, but appeared to have a central metallic core.

Sample 8 was the first sample to indicate any appreciable amount of material on the 1- μ screen. The charcoal trap downstream is being analyzed for uranium to determine if any passed through the 1- μ filter. A portion of the pin was on the bottom of the crucible and is being examined metallographically in an attempt to determine whether the thermocouple wires (tungsten-tungsten-26% rhenium) melted. It is believed that the nuclear energy released in Sample 8 during the transient was sufficient to approach the atmospheric boiling point of uranium (3400-3500°C).

One series of classified experiments was irradiated during this period.

VI. PUBLICATIONS

Papers

AN EDDY CURRENT GAUGE FOR MEASURING ALUMINUM CORROSION

S. Mori, R. E. Loess, and J. E. Draley
Corrosion 19, 269t-271t (August 1963)

COUPLING CEMENTS FOR ULTRASONIC-WAVE VELOCITY MEASUREMENTS AT HIGH TEMPERATURES

E. S. Fisher and C. J. Renken
J. Acoust. Soc. Amer. 35, 1055 (July 1963). Letter

STUDIES ON TTA COMPLEXES WITH METAL IONS. II. INVESTIGATIONS OF SOME TETRAVALENT COMPLEXES IN THE SOLID STATE

Yehuda Baskin and N. S. K. Prasad
J. Inorg. Nucl. Chem. 25, 1011-1019 (August 1963)

FREE CONVECTION HEAT TRANSFER UP TO AND NEAR-CRITICAL CONDITIONS

V. E. Hold and R. J. Grosh
Nucleonics 21, 122-125 (August 1963)

ELASTIC NEUTRON SCATTERING FROM Fe, Ni, AND Cu

S. A. Cox
Bull. Am. Phys. Soc., Ser. II, 8, 478 (August 1963). Abstract

ANL Reports

ANL-5800, REACTOR PHYSICS CONSTANTS
2nd Edition

ANL-6648 CHEMICAL ENGINEERING DIVISION SUMMARY REPORT,
October, November, December, 1962

ANL-6676 TABULATIONS OF CALCULATED CRYSTALLOGRAPHIC
DATA FOR ALPHA PLUTONIUM
Alan F. Berndt and Lowell T. Lloyd

ANL-6693 THERMAL HYDRAULIC PERFORMANCE CHARACTER-
ISTICS OF EBWR (0 to 100 Mwt)
Michael Petrick and E. A. Spleha

ANL-6694 A 200-WATT CONDUCTION-COOLED REACTOR POWER
SUPPLY FOR SPACE APPLICATION
Donald R. MacFarlane

- ANL-6708 INTERIM REPORT: FARET EXPERIMENTAL PROGRAM
The FARET Program Group
- ANL-6711 PHASE RELATIONSHIPS IN THE SYSTEM URANIUM
OXIDE-LANTHANUM OXIDE
D. C. Hill, J. H. Handwerk, and R. J. Beals
- ANL-6727 FAST NEUTRON SCATTERING FROM Ta¹⁸¹
A. B. Smith
- ANL-6747 TABLES OF OXYGEN PRESSURES CALCULATED FROM
THE HYDROGEN-WATER SYSTEM AND FROM THE DIS-
SOCIATION OF CUPRIC OXIDE
L. M. Atlas and J. B. Moser