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LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Quarterly Status Report on the
Advanced Plutonium Fuels Program
April 1 to June 30, 1968
and Second Annual Report, FY 1968

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

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Report distributed September 12, 1968

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FOREWORD

This is the eighth quarterly and second annual report on the Advanced Plutonium Fuels program conducted at the Los Alamos Scientific Laboratory. Much of the work is aimed at problem areas associated mainly with LMFBR development; the remainder has broad applicability to general reactor technology.

Most of the investigations discussed here are of the continuing type. Results and conclusions described may therefore be changed or augmented as the work continues. Published reference to results cited in the report should not be made without obtaining explicit permission to do so from the persons in charge of the work.

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PROJECT 801

SODIUM TECHNOLOGY

Person in Charge: D. B. Hall
Principal Investigators: G. H. Best
R. H. Perkins
E. O. Swickard

I. INTRODUCTION

For the successful operation of high temperature sodium systems contemplated for use in fast, central station reactor concepts, impurities in the sodium must be monitored and controlled. Nonradioactive impurities such as oxygen must be maintained at low concentration levels to limit corrosion processes. Radioactive impurities introduced into sodium from failed fuel elements should be removed to facilitate "contact maintenance" and to minimize safety problems. To control the levels of these impurities, a knowledge of their behavior and interactions in sodium must be developed. Acquisition of this information has been subdivided in the LMFBR Program Plan into a number of task areas of research. The sodium technology program at LASL has projects which contribute to six of these areas. The broad task areas and current LASL projects within those areas are summarized below:

Task Area 1. Study of Compatibility of Materials with Sodium and its Impurities.

- A. Correlation of sodium and helium leak rates.
- B. Study of carbon transport in thermal convection loops.

Task Area 2. Study of Purification Methods for Nonradioactive Impurities.

- A. Study of Na_2O kinetics in cold traps.
- B. Study of oxygen, carbon, and nitrogen removal with the soluble getters magnesium, calcium, and barium.

Task Area 3. Study of Fission Product Behavior in Sodium.

The rates of dissolution, distribution, plating out, and gettering of fission products are being investigated. The following programs are being pursued:

- A. Study of transport and distribution of fission products in flowing sodium.
- B. Study of transport and distribution of fission products in static sodium (capsule experiments).
 1. Study of ^{137}Cs distributions.
 2. Study of fission products release rate in trace-irradiated ceramic fuels.

Task Area 4. Study of Nonradioactive Impurity Sampling and Analytical Methods.

- A. Plugging indicator studies.
- B. Investigation of vacuum distillation, gamma ray analysis, d.c. resistivity meter, EMF cells; and development of remotely-operated distillation sampler for EBR-II.

Task Area 5. Study of Basic Chemistry and Physical Properties.

- A. Study of gas diffusion through metals into sodium.

Task Area 6. Study of Blanket and Maintenance Atmospheres.

- A. Development of a high temperature quadrupole mass spectrometer for cover gas analysis.

Details of the work in each of these programs are presented below.

II. STUDY OF COMPATIBILITY OF MATERIALS WITH SODIUM AND ITS IMPURITIES.

A. Correlation of Sodium and Helium Leak Rates (D. C. Kirkpatrick, J. P. Brainard)

1. General

The correlation of sodium leak development with measured helium leak rates observed during acceptance testing provides information on the degree of component integrity which must be attained for safe, long-term sodium plant operation. No firm criteria now exist that establish acceptable levels of leak-tightness for various situations.

This study uses fabricated stainless steel leaks and leaks that occur naturally in stainless steel bar stock. Selected samples having a range of helium leak rates are incorporated into small sodium systems (cells) which are held at a pre-determined temperature until sodium leakage occurs. From these observations it may be possible to establish, for mass spectrometer acceptance tests on sodium system components, the maximum tolerable helium rate which is consistent with adequate long-term containment of sodium by that component.

2. Results in FY 1968

A powered hydraulic press for fabricating leaks was obtained. The press has a control system which permits a known force to be applied to a sample for a prescribed time. A die with changeable inserts for different leak configurations was made for use with this press. Stable leaks in the range 10^{-4} to 10^{-5} atm-cm³/sec (helium) have been produced from stainless steel tubing.

A vacuum oven (Fig. 1) was set up to bake out volatile contaminants from bar stock samples. The oven is made of stainless steel and has an 8.5-liter working volume. The maximum temperature attainable is at least 700°C with existing power supplies.

Equipment for the first leak tests is shown in Fig. 2. Sodium cells are behind the left-hand metal panel. The mass spectrometer (lower left in figure) is continually calibrated during the experiment.

Stainless steel reaction chambers filled with air at ambient pressure are placed around the leak of each cell to simulate typical sodium system

Fig. 1. Vacuum oven for baking porosity leaks to remove volatile contaminants.

Fig. 2. Apparatus for first sodium-helium leak correlation experiment.

service conditions. The mass spectrometer (operating at room temperature) samples the reaction chamber gas periodically. Although sodium or sodium oxide cannot be detected with the room temperature mass spectrometer, a sodium leak can be observed by

the accompanying decrease of oxygen concentration in the reaction chamber. Less than 15 mg of sodium will react with all oxygen in the air in the 25 cc reaction chamber. Tests of this method of detecting the occurrence of sodium leakage indicated that a leak rate of 1 mg Na/24 h into the reaction chamber is detectable.

Four cells and their associated leaks are now in test at 400°C. Data on the test specimens are given in Table I.

Table I

Pre-Test Characteristics of Na Leaks		
Cell No.	Type of Leak	Initial He Leak Rate (room temp)
1	Fabricated (compressed tube)	1.1×10^{-4} atm-cm ³ /sec
2	Fabricated (compressed tube)	none (control specimen)
3	Porosity in bar stock	1.7×10^{-4} atm-cm ³ /sec
4	Porosity in bar stock	none (control specimen)

These leaks were stable under thermal cycling (20-500°C) under vacuum. While they are "large" leaks by comparison with those considered acceptable in sodium system components, it was observed that they may be blocked by traces of moisture. Thus they could readily escape detection during mass spectrometer testing; the leaks are, however, readily re-established by heating in a vacuum.

Prior to the introduction of sodium, the cells were filled with helium and heated to 400°C. During this procedure, the reaction chambers contained air to insure that their stainless steel inner surfaces would be pre-oxidized. In subsequent testing with sodium in the cells, the occurrence of oxygen-depletion in the reaction chamber should be unambiguously associated with the entrance of sodium. Apparently there was also some oxidation in the porosity leak during this phase of testing, for its leak rate decreased by a factor of 10^4 (to $\sim 2 \times 10^{-8}$ atm-cm³/sec) after three days; subsequently the leak became undetectable. The fabricated leak was however unaffected. It was established in separate tests that a porosity type of leak is subject to

plugging when heated in air oxidizing atmosphere and is readily re-established by heating in a hydrogen atmosphere.

After these preliminary tests, the cells were filled with hot trapped sodium and put in test at 400°C. No leakage has been observed during the two month test time accumulated to date. It is thought that the porosity leak was effectively sealed by the pre-oxidation during the preliminary testing, and that the fabricated leak may be plugged by sodium oxide during the current test. At the low test temperature (400°C) this postulated state of affairs may be a stable one. At higher temperatures, this might not be the case. Four simplified cells are now being constructed for 650°C tests.

B. Study of Carbon Transport in Thermal Convection Loops (J. C. Biery, C. R. Cushing)

1. General

Studies have indicated that the use of carbon beds may be useful in the gettering of ¹³⁷Cs in sodium systems. Carbon, however, is slightly soluble in sodium and can carburize austenitic stainless steels and refractory metals. Therefore, the purpose of this study is to determine the conditions under which the carbon mass transfer rates are sufficiently low to allow the use of carbon beds in a sodium system.

The carbon transfer rates from carbon rods will be studied in thermal convection loops. The Type 304 or 316 stainless steel loop itself will serve as the carbon sink when these alloys are studied and vanadium alloy sleeves will serve as getters when vanadium is studied.

2. Results in FY 1968

The first thermal convection loop has been assembled, helium leak checked and found tight. The loop is in its containment box and is awaiting the wiring of the thermocouples and the addition of the trace heaters prior to the application of the insulation.

III. STUDY OF PURIFICATION METHODS FOR NONRADIOACTIVE IMPURITIES.

A. Study of Na₂O Kinetics in Cold Traps (C. C. McPheeters, J. C. Biery)

1. General

Nuclear reactors which will incorporate liquid sodium as the heat transfer fluid will require efficiently designed cold traps because of the large sodium volumes involved. Minimum cold trap sizes adequate to achieve the required cleanup rates and impurity holding capacities are of interest because of the cost of large component construction. In order to design minimum-size cold traps, the mechanisms of impurity removal and the mass transfer coefficients must be known. It is the purpose of this study to determine the mechanisms of impurity precipitation in cold traps and to measure the mass transfer coefficients involved. With adequate knowledge of these rates and mechanisms, cold traps can be designed to accommodate the required amount of impurity deposits and to meet the required system cleanup rates.

Mass transfer coefficients are being determined by observing cleanup rates in a sodium system with cold traps of simple geometries. These cold traps are operated at various temperatures and flow rates to determine the effect of these variables on the mass transfer coefficients. The test system is an isothermal, forced-convection loop containing vacuum-distillation apparatus, an oscillating plugging indicator, and two United Nuclear Corporation oxygen meters for determination of oxygen concentration in the sodium.

The first cold trap design being tested consists of three concentric tubes.¹ The annulus between the outer two carries NaK which removes heat from the cold trap. Sodium flows down the inner annulus where it is cooled and then up the central tube where it is reheated. A notable feature of this design is the absence of any form of extended surface or "packing." The packing was omitted in order to provide a simple surface area on which the oxide could precipitate. Packed cold traps will, of course, be tested during this study also.

Cold trap test runs consist of an equilibration period at an initial temperature followed by a rapid change to a new temperature and flow rate. Oxygen concentration data are taken at small time intervals with all the available analytical techniques until the system concentration reaches the new equilibrium level. The resulting oxygen concentration data as a

function of time are then used to determine the mass transfer coefficients.

2. Results in FY 1968

Most of the year's work has been reported in detail in previous quarterly reports^{1,2,3} and is summarized below in section (b). A substantial amount of new data was obtained late in the year, and these are described below, separate from the more general accounts of the year's progress.

a. Experimental Results in Fourth Quarter of FY 1968

Development of the oscillating plugging indicator² has allowed very consistent measurement of impurity saturation temperatures. In the determination of rates of change of oxygen concentration, reproducible and consistent concentration measurements, such as those produced by the oscillating plugging indicator, are particularly valuable.

Additional dissolution and precipitation runs were made with the unpacked annular cold trap during the last quarter reporting period. Run 1-16 (Fig. 3) was a dissolution run with an initial oxygen concentration of 1.3 ppm, a final concentration of 14.8 ppm and a sodium flow rate of 0.35 gpm. The line through the data points is that predicted by the theoretical model^{2,3} with the mass transfer coefficient, $k = 6.4 \times 10^{-6} \text{ g O/cm}^2\text{-h-ppm}$. This value is 25% lower than the values obtained with the 1.0 gpm dissolution runs. The flow velocity (or Reynolds number) seems to have an effect on the dissolution coefficient; therefore, the dissolution process is probably diffusion rate limited. The mass transfer coefficient for precipitation is also affected by sodium velocity, and it is, therefore, also diffusion limited. These observations imply that the dissolution and precipitation coefficients should be equal at the same temperature and flow conditions. Further experimental work is necessary to determine accurately the flow dependence and temperature dependence of the mass transfer coefficients.

Run 1-17 (Fig. 4) was a precipitation run in which the initial oxygen concentration was 14.8 ppm, the final concentration was 1.4 ppm and the sodium flow rate was 0.5 gpm. No change in oxygen concentration was observed until about one third of a "system turnover" had taken place. The curve represents the theoretical prediction with a mass

Fig. 3. Transient oxygen concentration data from dissolution Run 1-16. Mass transfer coefficient for run = 6.35×10^{-6} g O/(cm²-h-ppm).
 C = oxygen concentration in sodium held in system storage tank, ppm;
 C_e = oxygen concentration in sodium in equilibrium with Na₂O at coldest temperature in cold trap, ppm; C_0 = initial oxygen concentration of sodium in system storage tank, ppm; M = sodium in system, lbs; t = time of run, h; W = flow rate, lb/h.

transfer coefficient, k of 72×10^{-6} g O/cm²-h-ppm; this is a factor of six higher than the values calculated from previous, similar runs. The lower values found earlier could have been caused by oxide breakaway in the cold trap during the runs, or by an oxygen source such as air introduction during sampling or oxygen release from stainless steel walls. Because of these uncertainties in the transfer coefficients, a new series of cold trap runs have been initiated. The oscillating plugging indicator will be utilized as a continuous oxygen concentration monitor during these experiments. The series of tests will determine the effect of Reynolds number at constant temperature, and the effect of temperature at constant Reynolds number on the mass transfer coefficients.

Fig. 4. Transient oxygen concentration data from precipitation Run 1-17. Mass transfer coefficient for run = 72.0×10^{-6} g O/(cm²-h-ppm).

b. Na₂O Cold Trap Design

Firm plans have been made for installation of a flexible "cold trap testing station" on the cold trap loop. The unit is now being designed. The testing station will consist of a fixed outer tube into which NaK-cooled inserts, or trap sections, are placed. Varying the size and geometry of the insert will permit the effect of a wide range of sodium velocities and flow characteristics to be studied. Packing can be placed in the annulus between the insert and the outer tube to study the effects of extended surface area.

A vacuum chamber will be installed above the cold trap for insert removal and examination. Radio frequency heating will evaporate residual sodium so that axial distribution of the remaining residue can be directly observed. Identification of the residues can be made by standard techniques of chemical and x-ray diffraction analysis.

c. Behavior of UNC Oxygen Meters Utilized on Cold Trap Loop

The electrochemical liquid metal oxygen meters developed by United Nuclear Corporation have a great potential value in measuring the rate of change of oxygen concentration during cold trapping runs. Five of these meters have been used in the cold trap testing program. During their first two months in service, their response to changes in oxygen concentration has been in agreement with that theoretically predicted. After about two months, however, a response lag was observed. This response lag is illustrated in Fig. 5, where the log of the oxygen concentration, as determined by the oscillating plugging indicator, is plotted versus the oxygen meter emf. (Distillation analyses made during the concentration transient were in excellent agreement with the plugging meter readings.) A straight line

Fig. 5. Hysteresis effect of oxygen meter TP-186. The arrows indicate the direction of the changes with time. The starting concentration was 1.3 ppm oxygen.

connecting the two extremes of the hysteresis loop (Fig. 5.) would agree well with the theoretical slope of the oxygen meter calibration curve; i.e., the oxygen meter calibration was essentially theoretical, but response to concentration changes was sluggish.

The response lag cannot be explained in terms of an inhibiting impurity in the sodium because, in three separate instances, installation of new oxygen meters resulted in restoration of theoretical and rapid response to oxygen concentration changes. The fast response of the new meters then also deteriorated after six to eight weeks.

d. Computer Simulation of Cold Trap Dynamics

Two computer programs were written during the year to help analyze cold trap rate data. The first program simulated the whole system by following an element of fluid about the system. Slug flow and uniform oxygen concentrations were assumed in the element of fluid. In the cold trap, oxygen was transferred into and out of the element to the cold trap wall by assuming the rate of transfer to be the product of surface area concentration difference between the fluid element and the fluid in equilibrium with the wall, and a mass transfer coefficient. The coefficient was assumed to be constant in the cold trap and to be equal for dissolution and precipitation. The constant was adjusted until the overall experimental transient concentration curve was reproduced. The computer program took into account delay times in pipes, partial mixing in the supply tank, and precipitation and redissolution of the oxide on the walls of the cold trap.

The second program was a two-dimensional finite difference simulation which calculated both radial and longitudinal concentration profiles within the annular portion of the cold trap. This program has given insight into the flow and mass transfer processes occurring within the cold trap being studied. By solving the continuity equation to obtain concentration profiles in both the radial and longitudinal direction, mass transfer coefficients were computed from the overall calculated oxygen transfer and the average concentration difference as determined from the computed profiles. Run No. 4 was simulated with this program, and the results indicated that there must be considerable fluid cross-flow in the radial direction. The Reynolds number at 1 gpm was less than 1000 and in the laminar flow range. However, to obtain a match between observed and calculated mass transfer coefficients the radial diffusivity had to be increased arbitrarily by a factor of 70. This "adjustment factor" decreased to about 10 in

the 0.1 gpm runs. The radial flow probably resulted from the nonsymmetrical introduction of the sodium to the annular space. As indicated by the above factors, the cross flow or radial eddy effect became more pronounced as the velocity was increased.

The program was also used to study the effect of velocity on mass transfer coefficients in the laminar flow range. The program indicated that the velocity effect was small; it appears that the mass transfer coefficient is proportional to the 0.1 - 0.15 power of the fluid velocity in the trap.

e. Summary of Results in FY 1968

A total of seventeen precipitation and dissolution cold trapping runs were completed in the test loop during the 1968 fiscal year. The precipitation runs covered a range of temperatures from 115°C up to 186°C, and the dissolution runs were performed at 213, 219, and 233°C. Precipitation runs were performed with sodium flow rates ranging from 0.1 gpm (0.12 cm/sec) to 100 gpm (1.2 cm/sec); dissolution runs were made at 1.0 gpm and 0.35 gpm flow rates. The results and conditions of all the runs completed to date are summarized in Table II.

Table II
Summary of Cold Trap Operating Parameters and Results
Cold Trap Number 1

Run No.	Min. Cold Trap Temperature (°C)	Na Flow Rate (gpm)	Initial Oxygen Concentration (ppm)	Final Oxygen Concentration (ppm)	Mass Transfer Coefficient (g/cm ² -h-ppm) x 10 ⁶
1-2	213	1.05	4.0	16.8	8.4
1-4	180	1.0	41	5.7	27.6
1-6	186	0.95	42	6.9	28.4
1-7	180	0.25	58	5.7	4.48
1-8	142	0.5	42	2.2	14.3
1-9	160	0.5	48	3.3	16.6
1-10	171	0.1	43	4.4	1.26
1-11	196	0.1	46	9.1	1.23
1-12	146	0.1	50	2.3	1.35
1-13	195	0.25	47	8.8	2.67
1-14	233	1.0	29	3.0	10.6
1-15	157	1.0	13.6	1.3	16.7
1-16	218	0.35	1.3	14.8	6.37
1-17	115	0.5	14.8	1.4	72.0

The results obtained during this fiscal year indicated that two important conclusions may be made. The mass transfer coefficient is a function of velocity of sodium in the cold trap. For laminar flow the coefficient increases with increasing velocity approximately as the square root of the Reynolds number. This velocity dependence indicates that the process is diffusion rate limited. The second

important observation is that the mass transfer coefficient is temperature dependent. The coefficient increases with increasing sodium temperature. Arrhenius plots indicate that the activation energy for mass transfer was approximately 3 kcal/mole. This value agrees well with the activation energy for diffusion of oxygen in sodium which is further evidence of a diffusion controlled process.

Mass transfer coefficients for Na₂O for deposition on a plugging indicator orifice were calculated to determine values at high sodium velocities. The coefficients determined at high velocities were much greater than those determined at cold trap velocities. At sodium velocities of 100 to 500 cm/sec, the mass transfer coefficients were a factor of 10³ greater than that determined with the cold trap experiments at a velocity of 1.2 cm/sec.

The trend of increased mass transfer coefficients with increased sodium velocity has led to design of an experimental cold trap capable of operating at high sodium velocities. Increasing the sodium velocity causes problems in designing the cold trap precipitation zone and the heat transfer regions. Small cross sections are favorable for high velocities and good heat transfer; however, large cross sectional areas are required for large oxide holding capacity. The experimental cold trap will compromise the oxide holding capacity in order to achieve the high velocities.

B. Study of Oxygen, Carbon, and Nitrogen Removal with Soluble Getters (V. J. Rutkauskas, G. E. Meadows, L. A. Waldschmidt)

1. General

For large sodium-cooled reactor systems, it may be desirable to use soluble getters for control of oxygen and other dissolved impurities in lieu of the more conventional hot and cold trapping techniques. The soluble (calcium and barium) getters of interest occur in the sodium coolant either naturally, or are produced during reactor operation (as with metal magnesium). The techniques for the controlled additions of these getters, maintenance of fixed getter levels, and the selective removal of depleted getter metals and other impurities from dynamic sodium systems must be developed if their usefulness is to be evaluated; and the significant chemical reactions occurring in a sodium system containing

these soluble getters must be understood and controlled. This mode of purity control has the potential for effectively controlling not only oxygen, but also carbon, hydrogen, nitrogen, and possibly metallic impurities.

2. Results During FY 1968

Assembly of the mechanical portion of the Analytical Loop No. 2 experimental facility which will be used for solution gettering studies and for development and evaluation of prototype analytical instrumentation is approximately 80% completed. The instrumentation and control circuitry associated with the completed elements of the system has been installed. Analytical procedures are being investigated to determine trace quantities of Ca and Mg metal in bulk sodium samples using the atomic-absorption spectrophotometric analytical procedures. (See Section V and Project 808, Section X.)

IV. STUDY OF FISSION PRODUCT BEHAVIOR IN SODIUM

A. Transport and Distribution of Fission Products in Flowing Sodium (J. C. Clifford)

1. General

The behavior of radioactivity released to sodium from failed or vented fuel elements may limit access to portions of the primary coolant system and may affect the consequences of a loss-of-coolant incident. Depending on the fission-product release fraction anticipated in either circumstance, it may be desirable to scavenge these species (as well as uranium and plutonium) from the coolant.

The immediate goals of this investigation are: (1) to identify sodium-soluble fission-product species and (2) to examine the effects of primary-coolant-system construction materials, design features, and operating conditions on these species.

2. Results in FY 1968

Studies of the distribution of long-lived fission products in sodium have been continued with major emphasis on ^{137}Cs .

a. Natural Convection Cold Trap Loop

A 4300-h experiment in which activity was released from plutonium-based fuel in a small forced-convection sodium loop containing a natural convection cold trap³ has been terminated. (The trap

previously has been referred to as a diffusion cold trap, but rate data for ^{137}Cs indicate that convective transport is the controlling mechanism in the trap.) In Table III the distribution of ^{137}Cs in this loop after 2300 h of operation is compared with the distribution determined during an earlier experiment in the same loop (after 2800 h). The earlier experiment utilized a full flow cold trap of approximately the same effective volume as the natural flow trap and the same type fuel⁴ as the source of activity. During the period of interest in the two experiments the loop hot leg temperature was approximately 500°C, the cold leg temperature was approximately 300°C and the cold traps operated in the range 110 to 175°C.

Table III

Comparison of ^{137}Cs Distribution in Two Cold Trapped Sodium Systems with Comparable Temperature Distribution

Location	^{137}Cs Activity (mCi)	
	Full Flow Cold Trap Experiment	Natural Convection Cold Trap Experiment
Loop Sodium	1.4	2.1
Cold Trap	1.1	1.3
Stainless Steel Surfaces	0.5	0.6
TOTAL*	3.0	4.0

* ^{137}Cs content of the fuel is estimated to have been 3.4 mCi in the full flow experiment and 4.5 to 9 mCi in the natural convection experiment. The latter values represent a considerable decrease from that reported earlier in LA-3820-MS;³ figures given in that report were wrong because of an error in the estimate of specific power and from segregation of ^{137}Cs in the fuel.

The sodium inventory was approximately the same in both cases, while the fission product inventory was a factor of 2 higher in the fuel for the natural circulation trap experiment. Although the rate at which ^{137}Cs accumulated in the cold trap during the two experiments was significantly different, the activity distributions, as determined by gamma scanning and by destructive analyses of traps, are similar enough to suggest that equilibrium was approached in both experiments.

After 2300 to 2500 h, approximately one-third of the ^{137}Cs was found in each cold trap, one-half was associated with the flowing sodium, and the

remainder was distributed around the system on stainless steel surfaces.

In addition to indicating the general distribution of ^{137}Cs , the natural convection cold trap experiment was intended to determine qualitatively whether oxygen in a sodium system influenced this distribution. The experiment consisted of: (1) establishing a ^{137}Cs equilibrium in a low oxygen system, (2) adding a large amount of NaOH to the system in an attempt to upset this equilibrium, and (3) adding zirconium foil to the high temperature section of the loop to remove oxygen from the cold trap and observing ^{137}Cs redistribution. The addition of 100 ppm oxygen to the system had a detectable, but trivial effect on the amount of ^{137}Cs in the cold trap; there was a slight loss of ^{137}Cs from the trap after the addition. The relative distribution of activity within the trap did not change, within the precision of the measurements. The addition of the zirconium hot trap resulted in an increase in cold trap cesium activity, but no change in relative distribution of cesium within the trap. The net result of the experiment, over a 4300 h period, was that the final ^{137}Cs inventory could have been predicted from rate data obtained before any oxygen additions or removals were made. Two conclusions appear possible. Either (1) oxygen has no effect on ^{137}Cs distribution, or (2) the majority of the oxygen added to the system was absorbed on loop surfaces and very little reached the trap. The experiment is being repeated using larger oxygen additions.

After completion of the oxygen addition experiment, the natural circulation cold trap loop was used for a preliminary study of adsorption of ^{137}Cs on stainless steel surfaces. Specimens of "as received" and heavily oxidized Type 347 stainless steel, in the form of 2 mil-thick strips, were rolled into bundles and immersed in 225°C sodium containing ^{137}Cs . Spacing between foil layers was provided by winding corrugated and flat sheet together in each bundle. An initial ^{137}Cs concentration of approximately 3 $\mu\text{Ci/g}$ of sodium was provided by dissolving carrier free $^{137}\text{CsCl}$ in sodium at 500°C.

Results from this experiment showed considerable scatter because of several temperature fluctuations in the test section during the 1600 h duration of the test. In general, though, the presence of a

heavily oxidized surface appears to inhibit ^{137}Cs absorption and to alter, slightly, the equilibrium partition of activity between the stainless surfaces and sodium. There is some evidence to suggest that the rate of deposition and the initial distribution of cesium also are affected by flow rate. Cesium activity added to sodium as the chloride appears to behave in the same manner as cesium extracted from the metal fuel by sodium.

b. ^{137}Cs Adsorption Loop

The natural circulation cold trap loop is not suitable for additional cesium adsorption experiments because of difficulty in controlling temperatures at low sodium flow rates and because of flow distortions in the sample test section. The experiments are being transferred to another loop which was put in operation recently (Fig. 6). In this system, sodium containing trace amounts of ^{137}Cs (1-10 $\mu\text{Ci/g}$) flows

Fig. 6. Sodium loop for ^{137}Cs adsorption experiments.

up through a 2-in.-diameter test column containing the absorbers (coils of metal foil fastened on a stringer). The column can be scanned with a NaI(Tl) detector and single channel analyzer to determine the distribution of activity. After leaving the test section, sodium passes through an expansion tank, a pump, a flowmeter, and a resistance heater.

A cold trap on a bypass line provides oxygen control for the loop. The main flow circuit is approximately isothermal (the test column is isothermal) and can be operated in the range 125-600°C. Initially, the loop will be used to study the effects of temperature on the deposition of ^{137}Cs onto Type 316 stainless steel, nickel, zirconium, and mild steel. A charge of ^{137}Cs has been added to the loop in preparation for the first experiment, which will be started after modifications to a shielded, 3 x 3 in. NaI scanning system have been completed.

c. Trace Irradiated Fuel Loop

Another small, forced-convection sodium loop, whose principal sections can be scanned for gamma-emitting isotopes,² has been completed and is operating satisfactorily. The loop will be used to study the release and distribution of fission products ($\tau \geq 8$ d) from trace-irradiated plutonium-containing fuels. Mechanical, electronic, and vacuum difficulties with gamma scanning equipment were encountered and have been resolved, but Ge(Li) detector problems continue. When a 40 cc Ge(Li) detector and accessories are delivered the scanning system should become operable. In the meantime, the sodium loop is being prepared for a short experiment to examine the attrition of unirradiated (U,Pu)O₂ particles in flowing sodium. Materials for this experiment are on hand.

B. Study of Transport and Distribution of Fission Products in Capsule Experiments with Single Isotopes (L. A. Geoffrion, J. M. Williams, J. C. Biery)

1. General

Capsule experiments have been designed to determine the distribution of gamma-active isotopes in the sodium/stainless steel/helium/adsorber system as a function of time and temperature. Gamma-ray scanning permits a study of transport rates, adsorption and desorption phenomena, and the equilibrium distribution between phases to be made. The isotope ^{137}Cs is the first radioisotope to be studied in these experiments because it is a major fission product released from irradiated nuclear fuels, and its long (27.7-yr) half-life simplifies measurements. Other candidates for study, using these experimental techniques, are ^{131}I and ^{140}Ba - ^{140}La .

Observations of the approach to equilibrium as a plane ^{137}Cs source diffuses into a cylindrical column of sodium permits estimates of transport and adsorption rates, distribution coefficients, and diffusion coefficients. Since this method of measurement allows a total mass balance over the system, it is possible to determine these parameters quantitatively.

2. Results During FY 1968

Experiments were run with two capsules made from 1-in.-diam Type 304 stainless steel tubing. Planchets containing 1 mCi of $^{137}\text{CsCl}$ were placed in the bottom of the capsules, and redistribution of gamma activity was followed with a gamma scanner as the capsules were subjected to varying thermal conditions. The capsule for experiment No. 1 was 8-in. long and contained 4.9 in. of sodium; that for experiment No. 2 was 12-in. long and contained 6 in. of sodium. Oxygen concentration in the sodium was less than 10 ppm.

The gamma scanning system consisted of a shielded NaI detector behind a 0.050 x 1.00 in. collimating slit. The position of the capsule-furnace assembly in front was varied to yield axial and diametrical scans. The slit was oriented with the 0.050 in. dimension perpendicular to the scanning direction.

Data from the two experiments indicate some of the characteristics of cesium behavior in a low oxygen sodium-stainless steel system. Table IV summarizes observations. From the data in Table IV, these conclusion may be drawn:

a. CsCl dissolution into sodium is slow at 200°C, but increases 25-30 fold when the temperature is raised to 300°C. The initial rate of dissolution from the planchet at 200°C (first 40 h) was 1.1×10^{-8} g Cs/cm²-h, but about 500 h later, the rate had decreased to 0.07×10^{-8} g Cs/cm²-h. If this is a reaction-limited process, the activation energy for the dissolution step is about 27 kcal/mole.

b. In isothermal systems above 150°C, the cesium does not segregate appreciably on the walls. Segregation of some cesium to the bottom of the capsule was observed only when the temperature was reduced to 120°C. Even at this temperature the remaining cesium appeared to be dissolved in the sodium with no adsorption on the walls.

Table IV
Summary of Experimental Data

Capsule	Temperature-°C			Time Hours After Temperature Change	% Cs Dissolved	% Cs on Planchet	% Cs in Bulk Sodium and on Walls	% Cs at g/l Interface	% Cs at Top of Capsule	Segregation to Side Walls
	Bottom	gas/liquid Interface	Top							
1 in. x 8 in.	200	200	200	200	74	26	72	1.6	0	No
	500	500	500	2½	99.75	0.25	99.50	0.25	0	No
				141	99.50	0.50	99.1	0.44	0	No
Capsule (Experiment No. 1)	300	475	500	293	99.2	0.77	99.2	~0	0	No
	500	385	235	328	97.4	2.6	92.8	1.8	2.8	Yes
4.9 in. of Sodium	500	500	500	2	99.5	0.5	99.0	0.5	0.05	No
	400	400	400	141	99.3	0.7	98.9	0.4	0	No
	300	300	300	72	99.3	0.7	99.1	0.2	0	No
	200	200	200	66	99.4	0.6	99.4	~0	0	No
	120	120	120	93	99.5	0.5	99.5	~0	0	No
	25	25	25	90	96.3	3.7	96.3	~0	0	No
					95.5	4.5	94.6	0.9	0	No
1 in. x 12 in.	200	200	200	5	2	98			0	No
				48	20	80			0	No
				148	49	51			0	No
Capsule (Experiment No. 2)				240	63	37			0	No
				312	70	30		1.4	0	No
6 in. of Sodium				408	74	26		1.8	0	No
				527	77	23			0	No
	300	300	300	2	91	9			0	No
				23	94	6			0	No
				124	98.8	1.2	97.4	1.4	0	No
				262	99.0	1.0	97.6	1.4	0	No
	400	400	400	191	99.4	0.6	98.5	0.9	0	No
	500	500	500	239	99.5	0.5	98.8	0.7	0	No
	500	340	120							Yes
				51	97.7	2.3	93.1	2.5	2.1	Yes
				189	98.3	1.7	91.0	2.1	5.2	Yes
	500	500	500	23	99.3	0.7	98.0	1.3	0	No
	505	375	255	72	98.4	1.6	95.7	2.3	0.4	Yes
				165	98.0	2.0	94.9	2.5	0.6	Yes
	500	500	500	88	98.6	1.4	97.5	1.1	0	No
				166	99.3	0.7	97.8	1.5	0	No
	503	410	383	63-641	98.6	1.4	96.6	1.9	0.1	Yes

c. The behavior of the cesium in the presence of a temperature gradient depended on the direction of the gradient. A uniform distribution of cesium

persisted as long as the bottom of the capsule was cool and the gas filled region at the top was hot. When the gradient was reversed, cesium segregation

to the gas/liquid interface, and to the top of the capsule occurred; there was also a small concentrating effect at the bottom of the capsule. Radial scans also indicated that significant quantities of cesium segregated to the stainless steel walls. The movement to the top of the capsule and the interface was accentuated with increased gradients. Up to 5% of the cesium segregated to the top with a temperature gradient of 39°C/in. in the gas space and the top at 120°C.

d. The cesium redistributed quickly and reversibly when the system was returned from the "top-cold" temperature gradient condition to an isothermal state.

e. The segregation of ^{137}Cs at the gas/liquid interface and at the top of the capsule appear to be associated with the phenomenon of impurity adsorption at liquid interfaces. (General thermodynamics arguments would predict that impurities should be found at such interfaces, where their effect on the surface tension lowers the energy of the system.) From the data of Experiment No. 2, the percentage of ^{137}Cs adsorbed at the liquid-gas interface can be linearly correlated with the surface tension of sodium at the temperature in the interface region. As the temperature of the interface decreased, the surface tension and the impurity concentration (adsorbed ^{137}Cs) increased. The observed constant of proportionality between ^{137}Cs adsorption and surface tension is, over the range of surface tensions from 160-200 dyn/cm, 3×10^{-5} (system Cs)/dyn/cm or 9×10^{-10} (g $^{137}\text{Cs}/\text{cm}^2$)/(dyn/cm). The slope of the adsorption curve for the top of the capsule showed a similar surface tension dependence. The movement of ^{137}Cs up to the top of the capsule under temperature gradient (top cool) conditions may indicate that the top was at least partially wet with sodium while it was dry under isothermal, or "top-hot," conditions.

f. At 120°C, the large percentage of segregation of ^{137}Cs to the top of the capsule under temperature gradient conditions, and to the bottom of the capsule under isothermal conditions, cannot be explained by surface tension phenomena alone. Since the saturation temperature for Na_2O in these capsules was probably between 120 and 150°C, the observed segregation under these conditions may

have been associated with the precipitation of Na_2O .

g. At 500°C, 5×10^{-9} g $^{137}\text{Cs}/\text{cm}^2$ adsorbed on the stainless steel at the bottom of the capsule. Under temperature gradient conditions with the bottom still at 500°C, the segregated ^{137}Cs at the bottom increased by a factor of 3 to 4. A corresponding increase was noted on all capsule surfaces below the liquid surface. No explanation for this is apparent.

C. Study of Transport and Distribution of Fission Products in Capsule Experiments with Irradiated Fuel (J. C. Biery, C. R. Cushing)

1. General

Rupture of nuclear reactor fuel elements containing ceramic Pu-U pellets could allow fission products to be leached from the pellets by the sodium coolant. The release rates of these fission products should be known to evaluate contamination problems in the sodium system. Fission products mass transfer rates from U-Pu ceramic fuel pellets to sodium as a function of temperature, sodium conditions, and pellet composition are being studied.

In a typical experiment the neutron irradiated pellet is enclosed with 3 to 10 in. of sodium in a 12-in. long capsule. The distribution of fission products as a function of time and position in the capsule is determined by gamma scanning the capsule. The temperatures for such experiments range from 650 to 900°C. Isothermal conditions or longitudinal temperature gradients up to 25°C/in. may be used.

2. Results During FY 1968

An experiment designed to study fission product mass transfer from an irradiated (U,Pu)C pellet into sodium was started in December 1967. A 0.260-in.-diam x 0.244-in. long pellet was irradiated in the Omega West Reactor (6.7×10^{16} fissions in sample, yielding 3.5×10^{15} atoms of ^{137}Cs). The pellet was placed in contact with a 7-in. column of sodium in a 0.430-in.-diam Type 304 stainless steel tube. The temperature at the pellet was 800°C, and at the top of the sodium column it was 700°C. The oxygen concentration initially in the sodium was less than 10 ppm.

Counts of the pellet and of the sodium 3 in. above the pellet were made 10 and 11 days after

startup. The slit size on the scanner was $\frac{1}{2}$ in. high by $\frac{3}{4}$ in. wide. Measurable amounts of ^{131}I , ^{137}Cs , ^{140}Ba - ^{140}La were detected in the sodium. After 11 days, 1.4% to 2.9% of the total inventory of these isotopes had transferred to the sodium. No detectable quantities of ^{95}Zr , ^{95}Nb , and ^{103}Ru were found in the liquid phase.

No additional scans of the capsule could be made because of difficulties with the solid-state detector system. However, the pellet and capsule were held at temperature for a total of 95 days (2280 h). After termination of the experiment the cooled capsule was scanned with a second germanium crystal system. After scanning, the pellet-containing section of the capsule was cut off, the sodium was melted out, and the capsule was rescanned. The results of the scans were as follows:

Percent of ^{137}Cs extracted into sodium: 2.9%

Percent of extracted ^{137}Cs remaining on capsule wall after removal of sodium: 4.0%

In a previous similar experiment⁵ the fission product transfer appeared to be limited by solid-state diffusion in the pellet. In that experiment the temperature ranged from 800 to 650°C over a period of 1500 h; only 0.03% of the ^{137}Cs was extracted. A diffusion coefficient of 3.3×10^{-17} cm²/sec was calculated for the ^{137}Cs . This value appears reasonable when compared with previously determined coefficients for fission product diffusion in UO_2 pellets.

The ^{137}Cs transfer in the most recent experiment was two orders of magnitude greater than that experienced in the previous experiment; and the transfer did not appear, at least initially, to be solid-state diffusion controlled. For instance, the diffusion coefficient calculated for the transfer measured in the current experiment was 2.5×10^{-13} cm²/sec, a value larger by 10^4 than seems reasonable; the penetration thickness was 57 μ .

Three possible explanations of the atypically rapid release of ^{137}Cs in the recent experiment are: (1) Sodium has been observed to penetrate into carbide pellets. If the pellet were sodium logged, fission product release would be greatly enhanced by the increased sodium-solid phase surface area and the possibility for liquid phase diffusion to occur. (2) The pellet may have developed microcracks

which would allow greater sodium-solid contact.

(3) The pellet was exposed to air for short periods before it was loaded into the capsule; and, although the pellet appeared unaffected, surface oxygen attack may have enhanced release of fission products. The fact that the quantity of ^{137}Cs extracted into the sodium did not increase appreciably after 11 days tends to support the third hypothesis.

Very little ^{137}Cs adsorbed onto the walls of the Type 304 stainless steel capsule during the experiment. As indicated above, the post-scan showed 4% of the extracted ^{137}Cs remaining on the walls after the sodium was melted out. A portion of this quantity of ^{137}Cs was probably dissolved in the residual sodium still attached to the capsule walls and may not actually have been adsorbed on the capsule walls.

V. STUDY OF NONRADIOACTIVE IMPURITY SAMPLING AND ANALYSIS METHODS

A. Plugging Indicators Studies (C. C. McPheeters, J. C. Biery)

1. General

Plugging meters have been used on sodium systems for many years. They are relatively simple to design, install, and operate; however, the meaning of the data obtained from these instruments has not always been clear, and as a result, the value of the instrument has sometimes been questioned. The work reported below indicates that the plugging meter is a valuable instrument and that it can be used with confidence. Three areas of investigation are covered:

- Studies of the bare orifice meter.
- Observations of the operating characteristics of the oscillating plugging meter.
- Determination of mass transfer coefficients from plugging meter data.

2. Results During FY 1968

a. The Bare Orifice Meter

The plugging meter orifice assembly which was used in these studies is shown in Fig. 7. It is a regenerative type of plugging indicator in which the sodium flows down the center tube and loses heat to the sodium flowing up the outside annulus. The plugging meter is cooled by blowing air around the outside annulus. Auxiliary heating is provided by electrical units on the outside of the meter. Four orifices are situated at the bottom of the inner tube; each is 0.132-cm-diam. Sodium velocities through the orifice can be varied from 50 to 500 cm/sec.

Figure 8 shows data from a typical type of plugging run. Initially the orifice is bare, (i.e., free from sodium oxide deposits), and the temperature of the sodium is well above the sodium oxide saturation temperature. The run is started by cooling the sodium until a temperature below the saturation temperature is reached; nucleation and precipitation of sodium oxide then occur on the orifice. At this temperature, or often at some lower temperature, a decrease in sodium flow can be detected. The temperature at which flow reduction occurs is usually taken to be the normal plugging temperature. The meaning of this temperature and its relationship to the

Fig. 7. Cross section view of plugging indicator orifice assembly.

Fig. 8. Normal plugging run with decreasing sodium temperature and a bare orifice.

saturation temperature is the question that has to be considered with this mode of plugging indicator operation.

The effect of three parameters -- sodium velocity,

concentration differentials, and cooling rates -- on nucleation times and temperature depression are indicated in Figs. 9 and 10.

Fig. 9. Effect of velocity on nucleation time.

Fig. 10. Effect of cooling rate on plugging temperature in a bare orifice meter T_s saturation temperature.

In Fig. 9 the time required for nucleation to occur (at constant concentration differentials) is

indicated as a function of sodium velocity. For all concentration differentials, higher velocities produced shorter times to nucleation in this particular meter. Similar velocity effects have been observed by Russian workers.⁶ Figure 9 indicates that at 1-2 ppm differentials, very long times are required for the initial nucleation and precipitation of sodium oxide on the orifice.

The apparent value of the plugging temperature is influenced by the rate at which the sodium is cooled below the saturated temperature. Figure 10 illustrates this effect. At faster cooling rates, shorter times are required to achieve large ΔC concentration differentials before nucleation is initiated. Reproducible plugging temperature may be obtained with the bare orifice meter only if the cooling rates and the flow rates are carefully controlled and monitored.

As in the meter described here, it is common to place an auxiliary throttling valve upstream of the plugging meter orifice. If the system is operated so that there is substantial throttling by the auxiliary valve the sensitivity of the plugging meter (the percentage reduction in flow produced by a given amount of deposit on the meter orifice) is sharply reduced. Such effects are troublesome when plugging meter data are used for the determination of precipitation rate constants. The effect of auxiliary throttling is indicated in Fig. 11.

Fig. 11. Effect of throttling on sensitivity of plugging meter. These values are calculated by assuming the orifice coefficients remain constant.

Though the several parameters which affect the indicated plugging temperature in a bare orifice meter may be identified and controlled, each meter must be calibrated before it can be used as an indicator of oxide concentrations in sodium. Such calibration, done at controlled, known cooling rates and flow rates which will be adopted for all subsequent use of the meter, serves to eliminate errors in oxide analysis produced by uncertainty in the nucleation temperature, and in the relation between the nucleation temperature and the actual equilibrium value of the saturation temperature. Calibration data for the bare orifice meter of Fig. 7 are presented in Fig. 12. The oxide concentrations were

Fig. 12. Calibration curve for bare orifice plugging meter. The LASL curve was determined by V. J. Rutkauskas.⁷

determined by vacuum distillation analysis of sodium. Spread in the data are larger than the statistical variation characteristic of the distillation method because the flow and cooling rate control during the calibration were not optimum. However, the curve shows that such a meter will yield a plugging temperature which is typically 20-30°C lower than the equilibrium saturation temperature of the sodium.

b. Operating Characteristics of the Oscillating Plugging Meter

Many bare orifice meter problems can be minimized or eliminated if the meter is operated in the partially plugged mode. The French indicated in 1963⁸ and the British in 1966⁹ that the partially

plugged mode of operation gave satisfactory results on systems running with cold trap temperatures as low as 110-125°C. The work reported here verifies these results and indicates that a simple oscillating mode of meter operation can yield an unambiguous determination of the equilibrium saturation temperature. In this mode, a partial plug is first formed on the orifice, and the sodium flow is then adjusted to a preselected value. The partial plug is not stable, however, and may either dissolve away, or continue to grow. If it grows, the flow will decrease; the flow control device corrects this deviation from the set point by shutting off the meter cooling so that the partial plug begins to dissolve. When flow increases because of dissolution of the sodium oxide plug and goes above the preset value the control circuit reactivates the cooling system. In this way an oscillating flow pattern is generated, and an oscillating temperature pattern results in the plugging meter. At the maxima and minima in the flow rate, the dissolution and precipitation rates are in equilibrium and by definition these are equilibrium values of the saturation temperatures for the particular sodium oxide concentration in the sodium.

In order to study the oscillating mode of plugging meter operation, the bare orifice meter (Fig. 7) was modified for oscillating operation by the addition of a simple flow control circuit to the system. (A high-low limit switch on the flow recorder was used to start and stop the fan which circulated an air stream on the plugging meter.) Typical flow and temperature records obtained with the oscillating meter (at a plugging temperature of 217°C) are shown in Fig. 13. Flow reversals occur at 216 to 218°C; the equilibrium temperature, is, therefore, determined with a sensitivity of $\pm 1^\circ\text{C}$ in a single cycle. The standard deviation of the equilibrium temperature obtained by averaging over several cycles is less than $\pm 1^\circ\text{C}$.

The period of oscillation is determined by the kinetics of the precipitation-dissolution reactions, and by the type of crystal precipitated on the orifice. For instance, after long-term exposure and recrystallization of the plug, there appears to be a decrease in the rates of mass transfer, and readings are obtained at less frequent intervals. Temperature maxima and minima remain the same, however,

Fig. 13. Oscillating meter temperature and flow for sodium with a 117°C Na₂O equilibrium temperature.

if there is only one impurity in the system.

With a second impurity in the system, there is a possibility the initial plug will slowly convert to the impurity having the higher saturation temperature. In the system operated at Los Alamos, there were apparently two species of precipitate: a sodium oxide plug seemed to form first; then after 4-5 h of operation the plug appeared to convert to a second type of precipitate, possibly sodium hydride. The equilibrium temperature in this case increased from 220°C to about 240°C. Once the second precipitate is formed the saturation temperature of the first precipitate cannot be subsequently monitored unless the plug is dissolved and a new precipitate is formed.

In Fig. 14 an oscillating run at a saturation temperature of 108°C is shown. The initial, partial plug cannot be generated at this temperature; it must be formed at an oxygen concentration typical of higher saturation temperatures and then be maintained while the oxide concentration and temperature of the system are gradually reduced. The kinetics of the plug at this low concentration (~ 1 ppm at 108°C saturation temperature) are much slower than at higher concentrations; thus readings of the equilibrium temperature are produced less frequently. The

Fig. 14. Oscillating meter temperature and flow for sodium with a 108°C Na₂O equilibrium temperature.

oscillatory form of the flow curve is not readily observed under these conditions, but flow does vary sufficiently for adequate temperature control about the 108°C point. Readings range in a $\pm 5^\circ\text{C}$ band and the standard deviation of the mean over 10 consecutive readings is about $\pm 1^\circ\text{C}$.

In summary, operating a plugging meter in the oscillating mode facilitates making precise, determinations of the temperature at which the dissolution and precipitation of sodium oxide in sodium are in equilibrium. Oxide concentration can then be obtained from standard solubility data; no meter calibration is necessary.

c. Mass Transfer Coefficients from Plugging Meter Data

Rate constants for precipitation of sodium oxide can be calculated by postulating a precipitation mode and some model for actual growth of the oxide on the orifice. The model for the following equations is based on the assumption that sodium oxide grows inward in a cylindrical layer from the inside of the orifice surface. The rate of deposition or dissolution of sodium oxide is indicated by Eq. 1.

$$\frac{dm}{dt} = kS(C - C_e) \quad (1)$$

where S is the surface area of the orifice, k is a

mass transfer coefficient, C is the concentration of the sodium coming into the orifice and C_e is the concentration of oxygen in the sodium in equilibrium with the orifice at its operating temperature. The mass of oxide on the orifice is associated with the fraction of the plug as indicated in Eq. 2.

$$\text{Plug fraction} = P_F = \frac{m}{A_o \ell \rho} \quad (2)$$

In Eq. 2, m is the mass of Na_2O precipitated on the orifice plate, ρ is its density, ℓ is the thickness of the orifice plate, and A_o is the cross-sectional area of the bare orifice. By differentiating Eq. 2 and substituting into Eq. 1, Eq. 3 results;

$$\frac{dP_F}{dt} = \frac{2k}{r_o \rho} \left(\frac{r}{r_o} \right) (C - C_e) \quad (3)$$

In this expression, r_o is the radius of the bare orifice, and r is that of the partially plugged orifice. The (r/r_o) term is also associated with the fraction of plug as indicated in Eq. 4.

$$\frac{r}{r_o} = (1 - P_F)^{1/2} \quad (4)$$

Substitution of Eq. 4 into Eq. 3, separation of the variables, integration, and finally rearrangement to isolate k as a function of the operating variables produces Eq. 5:

$$k_i = \frac{\rho r_o \left[\left((1 - P_{F_{i-1}})^{1/2} \right)^2 - \left((1 - P_{F_i})^{1/2} \right)^2 \right]}{(C - C_e) A_{V_i} (t_i - t_{i-1})} \quad (5)$$

In this form, the equation gives the value of the precipitation rate constant in any arbitrary i th portion of a plugging run. Time, t_i , is measured from the moment at which the temperature reaches the saturation temperature. P_{F_i} is deduced from the observed flow rate through the meter, with the use of Fig. 11.

Several plugging runs have been analyzed according to this equation, using the Rutkauskas solubility curve to determine C_e .⁷ The rate constants studied vary almost linearly with sodium velocity. (An 0.8 power for the velocity dependence would be expected from correlations of mass transfer coefficients with velocity in the turbulent range.) Also, the precipitation and dissolution rate constants appear to be equal. At 400 cm/sec k values as large as 2×10^{-2} g O/cm²-h-ppm have been observed.

B. Investigation and Development of Sampling and Analytical Techniques

1. General

The study and evaluation of sampling techniques and of analytical methods has several general objectives. These are:

- To develop an in-line sampling method which can be used on large sodium systems and which does not interfere with their operation.
- To develop analytical methods which are either specific for selected impurity elements, or which, if not specific, provide for unambiguous calibration.
- To develop operational instruments which will permit continuous monitoring of impurity levels in sodium during the intervals between the more precise analytical determinations which generally are not expected to provide continuous indications of sodium quality.

The vacuum distillation method has been extensively studied and it appears that it, while not specific for the determination of oxygen in sodium, can yield reliable data when used together with appropriate in-line, dynamic sampling methods. A method which is specific for oxygen and carbon, and of adequate sensitivity, utilizes (γ, n) activation of the sodium sample to permit identification of the contained impurities. While it may provide a standard against which other analytical methods may be compared, it is not suitable for "plant" use.

At the present time, the most commonly used commercially available instrument for continuous, semi-quantitative indication of sodium purity is the electrolytic cell oxygen meters. It does not appear that all the parameters which affect its operation are yet understood.

2. Results During FY 1968

- Remotely Operated Distillation Samples for EBR-II
(W. R. Wykoff, D. N. Dunning, V. J. Rutkauskas)

At the request of the AEC, part of the effort directed to a study of in-line sampling associated with the vacuum distillation analytical method has been re-directed to the design and construction of remotely operated, integral sampling and distillation units for installation on the primary coolant loop of EBR-II. A manually operated version of the sampling system is also being developed for the non-radioactive secondary sodium system of EBR-II. The sampling system design is a modified engineering loop version of the laboratory model integral full-flow

vacuum distillation sampling system currently in use on the Analytical Loop No. 1 and cold trap experimental facilities at the LASL. The entire sampling system will be fabricated of Type 304 stainless steel, and separation of sodium from the non-volatile impurities will be accomplished by induction heating. The work coil of the induction heater is located within the metal envelope surrounding the distillation zone.

A number of commercially available components have been ordered and fabrication of the superstructure, sample cup drive member, and additional components for the pilot version of the distillation apparatus has been completed. Fabrication of additional miscellaneous components required to complete the mechanical portion of the apparatus is continuing, and a mockup of this segment of the system is being assembled. The variation in the size of the 5 g samples obtained with the Integral full-flow sampling system has been $\pm 2\%$; the integral intermittent-flow sampling technique previously used yielded 5 g batches with a $\pm 10\%$ variation.

b. Sodium Analytical Methods Facility
(V. J. Rutkauskas, K. S. Bergstresser)

A summary of the status of this work is given under Project 808, Section X, as part of a general discussion of analytical methods.

c. Gamma-Ray Activation Analyses
(D. M. Holm, V. J. Rutkauskas)

1. Sodium Handling Equipment

The sodium handling equipment which will be used in the evaluation of the gamma-ray activation analytical technique for the determination of oxygen and carbon in sodium has been completely assembled and is undergoing preliminary operational checkout. A thief tube sampler system for removing the characterized sodium samples necessary to evaluate this technique has been installed on the Analytical Loop No. 1 experimental facility. The progress of experiments during the near future will be determined by schedules in effect at the linear accelerator used as a gamma ray source.

2. Radiation Detection Equipment and Techniques

A suitable system for detection of the positron emitting activation products from the (γ, n) reaction is being assembled. Two large NaI crystals were received and installed in their 11,000 -lb lead

shield. The crystals have been tested and their operation is satisfactory. Quantitative data on the characteristics of the detector, which are needed for use of the assembly, have been obtained.

Figure 15 is a simplified drawing of the NaI

Fig. 15. Schematic of NaI assembly.

assembly. Normally, the two 6-in.-thick, 13.5-in.-diam NaI crystals are optically isolated for use in the coincidence counting mode. (They may also be operated in parallel, in which case they function as a single cylindrical detector 13.5-in. in diam and 12-in. long.) As shown in Fig. 15, there is a well, or cavity, along the central plane; the 2.5-in.-diam hole accommodates a Ge(Li) high resolution detector at the center of the NaI assembly. (The 1-in.-diam section of the well admits a collimated

beam of gamma rays from the activated source.) The NaI assembly is used for suppressing the Compton component of the distribution in the Ge(Li) detector's response. For observing the decay of low-activity samples the Ge(Li) detector and its cryostat can be removed, and either opening may be employed for sample insertion. The two openings subtend at the assembly center only $\approx 1\%$ of the total 4π steradian solid angle. Thus, for samples at the center, the assembly is very nearly a 4π detector. A 2.5 x 6 in. NaI detector is available to plug the larger opening when desired. The flat end surface of each crystal is viewed by nine 3-in.-diam RCA 8054 photomultipliers.

To illustrate the resolution and full-energy efficiency, Fig. 16 shows spectra for the 662-keV

Fig. 16. Sample ^{137}Cs (662-keV) gamma-ray spectra from NaI assembly. Resolution and Compton suppression are much better for both crystals operated together as a 4π detector than for either crystal individually.

gamma ray of ^{137}Cs in the individual NaI crystals and for the two crystals combined as a 4π detector. The ratio of counts in the peak to the total counts is better (0.84) for the 4π configuration than for the individual crystals (0.72). The reason for this is that essentially all Compton-scattered gammas are fully absorbed in the 4π detector, but many are only partially absorbed in the individual crystals. Because of this complete absorption of gamma rays scattered from one crystal to the other by the Compton process, the Compton edges, clearly visible in the single-crystal spectra, virtually disappear in the combined-crystal spectrum. The overall resolution is $\approx 10\%$ for the ^{137}Cs 662-keV gamma ray.

In Fig. 17 the efficiency of the NaI assembly

Fig. 17. Gamma ray energy deposition probabilities for NaI assembly. For gamma emitters with two or more simultaneous gamma rays, the assembly has nearly approached 100% efficiency.

as a 4π detector is presented as a function of energy. Data were taken at energies up to about 2.0 MeV, the maximum energy of sources easily obtainable. However, the interaction probabilities are very nearly minimum at 2.0 MeV and will thereafter rise because of the rapidly increasing cross section for pair production. Thus, the probability for full-energy deposition has a minimum value of 0.65 (Fig. 17). The probability for depositing enough energy for a measurable signal is no less than 0.85, which implies a maximum probability for escape of ~ 0.15 . For gamma emitters with two or more simultaneous gamma rays, the assembly therefore approaches 100% efficiency for detection.

The principal use planned for the assembly is the measurement of the decay curves of pure positron emitters formed in activation analysis. From Fig. 17 the probability of the 4π detector absorbing the full energy of a 0.51-MeV gamma ray is found to be 0.79. Therefore, the probability that both 0.51 MeV photons from a positron annihilation will be fully absorbed is ≈ 0.62 . The common interference reaction products are positron emitters which also emit a gamma ray in coincidence with the positron (^{22}Na for example, with a 1.20-MeV gamma). If the area of the 1.02 MeV peak (resulting from the full-energy sum of both 0.51-MeV photons) is regarded as the true signal, it is evident that the high efficiency of the NaI assembly will remove most of the interference events from the signal channel. Figure 18 is a ^{22}Na spectrum from the 4π detector. The number of counts in the 1.02 MeV peak is only 10% of what it would have been if ^{22}Na were a pure positron emitter. Therefore, the NaI assembly reduces the interferences from ^{22}Na by 90%.

Fig. 18. ^{22}Na spectrum in NaI assembly. The assembly reduces interference from ^{22}Na by 90%.

When the assembly is used as a 4π anticoincidence detector, background ($\approx 10^3$ events/sec) in the rather large volume of the detector is much reduced by counting or analyzing only events in which there is ≥ 100 keV of energy deposited in each crystal. The 4π NaI assembly is an efficient device for suppressing the Compton distribution in Ge(Li) detector spectra. Figure 17 shows the efficiency of the NaI detector for eliminating Compton events. Compton scattered photons in the backward hemisphere have energies less than 0.51 MeV. For these, the efficiency is $\geq 98\%$. For higher-energy scattered photons in the forward hemisphere, the probability of capture drops to around 85%. Nevertheless, more than 90% of Compton events which result in a scattered photon entering the NaI are eliminated from the spectrum; no anticoincidence detector can completely suppress the "partial-energy" continuum of any gamma-ray detector. Scatterings in source and collimator result in some energy-degraded gamma rays reaching the detector; in addition, some of the scattered photons (particularly in the backward hemisphere where their energy is small) are absorbed in detector coverings before reaching the anticoincidence detector. With the degree of suppression given by the large NaI assembly, further improvement in the quality of spectrum measurements is best obtained by increasing the size (and therefore the full-energy efficiency) of the Ge(Li) detector. The ratios of the full-energy peak amplitude to the Compton edge amplitude observed in tests of two Ge(Li) detectors, of different sizes, illustrate this fact. This ratio for the 6-cm³ detector, which has been in use for several years, is increased from 5.8 to 18.5 by use of the NaI in anticoincidence. The ratio for a recently obtained 20-cm³ detector is improved from

12.0 to 75. In addition, the full-energy efficiency for the 20-cm³ detector is about an order of magnitude greater than for the 6-cm³ detector.

3. Atomic Absorption Spectrophotometric Analytical Procedure Development (G. E. Meadows, L. A. Waldschmidt)

Effort has continued on the development of atomic-absorption spectrophotometric analytical procedures for the determination of trace-level metallic impurities (other than sodium) remaining in the residue and condensate following distillation. In addition, procedures to determine trace metallic impurities in bulk sodium samples by the same method are being investigated. Attempts have been made to run these analyses in solutions containing high concentrations of sodium ion (approximately 10%) without going through a series of chemical separations to remove the sodium ion; the associated effect on sensitivity and accuracy of the analysis has been studied. Thus far, the results obtained with this technique have been very encouraging, and although it is difficult to predict whether or not this technique can be used routinely for all of the analyses which are currently being contemplated, it is being used on a semi-routine basis for potassium, calcium and magnesium.

4. Vacuum Distillation Development (V. J. Rutkauskas, G. E. Meadows)

Observations conducted on sodium samples removed for distillation analysis from Analytical Loop No. 1 have indicated that there is a minute quantity ($\sim 10^{-5}$ - 10^{-6} liter) of gas evolved from the sodium metal during the final stages of distillation. The evolution occurs while the sample is being distilled at constant temperature and is associated with the removal of the final portion of the sodium from the nonvolatile residue. The evolved gas has been analyzed quantitatively by mass spectrometric techniques and although the composition of the off-gas has not been positively identified there are several peaks which are known to be below a mass number of 40. Samples analyzed by gas chromatographic techniques have identified the evolved gas to be composed primarily of H_2 and CH_4 ; there is no trace of additional constituents in the range below mass 40. A continuing effort is being applied to characterize the off-gases by mass spectrometric and gas chromatographic techniques in an effort to positively identify the composition of the gas and make a quantitative analysis of the volumes involved.

In conjunction with this effort, a spot test for the determination of cyanides has been applied to sodium samples removed from the system. In this test the cyanide is decomposed by acid to form cyanogen (C_2N_2) and the cyanogen release results in a colored complex formed on copper acetate-orthotolidine test paper. Sodium samples were dissolved in water, acidified, and metallic zinc was added to facilitate the cyanogen release. Positive results were obtained with additions of 1 ppm by weight of potassium cyanide to 5 g sodium samples. The results obtained with this technique on sodium samples removed from the loop have indicated that if cyanide is present it is below the limit of detectability.

5. Spectrochemical Analysis of Sodium

A summary of this work is presented under Project 808, Section X.

VI. STUDY OF BASIC CHEMISTRY AND PHYSICAL PROPERTIES: DIFFUSION OF GASES IN METAL (J. P. Brainard, D. Kirpatrick)

A. General

Very little quantitative information is available on the diffusion of gases in reactor system containment materials, although the phenomenon has been observed in several high-temperature, liquid-metal-cooled systems. Diffusion of nitrogen through stainless steel in such systems may be misinterpreted as evidence of an air leak in the plumbing. If quantitative information on diffusion were available, the expected rate of nitrogen influx could be estimated, and the existence of small hard-to-find leaks might be substantiated or dismissed by comparing the expected and observed rates of nitrogen accumulation in the system.

A program for determining the diffusion rate of nitrogen in stainless steels has therefore been undertaken.

B. Results in FY 1968

Work to date on this project has consisted entirely of literature survey, experiment design, the evolution of measuring techniques, and hardware procurement. Most of the details have been presented during the year,^{1,2,3} and only the overall development of the program is given here.

It was initially thought that the diffusion of gas through the walls of a metal chamber might be

determined by measuring pressure drops through a series of known flow conductances. A flow meter capable of detecting flows as small as 1×10^{-8} torr-liter/sec, in the pressure range of 2×10^{-9} - 9×10^{-5} torr, was designed, constructed and tested. It was estimated that permeation rates of 1×10^{-11} torr-liter/sec-cm² could be measured.

As the work progressed, however, it became evident that a more straight forward approach would be to use a mass spectrometer to measure permeation as a function of time. This method has the further advantage that the diffusion species may be unambiguously identified and the occurrence of leakage in addition to diffusion might be more readily recognized.

The plans for the experiment were modified so that this second technique might be used, and design and procurement was initiated. Most of the equipment for the first experiment is now ready to assemble.

VII. STUDY OF BLANKET AND MAINTENANCE ATMOSPHERE

A. Development of a High Temperature Quadrupole Mass Spectrometer for Cover Gas Analysis (C. R. Winkelman, J. P. Brainard)

1. General

The purpose of this research is to develop a method for continuous on-line analysis of high temperature (up to 650°C) cover gas in an LMFBR. The analyzer must be capable of detecting impurities such as nitrogen, oxygen, hydrogen, carbon dioxide, methane, and fission products in the cover gas with a sensitivity varying from the part-per-million range to the percent range. A response time of about one minute is necessary if the analytical data are to serve as the error signal furnished to activate devices for continuous control of cover gas composition.

A mass spectrometer was obtained in order to meet the above requirements. It is believed that reasonably representative sampling can be accomplished by transporting the sample gas in sodium loop containment materials and at sodium loop temperatures until it has passed through the spectrometer for analysis.

2. Results in FY 1968

The work began this year with an instrument which injected heated gas into a heated quadrupole residual

gas analyzer and associated vacuum envelope and pumps. This heated system was made primarily of stainless steel and was eventually to be run at the cover gas temperature. Problems with the equipment soon became evident even though it was operated only up to 200°C maximum.

Since the vapor pressure of materials increases exponentially with temperature, ultra high vacuums necessary for low background measurements were not attainable at 650°C. Also, signal to noise ratio decreased with temperature due to the increase in electron multiplier dark noise, and current leakage across insulators became significant for the ppm measurements. In addition, there is the elution problem in which previous gas absorbed on the analyzer walls is mechanically bumped off when a new gas sample is introduced. Hence, the sample takes much longer than a minute to come to equilibrium with the analyzer walls.

All of the above problems can be eliminated or minimized by collimating the high temperature gas into a molecular beam and introducing this beam in a one pass sweep through the ionization region of the mass spectrometer. This new direction in equipment development will enable the mass spectrometer to be operated at room temperature and will minimize elution. Two additional supporting vacuum systems are required; one is used to collimate the gas beam before the introduction, and the other is used to absorb the beam after it is analyzed. The cover gas sample will be brought to the analyzer by means of a capillary tube made out of the sodium loop containment material and heated to the temperature of the cover gas.

A simple but crude sample beam has been injected into the quadrupole ionization source as a first test of the above ideas. It was found that the signal to background ratio was improved by an order of magnitude. Using the sample beam method, sensitivity will not be affected by pumping speed. We are, therefore, increasing the pumping speed in the mass spectrometer in order to lower further the background and hence increase signal to background ratio. A new vacuum envelope around the mass spectrometer is under construction which will improve the sample beam alignment. The introduction system is being designed to incorporate a 600°C capillary introduction tube and a static sodium system in order to

admit sodium vapor as well as the cover gas to the analyzer. Literature search is being carried out to obtain information on gas flow through a nozzle, where a transition from viscous to molecular flow occurs. This survey will facilitate the designing of an improved molecular beam.

Two gas mixing systems have been purchased and received. One is a static mixer and the other a dynamic mixer. They both can mix contaminants from ppm levels to percent levels in a carrier gas. The dynamic mixer was interfaced to the initial gas analyzer and was instrumental in finding the problem in that analyzer.

The calibration of mass spectrometers is temperature dependent whether the spectrometers are heated, the sample gas is heated, or both. Literature search has provided us with possible methods of compensating for temperature effects in the gas analysis.^{10,11,12} This compensation will allow the calibration of the cover gas at one temperature to be extended to other temperatures.

A digital averager to handle the analyzer data has been received and interfaced with the mass spectrometer.

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PROJECT 807
CERAMIC PLUTONIUM FUEL MATERIALS

Person in Charge: R. D. Baker

Principal Investigator: J. A. Leary

I. INTRODUCTION

The principal goals of this project are to prepare pure, well characterized plutonium fuel materials, and to determine their high temperature properties. Properties of interest are (1) thermal stability, (2) thermal expansion, (3) thermal conductivity, (4) phase relationships by differential thermal analysis, (5) structure and phase relationships by x-ray diffraction, high temperature x-ray diffraction, neutron diffraction and high-temperature neutron diffraction, (6) density, (7) hardness and its temperature dependence, (8) compatibility including electron microprobe analysis, (9) compressive creep (deformation).

In addition to phase equilibria and general properties, specific thermodynamic properties such as free energy of formation by vaporization equilibria in the 1000-2000°C temperature range with mass spectrometer identification of vapor species, free energy of formation by electromotive force measurement in the 450-1200°C temperature range, and heat capacity and heat of transition are being determined.

II. SYNTHESIS AND FABRICATION

(M. W. Shupe, A. E. Ogard, R. L. Nance, W. Jones, D. Kelley)

1. Carbides

Single phase $U_{1-x}Pu_xC$ can be synthesized by a process in which arc melting of the U, Pu, and C is the first step in the process. However, a large amount of operator control and technique is necessary during arc melting to maintain the desired (U + Pu)/C ratio. A process utilizing arc melting but also requiring less stringent operator control was desired. Results

obtained during this reporting period have shown that mixtures of monocarbide and sesquicarbide can be converted to the pure monocarbide by reaction of the excess C with H_2 at 850°C.

During the arc melting of U, Pu and C the melt is contaminated to a slight degree by the material of the electrode. In this process a graphite electrode is used to produce a hyperstoichiometric carbide intentionally. This arc melted button is annealed for 24 h at 1600°C, ground in a WC vibratory mill and screened to -230 mesh (< 64 μ) size. This powder is then reacted with H_2 at 850°C to remove the excess C before processing into pellets.

In Table 807-I the chemical compositions of pellets produced by this process are shown. The results of both the initial C-rich powder and the final pellets are listed. In the first 12 lots a reaction time of 0.4 h/g carbide was used. In about one-third of the lots this time was insufficient so that further reaction of the pellets with H_2 was required. In lots 13 through 22 a reaction time of 0.6 h/g carbide was used. Complete reaction of the excess C was noted in all cases. The results shown in Table 807-I indicate that excellent control of the U and Pu concentrations can be obtained. Recent lots indicate that the O and N concentrations are about 200 ppm each. Additional information on the physical characterization of these pellets is given in the section on Program 808 of this report. A photomicrograph of a typical pellet is shown in Fig. 807-1. The effect of H_2 reduction on pellet microstructure

Table 807-I
The Effect of Hydrogen Treatment on the Composition of
 $U_x Pu_y C_z$

Initial Powder				Pellets Made from H_2 Reacted Powders					
Lot No.	x	y	z	x	y	z	O ^(a)	N ^(a)	Microstructure ^(b)
1	0.794	0.206	1.01	0.794	0.206	0.97	0.008	0.009	MC, I
2	0.800	0.200	1.00	0.800	0.200	0.98	...	...	MC, I
3	0.796	0.204	1.00	0.797	0.203	0.94	...	...	MC, I
4	0.796	0.204	0.98	0.795	0.205	0.98	0.007	0.003	MC
5	0.795	0.205	0.96	0.800	0.200	0.97	...	...	MC
6	0.799	0.201	1.05	0.798	0.202	0.99	0.004	0.005	MC, I
7	0.799	0.201	1.00	0.798	0.202	0.98	...	...	MC, I
8	0.797	0.203	1.00	0.796	0.204	0.96	0.015	0.001	MC
9	0.797	0.203	1.01	0.797	0.203	0.95	0.011	0.008	MC, I
10	0.792	0.208	1.02	0.793	0.207	0.99	...	...	MC, I
11	0.794	0.206	1.03	0.796	0.204	0.99	0.009	0.005	MC, I
12	0.796	0.204	0.99	0.796	0.204	0.99	0.004	0.007	MC
13	0.796	0.204	0.99	0.795	0.205	0.97	0.005	0.009	MC
14	0.796	0.204	0.99	0.796	0.204	0.97	0.003	0.005	MC
15	0.800	0.200	1.02	0.800	0.200	0.97	0.005	0.006	MC
16	0.796	0.204	1.03	0.797	0.203	0.97	...	...	MC
17	0.799	0.201	1.00	0.798	0.202	0.98	...	...	MC
18	0.799	0.201	1.00	0.798	0.202	0.97	0.009	...	MC
19	0.792	0.208	0.99	0.797	0.203	0.98	0.008	0.003	MC
20	0.792	0.208	0.99	0.795	0.205	0.95	0.009	...	MC
21	0.797	0.203	1.01	0.793	0.207	0.96	0.003	0.003	MC
22	0.797	0.203	1.01	0.792	0.208	0.97	0.004	0.004	MC
Avg.	0.796	0.204	1.00	0.796	0.204	0.97	0.007	0.005	
	± 0.002	± 0.002	± 0.02	± 0.002	± 0.002	± 0.01	± 0.003	± 0.002	

Notes: (a) atomic ratio referred to (U + Pu)
(b) I indicates < 0.5 v/o impurity phase

Fig. 807-1 Single Phase $U_{0.8}Pu_{0.2}C$
(380X, Nitric-Lactic-Acetic Acid Etch)

is shown in Fig. 807-2. Typical purities of the monocarbides that were prepared are shown in Table 807-II.

When higher carbides are eliminated from the monocarbide structure, small amounts of metallic impurities are detectable in the microstructure. Generally, these are somewhat enriched in Pu relative to the Pu/U ratio in the MC matrix. It is unlikely that this is detrimental for fuel-clad compatibility, inasmuch as the Pu is more stable in the traces of intermetallic compounds that are detectable. As shown in Table 807-II, the purity of the monocarbide is primarily determined by the purity of the U melting stock. The less pure melting stock (columns 2 and 3) was used to

H₂ Reduced (380 X)

H₂ Reduced (900 X)

No H₂ Treatment (380 X)

No H₂ Treatment (900 X)

Fig. 807-2 Photomicrographs of Pellets Produced from U_{0.8}Pu_{0.2}C Powders before and after Reaction with H₂.

Table 807-II

Spectrochemical Analysis of Enriched Uranium Melting Stock and (U, Pu)C Products

Element	Element Conc. (g/10 ⁶ g Pu)			
	Melting	MC	Melting	MC
	Stock	Pellets	Stock	Pellet
Li	< 0.5	< 1	< 0.2	< 1
Be	< 0.1	< 1	< 0.1	< 1
B	< 0.2	< 1	< 0.4	< 1
Na	2	< 2	3	< 2
Mg	2	< 5	5	< 5
Al	15	< 10	15	< 10
Si	150	200	75	65
P	< 50	< 50	< 50	< 50
Ca	< 2	< 5	5	< 5
V	30	< 5	10	< 5
Cr	3	< 10	10	< 10
Mn	3	5	10	5
Fe	70	60	90	55
Co	< 5	< 5	< 5	< 5
Ni	300	40	10	15
Cu	5	100	3	50
Mo	< 25	< 10	< 25	< 10
Cd	< 1	< 10	< 1	< 10
Sn	< 1	< 2	< 1	< 2
Pb	< 1	< 2	< 2	< 2
W	< 100	< 10	< 100	40

Table 807-III

Particle Size Distribution of Hydrogen Treated (U, Pu)C Powders (Recording Sedibalance Results)

Lot No.	Maximum Size		Tap Density, g/cc	Mass Median Dia. (μ)		
	Mesh	(μ)		Dia.	(+1σ)	(-1σ)
6-45-1	325	44	...	6.0	20.2	4.0
6-45-2	325	44	...	6.7	12.8	2.5
6-74-1	230	64	3.8	7.9	19.5	5.6
6-81-1	230	64	3.3	7.4	21.0	5.4
6-86-1	230	64	2.8	7.6	18.4	5.2
6-88-1	230	64	2.9	7.0	15.8	4.8

Table 807-IV

Analysis for N₂ and O₂ as a Process Contaminant (ppm by wt.)

	N	O
Arc Melted Ingot	68	13 ± 2
Annealed Ingot	...	33 ± 40
Crushed Powder	49	...
Blended Powder	98	185 ± 46
H ₂ -Reacted Powder	185	236 ± 40
Sintered Pellet	240	250 ± 40

to prepare lots 1 through 8, (Table 807-I). Most of the trace of impurity phase in these carbides could be traced to the high Si in the U, and to Cu pickup from powder sieves. Use of purer U melting stock and elimination of Cu sieves has essentially eliminated these metallic phases in the microstructure. However, an occasional trace impurity can be found metallographically in even the purest preparations, as shown in Fig. 807-3. The 380X photomicrograph in the upper right hand corner shows that this type of precipitate, although identifiable, represents an insignificant volume fraction of the U_{0.8}Pu_{0.2}C.

Some lots also were prepared using a W electrode in place of the graphite electrode. Although the W content can be kept to < 50 ppm by exercising special care, occasionally there is gross W pickup from the electrode. As shown in Fig. 807-4, the

W appears as a second phase in combination with Si and Pu.

Analysis of particle size distribution of H₂ reduced (U, Pu)C powders are shown in Table 807-III. The arithmetic mean diameters of 4 lots show a consistency of particle size while controlling pulverizing conditions. This allows sufficient control over sintered pellet dimensions. A powder such as lot No. 6-86-1 when sintered at 1800°C for 2 h then 1400°C for 4 h in Ar resulted in a diameter of 0.266 in. and a density of 90% of theoretical.

The contamination of U_{0.8}Pu_{0.2}C by N₂ and O₂ during various processing steps has been determined. The results shown in Table 807-IV indicate that pellets containing less than 300 ppm of either N or C can be produced.

Fig. 807-3 Electron Microprobe Examination of Single Phase $U_{0.8}Pu_{0.2}C$ Containing 120 ppm of Fe Plus Si

Figure 1a. Photomicrograph showing inclusion in Sample CMB-11-KAJ-68-0110 (430x). Photo is mirror image of electron microprobe photos. Area examined with the microprobe is darkened.

Figure 1b. Pu x-ray intensity distribution, same area (3000x). Note that inclusions are enriched in Pu.

380X

Figure 1c. C x-ray intensity distribution, same area. C intensity from inclusions is equal to background.

Figure 1d. Si x-ray intensity distribution, same area. Si intensity from matrix is equal to background.

Figure 1e. Fe x-ray intensity distribution, same area. Fe intensity from matrix is equal to background.

Fig. 807-4 Electron Microprobe Examination of $U_{0.8}Pu_{0.2}C$ Containing > 1000 ppm W and 350 ppm Si Impurities.

Figure 3a. Photomicrograph showing large white inclusion in Sample CMB-11-KAJ-67-0257 (430x). Photomicrograph is mirror image of electron probe photos. Area examined with the microprobe is darkened.

Figure 3b. Pu x-ray intensity distribution, same area (1500x). Note that the white inclusion is enriched in Pu, and the area around the inclusion is slightly depleted in Pu, relative to the matrix.

Figure 3c. U x-ray intensity distribution, same area. Note that the white inclusion is depleted in U.

Figure 3d. C x-ray intensity distribution, same area. C x-ray intensity from inclusion is equal to background.

Figure 3e. Si x-ray intensity distribution, same area. Si intensity from matrix is equal to background.

Figure 3f. W x-ray intensity distribution, same area. W intensity from matrix is equal to background.

The following conclusions can be drawn from these results:

1. Single phase $U_{0.8}Pu_{0.2}C$ exists at a slightly substoichiometric carbon composition. The single phase monocarbide C/(U + Pu) ratio of 0.97 ± 0.01 is readily obtained by reaction of excess C with H_2 . The reaction of the carbide with H_2 does not produce free actinide metal.
2. The U and Pu concentrations are not affected by the reaction of the excess C with H_2 , or by the sintering step.
3. A reaction time of 0.6 h/g carbide at $850^\circ C$ is needed to insure a single phase product if the starting material contains ~3% excess C.

A variety of carbides with various U, Pu, and C compositions also were prepared for use in the determination of high temperature physical properties. A special disc of ^{240}PuC 2 in. dia. x 1/16 in. thick was also prepared for neutron diffraction experiments.

2. Oxides

Several lots of $U_{0.8}Pu_{0.2}O_2$ powder have been prepared to be used as analytical chemistry intermediate reference standards as part of a cooperation program with the New Brunswick Laboratory. Six 35 g lots of varying purity and varying Pu/U ratio from 5/95 to 30/70, and one 200 g lot having the ratio $Pu/(U + Pu) = 20$ percent by wt. are required. The conventional ADU- $Pu(OH)_4$ coprecipitation procedure has been used, followed finally by high temperature firing of the powder in $5 H_2 - 95 Ar (H_2O/H_2 = 1.3 \times 10^{-2})$. The lattice dimensions of the high-fired small lots shown in Fig. 807-5 indicate uniform solid solutions are produced that follow Vegard's law. The O/M ratio of the nominally 20 percent PuO_2 composition is estimated to be 2.015 ± 0.01 .

Relative rates of solution of $U_{0.8}Pu_{0.2}O_2$ before and after firing at 1550° have been determined. The low fired powder had been heated in H_2 at 925° to reduce U_3O_8 to UO_2 . As anticipated, the high fired powder

Fig. 807-5 Lattice Parameters of (U, Pu) O_2 Solid Solutions (slightly hyperstoichiometric).

dissolved more readily than the low fired material, presumably because of solid solution formation at the high temperature. After 2 h in hot 15 M HNO_3 , 99.4% of the high fired material had dissolved, in comparison to 88.9 percent of the low fired material. All residues were dissolved completely by fuming with a $HF-HNO_3-H_2SO_4$ mixture. It should be noted that x-ray powder diffraction analysis indicated that the oxide was not a uniform solid solution after the 925° firing.

III. PROPERTIES

1. Differential Thermal Analysis (J. G. Reavis)

The study of potential high temperature fuel materials by use of the high temperature thermal analysis apparatus using optical sensors has continued. (U, Pu) C, PuC and UO_2-PuO_2 compositions have been studied. Melting behavior of (U, Pu) C compositions containing 0-50% PuC has been investigated. Melting of $PuC_{0.86}$, $PuC_{0.87}$ and $PuC_{1.6}$ has also been studied. Melting points and heats of fusion measurements have been made on UO_2 , $U_{0.8}Pu_{0.2}O_2$, PuO_2 , and ZrO_2 contained in sealed W capsules.

Melting of (U, Pu) Monocarbides

The melting process of (U, Pu) C compositions containing 0-50 m/o PuC has been studied by application

of DTA and metallographic techniques supplemented by macro observations of samples quenched from temperatures near the liquidus. The resulting solidus and liquidus temperatures are plotted on Fig. 807-6 as a function of composition. UC was found to have a solidus at 2520°C and a liquidus at 2540°C compared to the congruent melting point of 2525°C reported by Witteman and Wallace.⁽¹⁾ When the 20°C uncertainty in temperature measurement is considered, this appears to be excellent agreement.

Other liquidus and solidus temperatures observed generate liquidus and solidus lines much as would be expected in a binary system exhibiting continuous solid solution formation as is encountered in the (U, Pu) system. Liquidus and solidus temperatures for the particularly important composition $U_{0.8}Pu_{0.2}C$ are 2485°C and 2285°C, respectively, with an uncertainty of $\pm 20^\circ$.

To elucidate the melting process, a thorough study of $U_{0.8}Pu_{0.2}C$ pellets was made by use of metallographic techniques. Two lots of pellets, shown by analysis to be $U_{0.81}Pu_{0.19}C_{0.95}$ and $U_{0.81}Pu_{0.19}C_{0.99}$, were sintered at 1600°C. Individual pellets were then heated to temperatures in the range 2200°C to 2475°C, equilibrated 1 minute and cooled at about 1000 deg/min to temperatures below 1000°C. Photomicrographs of microstructures produced by this treatment are shown

in Fig. 807-7. Although the $MC_{0.95}$ samples as sintered at 1600°C contained < 1 v/o of a second metallic phase (principally W, Si, Fe, with some Pu) samples quenched from 2200°C and 2225°C do not show the presence of this phase. Additional samples (not shown) heated to 2200°C and cooled slowly to 2000°C and to 1800°C and quenched showed this phase had not reappeared at 2000°C but had returned at 1800°C. Thus this metallic phase does not precipitate until a temperature between 1800°C and 2000°C is reached. The 2250°C photomicrograph shows the first evidence of what is believed to indicate melting followed by coring during resolidification. Higher temperature samples show the progression of this process. The 2465°C sample had (by macro observation) almost completely melted. These observations lead to the assignment of values of 2250°C as solidus and 2475°C as liquidus of $MC_{0.95}$. Similarly, solidus and liquidus values of $MC_{0.99}$ were found to be 2300°C and 2485°C. The comparative values seem to indicate slightly higher values for $MC_{0.99}$ than for $MC_{0.95}$. Additional observations will include the composition $U_{0.8}Pu_{0.2}C_{1+x}$.

Melting Behavior in the Pu-C System

Several samples of $PuC_{0.86}$ and $PuC_{0.87}$ have been subjected to DTA. Thermal arrests consistently begin at $1605 \pm 10^\circ$ during heating. Macro observations of samples heated to slightly higher temperatures and quenched show the presence of a liquid phase at the higher temperatures, but the samples did not slump until the range 1650-1660°C was reached. This leads to the hypothesis that low temperature single phase monocarbide begins to decompose at about 1600°C into Pu_2C_3 plus liquid and that the Pu_2C_3 dissolves in the liquid phase at higher temperatures, liquefaction being completed at a temperature just above 1650°C.

The composition $PuC_{1.6}$ was also studied. This composition produced sufficient dicarbide to allow the $1650^\circ PuC_{1.5} + 0.5 C = PuC_2$ transition to be detected. DTA and macro observations showed the melting point to be $2035 \pm 10^\circ C$.

Heat of Fusion of (U, Pu)O₂

In a cooperative program with GE-Sunnyvale, the heat of fusion of $U_{0.8}Pu_{0.2}O_{1.97}$ has been determined.

Fig. 807-7

Fig. 807-8 Tungsten DTA Capsule
(0.550 in. O.D.)

Fig. 807-9 Thermal Analysis of $U_{0.8}Pu_{0.2}O_{1.97}$

Originally it was planned that ZrO_2 would be used as a reference material for which the heat of fusion was known. While the work was in progress a value of the heat of fusion of UO_2 determined by drop calorimetry was reported⁽²⁾ and this material was adopted as a reference material. DTA curves for the reference material and the fuel material were compared and the relative heats of fusion were calculated.

Samples of ZrO_2 , UO_2 , PuO_2 , and $U_{0.8}Pu_{0.2}O_{1.97}$ were sealed in W capsules as shown in Fig. 807-8. Each capsule contained 20 millimoles of oxide. These capsules were thermally cycled in a W furnace in the DTA apparatus. T and ΔT curves were recorded and

Table 807-V
Melting Data for Oxides in
Sealed W Containers

Oxide	Melting Temp., °C		$\Delta H_m^{(a)}$ kcal/mole	ΔS_m eu
	Solidus	Liquidus		
UO_2	2845	2860	18.2	5.8
$U_{0.8}Pu_{0.2}O_{1.97}$	2780	2820	19.4	6.3
PuO_2	2400	2445	24.0	9.0
ZrO_2	...	2685	20.1	6.8

(a) based on reference 2 value for UO_2

breaks in ΔT curves were evaluated as indicated in Fig. 807-9 which is a tracing of one of the recorder charts. This tracing indicates the determination of melting and freezing arrest temperatures and of the areas of the breaks in the ΔT curves. Areas of the ΔT breaks for different materials were compared after application of appropriate normalizing factors taking into account instrument amplification and the comparative amounts of energy absorbed or released by reference and fuel samples was calculated.

None of the W capsules failed even though cycled from 5 to 12 times through the melting points of the various oxides. The concentration of W was generally found to be about 1 w/o in the post-melting samples. Compositions of the oxides going into the capsules was $ZrO_{2.00}$, $UO_{2.00}$, $PuO_{2.00}$, and $U_{0.80}Pu_{0.20}O_{1.973}$.

Melting temperatures and heats of fusion of the oxides are listed in Table 807-V. Uncertainties in the melting temperatures are about $\pm 20^\circ$. The solidus and liquidus points for $U_{0.8}Pu_{0.2}O_{1.97}$ were 2780° and $2820^\circ C$, respectively. This is in good agreement with the values of $2760 \pm 16^\circ$ and $2790 \pm 16^\circ$ reported by Lyon and Bailly.⁽³⁾ Uncertainties in the heats of fusion arising from random errors are about $\pm 10\%$, while due to the limited number of reference materials for which heats of fusion are accurately known, systematic errors are indeterminate. The literature value⁽⁴⁾ of the heat of fusion of ZrO_2 is 20.8 kcal/mole, compared with the value of 20.1 calculated from comparison with UO_2 in this work. If the literature value for ZrO_2 is selected for reference, the calculated heats of fusion of the other oxides must be revised upward by about 4%. The entropy of melting of PuO_2 shown in Table 807-V is unusually high.

2. X-Ray Powder Diffraction

(C. W. Bjorklund, R. M. Douglass, J. L. Green)

X-ray powder diffraction techniques have been applied to two general areas: characterization of plutonium fuel materials, most of which has been discussed in other sections of this report, and studies of self-irradiation damage in plutonium compounds. A summary of the experimental procedures was included in a preceding report.⁽⁵⁾

α - Pu_2S_3 : A powder pattern obtained for a sample of plutonium sulfide was tentatively identified as that of orthorhombic α - Pu_2S_3 by comparison with limited data reported by Marcon and Pascard⁽⁶⁾ for the compounds α - Pu_2S_3 and α - Ce_2S_3 , which they found to be isomorphous. Attempts to refine the lattice dimensions calculated on the basis of this information were unsuccessful. Better agreement was obtained when the pattern was compared with that of a smaller cell calculated from single crystal data for α - Gd_2S_3 reported by Prewitt and Sleight.⁽⁷⁾ Justification for this procedure was based on the report⁽⁸⁾ that an α -rare earth structure existed for all of the sulfides of the rare earths from Ce to Dy, including Gd (the actual structure was not resolved). A subsequent sample of Pu_2S_3 prepared from the first by heating it to 950° in H_2 produced a powder pattern identical with the first pattern but with much better resolution in the high angle region. The resolution was improved again when the second Pu_2S_3 sample was heated in Ar at $\sim 1000^\circ\text{C}$, but a second phase grew in to complicate the pattern. Powder patterns of this material were made with Cu $K\alpha$ radiation and also with Fe $K\alpha$ radiation to spread the low angle reflections apart for better identification. The most probable values of the lattice dimensions calculated from measurements of only those reflections for which there were no known overlaps are:

$$a = 7.396 \pm 0.005 \text{ \AA}$$

$$b = 15.415 \pm 0.007$$

$$c = 3.998 \pm 0.002$$

Although the complexity of the patterns limited the number of reflections which could be used (15-20) in the lattice dimension calculations, good qualitative agree-

ment was obtained between the intensities and positions of the remaining reflections and the values calculated for a cell of these dimensions using Prewitt and Sleight's data for α - Gd_2S_3 . Very recently, Besacon, Adolphe, and Flahout⁽⁹⁾ confirmed the existence of α -rare earth sulfides from La through Gd and determined the structure of the La_2S_3 and Gd_2S_3 isomorphs from Wesenberg and precession photographs. They confirmed, apparently independently, the space group reported by Prewitt and Sleight, but their dimensions for α - Gd_2S_3 differed somewhat, particularly along the a axis.

Self-Irradiation Damage: The effect of self-irradiation damage on the lattice dimensions of several plutonium compounds is being studied as a function of time, temperature, and energy deposition. The compounds are divided into two groups: (1) those of "normal" Pu isotopic composition, including a dioxide, nitride, and a sesquicarbide, and (2) compounds in which the ^{238}Pu content has been increased to provide a 10-fold increase in the rate of energy deposition. This group includes several dioxides of similar composition, a monocarbide, and a two-phase monocarbide-sesquicarbide system. The effect of temperature on the dioxides in this group is also being studied.

Fig. 807-10 Self-irradiation Damage in Normal Pu Compounds

The results obtained for compounds of normal plutonium isotopic composition are shown in Fig. 807-10. Data for PuO₂ containing 3.75 at/o ²³⁸Pu are also included for comparison. The solid and dashed lines were obtained by fitting the data to the equation

$$a_t = A(1 - e^{-Bt}) + a_0 \quad (1)$$

where a_t is the lattice dimension at time t , a_0 is the lattice dimension at time zero, A is equivalent to Δa_t at saturation (or $t = \infty$), and B is a constant. The percent change in lattice dimension is readily calculated from this equation. A Los Alamos non-linear least-squares computer program (HAP)⁽¹⁰⁾ was used to fit the data to the equation, and the plotting subroutine was modified to permit plotting multiple sets of data on one frame. The present values of the lattice dimensions of normal PuO₂, PuN, and Pu₂C₃ are within 92, 98, and 69%, respectively, of the saturation values predicted by the equations.

The lattices of all of the compounds enriched with ²³⁸Pu (3.75% in the dioxides and 4.05% in the carbides) have expanded to the predicted saturation values. Irregularities were observed in the expansions of the monocarbides as shown in Fig. 807-11. The difference in overall lattice expansion of the two samples

Fig. 807-11 Data Points for Self-Irradiation Damage in Carbides.

might be expected since PuC has a relatively wide composition range. At the low carbon end of the range the compound is considered to be highly defected and more capable of accommodating atoms displaced by self-irradiation damage than the compound at the high-carbon end of the range.

Two equations were developed to relate the effect of temperature to the lattice expansion of PuO₂. An empirical equation

$$a_t = \left(\frac{A_1}{T} + A_2 \right) \left[1 - e^{-(A_3/T + A_4)t} \right] + a_0 \quad (2)$$

was found to apply reasonably well over the temperature range 25° to 400°. This equation was derived from Eq. 1 by the substitution of

$$A = \frac{A_1}{T} + A_2 \quad (3)$$

and

$$B = \frac{A_3}{T} + A_4 \quad (4)$$

ignoring a slight departure from linearity near 25° for A and B as functions of $1/T$. A more rational expression was subsequently derived to include the data obtained for PuO₂ stored at -198°C which would not fit Eq. 2. (More precisely, A and B in Eq. 1 were more nearly exponential functions of $1/T$ over the temperature range -198° to 400°C.) This equation

$$a_t = \frac{B_1 B_2 a_0}{B_2 + B_3 e^{-B_4/T}} \left[1 - e^{-(B_2 + B_3 e^{-B_4/T})t} \right] + a_0 \quad (5)$$

was derived by including a temperature term $(C(T) N^k)$ in the differential equation from which Eq. 1 has been derived; e.g.

$$\frac{dN^k}{dt} = B_2 N - C(T) N^k = B_2 (N_0 - N^k) - C(T) N^k \quad (6)$$

Here, $C(T)$ may be any appropriate function of T , B_2 is a temperature independent radiation damage rate constant, N is the number of undamaged atoms at time t , N^k is the corresponding number of damaged atoms and

Fig. 807-12 Self-irradiation Damage in PuO_2 (curves calculated by equation 5).

N_0 is the initial number of atoms. Equation 5 was derived by integration of Eq. 6. B_1 is a proportionality constant introduced by the assumption that $\Delta a/a_0$ is proportional to N^*/N_0 . The function $C(T)$ was assigned the form

$$C(T) = B_3 e^{-\frac{\Delta E}{kT}} \quad (7)$$

because most descriptions of annealing are generally formulated with equations similar to those of chemical kinetics. ΔE represents an average annealing activation energy, k is the Boltzman constant and $\Delta E/k$ is represented by B_4 in Eq. 5. The particular form of Eq. 5 in which a_t , rather than $\Delta a/a_0$, is the independent variable was chosen to avoid the necessity of punching new data decks for the computer program. A new subroutine was written for the computer program to adapt it to Eq. 5, and the following values of the parameters were calculated from the combined data for PuO_2 stored at -198° , 25° , 100° , 200° , and 400°C . (Estimated standard deviations are shown in parentheses.)

B_1	3.663×10^{-3}	$(0.4_6 \times 10^{-3})$
B_2	1.45×10^{-2}	$(0.3_3 \times 10^{-2})$
B_3	4.539×10^{-2}	(6.2×10^{-2})
B_4	1.260×10^3	$(0.8_2 \times 10^3)$
a_0	5.3930	(0.001 ₄)

ΔE was calculated from the value of B_4 to be ~ 0.1 electron volt. The experimental data and the curves calculated by means of Eq. 5 with the values of the parameters given above are compared in Fig. 807-12.

It was reported previously that a plot of the lattice expansion of the different compounds as a function of accumulated dose showed that only in the case of PuO_2 was the expansion independent of dose rate. Results to date confirm this observation.

3. High Temperature X-Ray Diffraction (J. L. Green)

X-ray equipment is being developed for use in the study of the high temperature crystallographic properties of plutonium ceramics. The basic x-ray equipment consists of a Picker powder diffractometer with associated electronics and x-ray generation equip-

ment. The diffractometer furnace is based on a strip heater having the sample mounted directly on the surface. At present, work is being done on carbon saturated carbides. Therefore, graphite heater strips are used. Metallic heaters are being fabricated which will allow the system to be used with other materials.

An initial series of lattice parameter determinations were carried out using high purity W powder. The purposes were (1) the evaluation of analytical extrapolation techniques for the correction of sample displacement errors, and (2) the evaluation of general precision and accuracy. The extrapolation techniques were tested by comparing least squared lattice parameters derived from data taken with the scattering center of the sample displaced by various known amounts from the focusing circle. The results shown in Table 807-VI indicate that the methods used are adequate. Also shown in Table 807-VI are the results for samples of the same batch of W powder mounted on a heater strip in the furnace and the average of 3 determinations using Debye-Scherrer techniques. A comparison of these data shows that the precision of the diffractometer results is within the range of $\pm 0.0001 \text{ \AA}$. This gives no definite information on the absolute accuracy, but comparison with the Debye-Scherrer data indicates that the overall accuracy is to the order of $\pm 0.0002 \text{ \AA}$ for these particular samples. This is adequate for any studies anticipated at present.

Table 807-VI

High Purity Tungsten Lattice Parameters

		$a_0^{(3)}$ ($\text{\AA}$)	$\sigma^{(1)}$ ($\text{\AA}$)
Measured	0	3.1651 ₉	0.00003
Displacement in mils	6.7	3.1652 ₃	0.00002
	2.6	3.1652 ₇	0.00002
Heater strip mount		3.1652 ₄	0.00003
Debye-Scherrer		3.1652	0.0002 ⁽²⁾

- (1) Estimated standard deviation computed by fitting routine.
- (2) Estimated overall accuracy.
- (3) No refraction correction made.

Power requirements and maximum temperatures for the diffractometer furnace have been investigated. Using a bare ATJ graphite heater strip, temperatures up to 2500°C have been attained. Although higher temperatures are possible, 2500 to 2600° probably is an upper useful limit for graphite heater elements. At 2500° the deposition of soot on the windows and radiation shields was significant. The rate of power dissipation for an element 1 in. long, 0.125 in. wide and 0.030 in. thick at 2500° was 1 KVA with an element current of 80 A.

The testing of the high temperature operation of the furnace and the development of sample preparation techniques have been done using NbC as a stand-in for (U, Pu)C. The method of sample preparation that is being used involves the use of naphthalene as a binder. The powdered sample is mixed with an appropriate amount of naphthalene dissolved in toluene. A thin layer of the slurry is then loaded onto the heater strip using a jig to control sample thickness and uniformity. The composite is then sintered in Ar. NbC samples prepared in this way are strong enough to allow handling and are mechanically stable during thermal cycling.

Several expansion coefficient determinations have been using NbC samples. The first trials were unsuccessful due to sample oxidation. After repairing several small mechanical leaks in the system, further experiments were run which were successful in that expansion coefficients in the range of 25° to 1800° agreed quite well with other data available on NbC. It was evident, however, that minor amounts of oxidation were still occurring at 1800° . This was presumed to be due to the diffusion of H_2O through flexible plastic cooling lines in the furnace and to impurities in the He cover gas. All elastomeric lines within or leading to the interior of the furnace have been replaced with flexible metallic assemblies and a uranium chip furnace has been installed in the He supply line. Final testing of this revised system is presently being carried out.

The inert atmosphere sample preparation and

furnace loading box is complete. The atmosphere is maintained by a small continuous flow of Ar through the box. A hot wire atmosphere tester in the box indicates that a gas purity of ≤ 10 ppm ($\text{O}_2 + \text{H}_2\text{O}$) can be maintained. The inert box and furnace assembly are now contaminated and committed to use with plutonium.

Techniques also have been developed for examining plastic mounted metallographic specimens at room temperature using the diffractometer. Several samples of various plutonium carbides have been scanned. Design and fabrication is under way on a sample enclosure that will allow room temperature examination of metallographic mounts or other powder specimens under an inert atmosphere. The system will also allow the rotation of the samples to help eliminate the effects of preferred orientation.

4. Neutron Diffraction (J. L. Green)

The room temperature structure of Pu_2C_3 was first described by Zachariasen⁽¹¹⁾ in 1944. It is body centered cubic and in space group $\text{I} \bar{4} 3 d$ and has 8 formula weights per unit cell. The Pu ions are located in the 16 fold (c) positions and the C atoms in the 24 fold (d) positions, both of which require one positional parameter for description. Based on x-ray intensity data Zachariasen was able to define the metal parameter as 0.050 ± 0.003 . Because of the small x-ray scattering amplitude of carbon relative to plutonium, he was not able to determine the anion position parameter. As in the case of PuC, Costa and Lallemand⁽¹²⁾ have suggested that a possible antiferromagnetic transition occurs in Pu_2C_3 at approximately 120°K .

In order to investigate these problems, two targets of carbon-saturated Pu_2C_3 were prepared and scanned. The early target was prepared using ^{239}Pu and was studied only at room temperature. The second was prepared using ^{240}Pu and was studied both at room temperature and at cryogenic temperatures.

A comparison of room temperature and low temperature data indicates that if a magnetic transition does occur, it was not experimentally observable.

Fig. 807-13 Room Temperature Neutron Diffraction Pattern for $^{240}\text{Pu}_2\text{C}_3$

Considerable crystallographic information on the structure can be derived from the room temperature data from both targets. Figure 807-13 is a schematic representation of the room temperature diffraction pattern for the ^{240}Pu target. Numerical intensity information was extracted from the counting data using a least-squares Gaussian fitting computer program. For the ^{240}Pu target, it was possible to obtain data for 46 diffraction peaks. The resolution of the ^{239}Pu target was not nearly as good due to the large fast fission neutron background; however, it was possible to obtain intensity information on 12 low angle reflections. These data were then used in a computer program which calculates the various crystal parameters by least-squares fitting the observed intensities. The results of these calculations are shown in Table 807-VII. The recent data on U_2C_3 by DeNovion et al.⁽¹³⁾ is shown for comparison.

Agreement between the two independent Pu_2C_3

Table 807-VII

Pu_2C_3 CRYSTALLOGRAPHIC PARAMETERS

	$^{239}\text{Pu}_2\text{C}_3$	$^{240}\text{Pu}_2\text{C}_3$	U_2C_3
x_{Pu}	0.050 ± 0.002	0.0492 ± 0.0005	0.0485 ± 0.0002
x_{C}	0.289 ± 0.004	0.2896 ± 0.0005	0.2872 ± 0.0005
b_{Pu}	0.77 ± 0.10	0.409 ± 0.007	—
$B(\text{thermal})$	$\sim 0.7 \text{ \AA}^2$	$0.69 \pm 0.06 \text{ \AA}^2$	$0.30 \pm 0.01 \text{ \AA}^2$
$R(\text{intensity})$	0.06	0.06	0.02
a_0	$8.132 \text{ \AA}$	$8.135 \text{ \AA}$	$8.089 \text{ \AA}$
C-C bond	$1.40 \text{ \AA}$	$1.39 \text{ \AA}$	$1.42 \text{ \AA}$

determinations is quite good. As expected, the atomic position parameters for Pu_2C_3 and U_2C_3 are very similar. The only major difference is in the value of the thermal parameter, B . Whether or not this difference is real is somewhat difficult to determine. The value of B is rather sensitive to the accuracy of the absorption corrections and also there appears to be a rather strong correlation between the value of B and the calculated value for the instrumental constant. A quantity of interest that may be computed from these data is the C-C bond length. The carbon atoms in the Pu_2C_3 type structure occur as dicarbide groups. This bond length is $1.39 \text{ \AA}$ in Pu_2C_3 and $1.42 \text{ \AA}$ in U_2C_3 . It is pertinent to point out that these are significantly longer than the value of $1.295 \text{ \AA}$ reported for U_2C_3 by Austin.⁽¹⁴⁾

5. Thermodynamic Properties of Pu Compounds by Electromotive Force Techniques (G. M. Campbell)

Nitrides: A galvanostatic technique for determining the Pu/Pu^{+3} equilibrium potential using a W microelectrode has been developed. The procedure involves electro-deposition of Pu metal from the fused salt electrolyte onto the microelectrode by a current of constant magnitude, followed by anodic stripping of the Pu metal at constant current. By recording the potential during the procedure and having a theoretical knowledge of the effect of diffusion on the Pu^{+3} concentration at the electrode surface, the equilibrium potential can be determined. Experiments which made use of a Pu/Pu^{+3} as well as those which made use of a U/U^{+3} as reference electrodes indicate the technique is probably accurate to $\pm 1 \text{ mV}$ in melts of high purity. The purity of the electrolyte is indicated by the residual current observed in the chronopotentiometric trace.

This galvanostatic technique has been used to determine the emf of the Pu/Pu^{+3} couple vs that of a PuN electrode in LiCl-KCl , PuCl_3 melt, over the temperature range 714 to 1031°K .

Since N_2 is known to react with Pu over the range of temperatures of these experiments the cell reaction is properly written as

However it is unlikely that the solubility of PuN in Pu is great enough to cause a significant difference in the emf at these temperatures. (As shown in the following section, mass spectrometric studies indicate there is no measurable effect.) For this reason the results are treated as if the cell reaction were

and the schematic representation of the cell is

The results from the three cells are given in Table 807-VIII. After correcting for the thermal emf of Ta vs W and for the difference between the measured pressure of N₂ and 1 atm the emf is plotted against temperature in Fig. 807-14. The least-squares line is represented by the equation

$$E = 7.90071 - 2.31690 \times 10^{-2} T + 2.517855 \times 10^{-5} T^2 - 9.1644 \times 10^{-9} T^3 (\pm 0.003 \text{ V})$$

with E in volts and T in °K.

The results of previous experiments by an indirect method⁽¹⁵⁾ gave 0.8745 (± 0.005) V for the emf at 700°K. The present experiments indicate that the emf at 700°K is 0.8765 (± 0.003) V which is in good agreement.

The phase change involving the most energy in this temperature interval is melting of Pu at 913°K. Since this involves only about one entropy unit, no change in the slope of the emf vs temperature curve is detectable.

The decrease in emf with increasing temperature below the melting point of Pu is larger than can be accounted for by consideration of the known thermodynamic properties of the constituents. This probably results from the condition of no equilibrium between the surface and the center of the PuN pellet.

Above the melting point of Pu the least-squares line shown in Fig. 807-15 from two cells is

$$E = 1.0672 - 3.258 \times 10^{-4} T (\pm 0.003 \text{ V})$$

This results in

$$-\Delta G_T^0 = 73.8 - 0.0225 T \text{ kcal/mole}$$

for the Gibbs free energy of formation of PuN.

Table 807-VIII
Data From Pu vs PuN Emf Cells

Cell No.	Emf meas. (volts)	Temp. (°K)	Pressure (atm)	Emf cor. for thermal emf and to N ₂ pressure of 1 atm
1	0.7425	950	0.720	0.7553
1	0.7450	950	0.716	0.7578
1	0.7380	968.5	0.749	0.7507
1	0.7488	968.1	0.734	0.7577
1	0.7375	987.2	0.751	0.7505
1	0.7415	986.2	0.751	0.7545
1	0.7310	1007.1	0.755	0.7444
1	0.7210	1025.9	0.755	0.7348
1	0.7295	1011.9	0.755	0.7430
1	0.7180	1031.6	0.755	0.7319
2	0.7382	954.2	0.728	0.7509
2	0.7424	944.4	0.714	0.7552
2	0.7494	929.3	0.707	0.7620
3	0.7596	846.0	0.774	0.7692
3	0.7688	827.2	0.746	0.7785
3	0.7795	810.3	0.742	0.7889
3	0.7885	792.4	0.739	0.7975
3	0.7925	775.5	0.742	0.8012
3	0.8046	753.5	0.741	0.8128
3	0.8259	734.5	0.752	0.8336
3	0.8508	713.8	0.737	0.8583
3	0.8733	698.4	0.739	0.8804
3	0.7648	830.1	0.786	0.7739
3	0.7524	865.3	0.786	0.7622

Fig. 807-14 Emf vs Temperature for the Cell
Pu(s, ℓ)(PuN) | Pu³⁺, LiCl-KCl | N₂(g), PuN(s)

Fig. 807-15 Emf vs Temperature for the Cell
Pu(l)(PuN) | Pu³⁺, LiCl-KCl | N₂(g), PuN(s)

Carbides: Three types of emf cells have been run involving electrodes containing the solid solution $(U_{0.8}Pu_{0.2})_2C_3$. They were

It has been determined that equilibrium is not established without electrode compositional change in cells of Type (I) and (II). Cells of type (III) are stable, however. Analysis of emf data on this type of cell shows that the activity of Pu in the solid solution is much smaller than that of U. Current experiments are being made to determine whether the emf of type (III) cells is sensitive to changes in the ratio x_1/x_2 .

6. Thermodynamic Properties from Vaporization Studies

(R. A. Kent)

The mass spectrometer-Knudsen cell assembly employed to study the vaporization of Pu and PuN has been described.⁽⁵⁾

Pu: Plutonium metal was vaporized from W Knudsen cells in the range 1426-1658°K and from a ThO₂ cup contained in a W cell in the range 1482-1579°K. The results of the chemical and spectroscopic analyses of the electrorefined⁽¹⁶⁾ Pu metal used are given in

Table 807-IX
Spectrographic Analysis of Plutonium

Element	Concentration, ppm by wt.	Element	Concentration, ppm by wt.
Al	3	Mg	2
Am	< 10	Mn	< 0.5
B	< 0.001	Mo	< 1
Bi	< 1	N	3 ± 1
C	15 ± 5	Na	< 2
Ca	< 2	Ni	< 0.5
Cd	< 5	O	20 ± 10
Co	< 1	Pb	< 1
Cr	1	Zr	< 10
Cu	< 0.05	Si	7
F	< 2	Sn	< 1
Fe	3	Ta	19
Ga	< 0.2	Th	< 15
H	10 ± 5	U	10
K	< 7.5	W	< 5
La	< 1	Zn	< 10
Li	< 0.005	Pu	100.00 ± 0.06 %

Table 807-IX. The mass spectrum consisted of Pu⁺ ions only, no PuO⁺ or Pu₂⁺ ions were observed. The temperature dependence of the ²³⁹Pu⁺ signal was determined and the Pu⁺ ion current data from both the W Knudsen cells and the ThO₂ cup were converted to pressure values by means of the relationship

$$P = K(IT) \quad (1)$$

where P is the pressure in atm, I the ion current, T the temperature in °K and K is the machine constant. Gold was used as the calibration standard and the usual corrections were made for the relative ionization cross sections⁽¹⁷⁾ and multiplier gains. The resultant equation is

$$\log P_{Pu} \text{ (atm)} = - \frac{17420 \pm 184}{T^{\circ K}} + (4.924 \pm 0.120) \quad (2)$$

where the uncertainties quoted are the standard deviations generated by the least-squares program. Equation (2) yields for the heat of entropy of vaporization of Pu at 1538°K 79.7 ± 0.8 kcal. mole⁻¹ and 22.5 ± 0.6 eu, respectively. The tabulated functions for Pu(g)⁽¹⁸⁾ and the estimated functions for Pu(s, A)⁽¹⁹⁾ used to convert these values to 298°K are listed in Table 807-X.

The resultant second law values are

$$\Delta H_V^{\circ} = 83.2 \text{ kcal. mole}^{-1} \text{ and } \Delta S_V^{\circ} = 29.4 \text{ eu.}$$

The free energy functions from Table 807-X were combined with the absolute pressure values to yield the third law heat of vaporization of $\Delta H_V^{\circ} = 82.9 \pm 0.1 \text{ kcal. mole}^{-1}$. The entropy of vaporization calculated from the thermodynamic functions is $\Delta S_V^{\circ} = 29.1 \text{ eu.}$

The vapor pressure data for Pu are presented in Fig. 807-16. As indicated in Fig. 807-16 the Pu pressures from the ThO₂ cup are approximately 7% lower than those obtained from the W Knudsen cells. These results are in accord with those obtained by Mulford.⁽²⁰⁾

Table 807-X
Thermodynamic Functions for Plutonium

Temp., °K	$\left(H_T^{\circ} - H_{180}^{\circ} \right) (s, A)$ cal. mole ⁻¹	$\left(H_T^{\circ} - H_{180}^{\circ} \right) (g)$ cal. mole ⁻¹	$-\left(\frac{F_T^{\circ} - H_{180}^{\circ}}{T} \right) (s, A)$ eu.	$-\left(\frac{F_T^{\circ} - H_{180}^{\circ}}{T} \right) (g)$ eu.
298	0	0	13.20	42.32
1000	8177	4330	19.14	45.10
1200	9877	5994	20.64	45.95
1400	11577	7842	21.91	46.76
1600	13277	9860	23.02	47.55
1800	14977	12020	24.00	48.30

Fig. 807-16 Vapor Pressure Data for Pu.

Fig. 807-17. Third Law Heat of Vaporization of Pu vs Temperature.

There are two possible causes for the lower Pu pressure from the ThO₂ cup. Analysis of the Pu residue showed a thin (1-5μ) skin, presumably of Pu₂O₃, on the surface of the Pu. Also, the Pu residue was δ-phase, indicating the dissolution of a few percent Th in the Pu. This would likely lower the Pu activity somewhat.

The third law ΔH_V° values are plotted vs temperature in Fig. 807-17. The lack of a temperature-dependent trend indicates the reliability of the estimated functions employed for Pu(s, l) and of the vapor pressure values.

From this study it is concluded that Pu vaporizes predominately to the monomer with a heat of vaporization of $\Delta H_{V298}^\circ = 83.0 \pm 0.5$ kcal. mole⁻¹.

The detailed results of this study are described in a separate LA report.⁽²¹⁾

PuN: Eight experiments were performed in which PuN(s)

was heated in W Knudsen cells in the range 1658-1976°K. The PuN samples used were fabricated by pressing pellets from PuN_{0.95} powder prepared by reacting N₂(g) with hydrided Pu.⁽²²⁾ Analytical results for the PuN powder are listed in Table 807-XI. The pellets were

Table 807-XI

Spectrochemical and Chemical Analysis of PuN Starting Material

Element	Concentration, ppm
Al	7
B	0.5
Ba	0.5
Bi	< 1
Ca	< 2
Cd	< 1
Co	< 1
Cr	< 1
Cu	2
Fe	20
Hf	< 1
La	< 1
Mg	10
Mn	< 0.5
Mo	< 1
Na	2
Ni	0.5
O	410
Pb	< 1
Si	20
Sn	< 1
Ti	0.5
U	1
V	0.5
Zn	< 10
Zr	< 1

heated in W crucibles under 0.5 atm N₂ for 15 h at 1600°C. Metallographic, chemical, and x-ray diffraction analyses of the resultant pellets indicated the PuN to be single phase, with stoichiometries of PuN_{0.96} to PuN_{0.99}, and with an average lattice parameter of 4.9055 ± 0.0003 Å.

When these pellets were heated in W Knudsen cells, the only sample ions observed were Pu⁺ and N₂⁺. The ion current data obtained when the temperature dependence of the ²³⁹Pu⁺ ion was determined were converted to pressure values in the usual manner by employing Au as the calibration standard and correcting for relative ionization cross sections and multiplier gains.

The equation obtained from 106 data points for the partial pressure of Pu(g) above PuN(s) is

$$\log P_{\text{Pu}} (\text{atm}) = -\frac{21958 \pm 98}{T^\circ \text{K}} + (6.436 \pm 0.005) \quad (3)$$

This equation leads to a heat of formation of Pu(g) above PuN(s) of $\Delta H_{1813}^\circ = 100.5 \pm 0.4 \text{ kcal. mole}^{-1}$.

It was more difficult to obtain data for N_2^+ because the nitrogen background peak was large. However, the temperature dependence of N_2^+ was determined, yielding a second law heat of $\Delta H_{1848}^\circ = 99.5 \pm 3.9 \text{ kcal. mole}^{-1}$.

Metallographic, chemical, and x-ray diffraction analyses of the residues after vaporization experiments indicated the samples to still be single phase PuN with stoichiometries $\text{PuN}_{0.96}$ - $\text{PuN}_{0.98}$, having an average lattice parameter of $4.9055 \pm 0.0003 \text{ \AA}$. As expected, the grain size of the PuN material increased during the vaporization process. No oxide or free metal could be detected in the microstructures. The Pu partial pressure values obtained as a function of temperature were reproducible when repeatedly taken at successively increasing and decreasing temperatures. Thus it was concluded that, in the range 1600-2000°K, PuN decomposes invariantly and, presumably congruently, according to the reaction

with a heat of $\Delta H_{1813}^\circ = 150.7 \pm 0.6 \text{ kcal. mole}^{-1}$.

As no heat capacity or entropy data exist for PuN(s), the thermodynamic functions were estimated from known data for UN, (23, 24) U, (25) and Pu. (19) These estimated functions were then employed to correct the second law value to 298°K. The value so obtained for the decomposition reaction is $\Delta H_{298}^\circ = 156.2 \text{ kcal. mole}^{-1}$.

For the reaction given by Eq. (4)

$$P_{\text{N}_2} = \frac{1}{2} P_{\text{Pu}} (M_{\text{N}_2} / M_{\text{Pu}})^{\frac{1}{2}} = 0.171 P_{\text{Pu}} \quad (5)$$

where M is the molecular weight of a given species.

The equilibrium constant for the decomposition reaction is then given by

$$K_{\text{eq}} = P_{\text{Pu}} P_{\text{N}_2}^{1/2} = 0.4135 P_{\text{Pu}}^{3/2} \quad (6)$$

When the values of K_{eq} were combined with the free energy functions for PuN and those for $\text{N}_2(\text{g})$ (26) and Pu(g), (18) the third law heat of the decomposition reaction is calculated to be $\Delta H_{298}^\circ = 156.1 \pm 0.2 \text{ kcal. mole}^{-1}$. The Pu partial pressure data are plotted in Fig. 807-18.

In a separate experiment a weighed, degassed pellet of PuN was heated to a constant temperature (1911°K) and the Pu^+ ion signal monitored as a function of time. At the termination of the run, the sample was reweighed and the pressure of Pu(g) calculated from the Knudsen equation. The third law heat of decomposition obtained from the weight loss experiment was $\Delta H_{298}^\circ = 155.9 \text{ kcal. mole}^{-1}$ in good agreement with the value obtained via the gold calibration.

In two other experiments, Pu metal was heated with PuN in a W Knudsen cell in the range 1544-1635°K. The second and third law heats of formation of Pu(g) obtained were $\Delta H_{298}^\circ = 82.6 \pm 1.4 \text{ kcal. mole}^{-1}$ and $\Delta H_{298}^\circ = 83.2 \pm 0.3 \text{ kcal. mole}^{-1}$, respectively. These values are in excellent agreement with the values obtained for the vaporization of Pu metal. Thus, the effect of solubility of N or PuN in Pu(l) is negligible in the temperature range of these experiments.

The third law heat of the decomposition reaction

Fig. 807-18 Vapor Pressure Data for Pu(g) Above PuN(s)

Fig. 807-19 Third Law Heat vs Temperature for the Reaction $\text{PuN(s)} = \text{Pu(g)} + \frac{1}{2} \text{N}_2\text{(g)}$.

is shown graphed vs temperature in Fig. 807-19. The lack of a temperature-dependent trend in the heat values indicates that the estimated thermodynamic functions for PuN(s) are more reliable than might be expected.

The heat of the decomposition reaction is taken to be $\Delta H_{298}^{\circ} = 156.1 \pm 2.5 \text{ kcal. mole}^{-1}$ from which one calculates the standard heat of formation of PuN(s) to be $\Delta H_{f298}^{\circ} = -73.1 \pm 3.0 \text{ kcal. mole}^{-1}$.

Further experiments designed to prove the congruency of the decomposition process are in progress. The results of the PuN study are described in detail in a separate report. ⁽²¹⁾

Carbides: As a prelude to the study of the Pu-U-C ternary system, a comprehensive investigation of the Pu-C binary system is in progress, in which the vapor pressure of Pu(g) over well characterized carbides is being determined as a function of the composition of the PuC_x phase, and as a function of temperature.

7. High Temperature Calorimetry (A. E. Ogard, G. Melton)

The high temperature heat contents and heat capacities of $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{1.98}$ are being determined as part of a cooperative program with GE-Sunnyvale. In addition, these properties are being determined for UO_2 & Al_2O_3 . To date the measurements have been completed up to $\sim 2400^\circ\text{K}$ in a drop calorimeter that was not enclosed in a glovebox. At these high temperatures, grain growth is extensive in the welds of the W capsules used to contain the oxides. Therefore the calorimeter has been relocated in a Pu handling enclosure, and the calorimeter has been recalibrated. It has been demonstrated that in the new assembly, calibration is independent of the rate heat input over the

range 700 to 2,000 cal/min., and independent of the integral heat input over the range 1,000 to 15,000 cal.

Carburization of the W capsule due to the use of a graphite resistance furnace limited the temperature of operation to $\sim 2400^\circ\text{K}$. A new furnace utilizing a W mesh heating element has been fabricated and is being tested.

In addition, components for a drop calorimeter operating in the temperature range of room temperature to 1300°K have been fabricated.

IV. ANALYTICAL CHEMISTRY

1. Spectrochemical Analysis of Impurities (W. M. Myers, C. B. Collier, R. T. Phelps)

A carrier-distillation technique involving the use of 6.4% Ga_2O_3 as a carrier and Co as an internal standard was developed for determining impurity elements in mixed carbides, mixed nitrides and mixed oxides of U and Pu. These materials are ignited to U_3O_8 - PuO_2 and excited by d.c. arc in an O_2 atmosphere. Concentrations of the following 21 elements are determined in the nominal range of 1 to 1000 ppm: Li, Be, B, Na, Mg, Al, Si, P, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Cd, Sn, Ba, Pb, and Bi. Additional impurities are determined by a second carrier-distillation technique which involves the use of 50% AgCl as a carrier. These are Ti, V, Co, Zr, Nb, Mo, Ta, and W.

The impurities commonly found in the materials (Al, Cr, Cu, Fe, Mn, Ni, Si, and W) are measured with 20% relative standard deviation, using photometry to evaluate the spectrograms. Measurement of concentrations by visual comparison of spectrograms is done faster but with a precision of 50% relative standard deviation.

The following materials with the number of samples indicated in parentheses were analyzed for impurity elements: $\text{U}_{0.8}\text{Pu}_{0.2}\text{C}$ (130), $\text{U}_{0.8}\text{Pu}_{0.2}\text{N}$ (1), $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_2$ (22), PuC (13), PuCl_3 (1), PuN (4), PuO_2 (10), and U (2).

2. Determination of U and Pu in Mixed Carbides, Nitrides and Oxides (K. S. Bergstresser, G. B. Nelson, and G. R. Waterbury)

Interest in determining U and Pu in these materials without prior separation resulted in applications of

controlled-potential coulometric and potentiometric titration methods to these assays. Repeated analyses of mixed carbide and oxide fuel materials showed that the precision (1σ) in measuring Pu was 0.04 relative percent by the controlled-potential coulometric method and 0.07 relative percent by potentiometric titration. The precision in measuring U by either method was about 0.08 relative percent, but the controlled potential coulometric method had a slight positive bias (+ 0.1 percent). The reliability was adversely affected by trace amounts of W, Fe, or carbonaceous residues left from dissolution of carbide materials. Ignition of the carbides to oxides in air at 950°C removed carbonaceous materials quantitatively, but chemical separation would be required to remove W or Fe if present in significant concentration. Both methods were applied successfully to analysis of various U-Pu materials, but the controlled-potential coulometric methods generally were preferred because of their good precision and the small sample (5 to 10 mg) required.

3. Determination of Oxygen in (U, Pu)O₂ (C.S. MacDougall, M.E. Smith, D.E. Vance, and G.R. Waterbury)

A method was developed in which O₂ was liberated as CO and CO₂ by inert-gas-fusion at 2000°C from an oxide fuel - C pellet and then measured gravimetrically. Repeated analyses of high-purity ThO₂, U₃O₈, PuO₂, and (U, Pu)O₂, using an automatic temperature programmer on the furnace control, showed that the method was not biased. The relative standard deviation was 0.1 percent in analyzing 1-g samples of non-Pu materials and 0.2 percent for Pu-containing materials handled in a glove box. Application to analysis of (U, Pu)O₂ fuel pellets required grinding of the pellets prior to weighing and blending with C. The entire operation was accomplished satisfactorily with an over all precision (1σ) of 0.2 relative percent.

Gas chromatographic and microwave discharge spectrophotometry finishes to measure the CO and CO₂ also are being investigated in an attempt to improve the precision of the measurements.

4. Determination of O/M Atom Ratios in (U, Pu)O₂ (J.W. Dahlby and G.R. Waterbury)

A gravimetric method reported by Lyon (GEAP Rpt. 4271, 1963) produced high O/M atom ratios (between 2.006 and 2.008) for UO₂ when this material was oxidized in air in the recommended manner and then reduced in He-H₂ as the sample was heated from room temperature to 950°C . Experiments performed using a thermo-balance showed that introduction of the reducing gas mixture while the sample was at 950°C produced UO_{2.001} and the standard deviation in the O/M ratios was 0.001. To test the method for analyzing (U, Pu)O₂ materials, mixtures containing 4 g of U and 1 g of Pu were oxidized in air and then reduced by He-H₂ at 950°C . Slightly erratic results were obtained. When the reducing gas mixture was introduced to the mixed oxides at a temperature between 980 and 1000°C , the O/M atom ratios obtained for eleven determinations averaged 2.001 with a standard deviation of 0.001. Application of the method to analysis of (U, Pu)O₂ fuel pellets was started.

As a check on the thermogravimetric method and also in an effort to have a second method available for O/M ratios, the direct measurement of the uranium, plutonium, and oxygen will be attempted on material prepared as a single batch. The analyses of (U, Pu)O₂ described in Sections 1 and 2 above indicate this may be possible with the degree of precision desired.

5. Determination of C in PuS (C.S. MacDougall, M.E. Smith, and G.R. Waterbury)

A combustion-manometric method was modified for application to the determination of C in the ppm concentration range in PuS. Modifications included selective trapping of the SO₂ and SO₃ formed in the combustion, and the use of Al foil envelopes to contain PuS powders during the combustion. Repeated analyses of PuS mixed either with Pu metal, having a known C content, or with C showed that the relative standard deviation of the method was about 10 percent for determining C in the ppm concentration range. Interference from the SO₂ and SO₃ was not observed with the modified method.

6. Applications of the Electron Microprobe
(E. A. Hakkila and H. L. Barker)

Approximately ninety-five samples of various carbides material from various preparatory experiments were examined to identify impurities, precipitates, inclusions and phases, and to determine homogeneity. In most, the matrices were homogeneous with respect to U, Pu, and C on a macroscale although a few were heterogeneous on a microscale. Samples enriched in C generally were heterogeneous, but metal-rich ceramics were homogeneous. Some isolated areas were found in the matrices that were depleted in U and dark in color, and other areas were light in color and depleted in Pu. Inclusions generally were enriched in Pu and depleted in U and C with respect to the surrounding matrix. Some inclusions contained Si, Fe, Cu, Ni, or W as impurities but not necessarily associated together. Si also was heterogeneously distributed along grain boundaries in some samples. Included among the phases identified were: (1) brown phases enriched in U, rounded white phases that were enriched in Pu and contained Si and W, white phases enriched in U, low density phases enriched in Pu, and flat white phases and gray phases that were enriched in Pu and did not contain Si or W. Precipitates generally were enriched in Pu relative to the matrix.

The diffusion zone of a UC-PuC diffusion couple was found to be approximately 200 μ wide. The C content in this zone was low as compared to either carbide. Grain boundary diffusion of Pu into the UC was observed.

White particles in a melted (U, Pu)O₂ matrix were identified as predominantly W containing some Fe. Two samples of (U, Pu)O₂ were examined to determine homogeneity and to identify impurity phases. The U and Pu were distributed homogeneously on a micro and macro scale. Major constituents in various impurity phases were: (1) W, Fe, Ni, and P, (2) Fe, Ni, and P, and (3) Fe, Cr, and S.

7. Determination of Oxygen with the Electron Microprobe

(E. A. Hakkila and H. L. Barker)

The sensitivity of the determination of O₂ with the electron microprobe equipped with a flow proportional detector was estimated from the intensities of the K α x-ray of O₂ measured for several oxide materials, including BeO, Al₂O₃, SiO₂, CuO, ZrO₂, UO₂, and PuO₂. The measured intensities indicated that probably no less than 1 to 2 percent of O₂ could be detected in a material such as (U, Pu)C. As these intensities are lower than should be obtained with this equipment, a new detector was ordered, and replacement of the detector window with a thin organic film was investigated.

8. Miscellaneous Analysis

Approximately 175 samples of (U, Pu)C materials from various preparatory operations and experiments were analyzed by controlled-potential, combustion, inert-gas-fusion, and Kjeldahl methods for one or more of the following elements: U, Pu, O₂, C, H₂, and N₂.

Eighteen samples of (U, Pu)O₂, having U/Pu atom ratios between 21/1 and 2.2/1 were analyzed for U and Pu by potentiometric and controlled-potential coulometric methods. The precision (1 σ) of these determinations was less than 0.1 percent.

PuN, PuO₂, PuC, Pu metal and U metal were analyzed by standard methods for constituents and impurities of interest.

Six Pu metal and two U metal starting materials were analyzed for C, O₂, and N₂. The concentrations of these elements were in the low ppm range, verifying that the materials were pure with respect to these elements.

A few samples of UO₂ were analyzed for major constituents, and twenty-three Pt foils were analyzed for O₂.

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PROJECT 808

COMPATIBILITY OF SODIUM-BONDED (U,Pu)C AND (U,Pu)N FUELS WITH CLADDING MATERIALS

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I. INTRODUCTION

(U,Pu)C and (U,Pu)N are regarded as attractive alternates to mixed oxides as fuels for commercial LMFBR application. The high heavy-atom densities and thermal conductivities of the mixed carbide and nitride make it possible for these fuels to outperform mixed oxides. Full exploitation of carbides and nitrides dictates the use of a gap between fuel and clad to accommodate fuel swelling (with minimal fuel-cladding mechanical interactions) and a high thermal conductivity path across the gap to limit fuel temperature. These conditions can be met by filling an annulus between fuel and clad with sodium.

Before a satisfactory sodium-bonded fuel element can be developed, however, information is required that will identify the number and severity of problems associated with sodium bonding and will suggest solutions to these problems. Problem areas that are being studied in this experimental program are:

1. The mechanisms and kinetics of carbon transfer to claddings through the sodium bond.
2. The significant fuel and sodium variables that affect compatibility.
3. The consequences of exposing fuel to coolant sodium.
4. The behavior of sodium-bonded fuel elements under irradiation.
5. The performance limitations of the sodium bond under high heat flux conditions.

Efforts are now concentrated on the mixed carbide fuel, though investigation of the nitride system will be initiated when suitable fuel becomes

available. Type 316 stainless steel is the base cladding material being studied, though vanadium alloys developed by ANL and Westinghouse also will be tested.

As prerequisites for this compatibility program a number of developmental efforts have been undertaken. These include establishment of (1) techniques for the production of single phase monocarbide pellets of known composition and dimensions, (2) techniques and equipment for fuel pin loading, bonding, and inspection, (3) techniques for removal of bonding sodium from fuel¹ and for metallographic examination of fuel, and (4) techniques and equipment for determining the distribution of fission products in irradiated fuel pins.

II. SYNTHESIS AND FABRICATION OF (U,Pu)C PELLETS (M. W. Shupe, A. E. Ogard, R. W. Walker, C. Emery, G. Moore, S. McClanahan)

A. General

Efforts have been directed toward standardizing the procedures for producing single phase monocarbide pellets (see Project 807) of known composition and dimensions. These pellets will be utilized in EBR-II irradiation experiments and for compatibility testing.

Basic process steps are:

1. Multiple arc melting of a physical mixture of ²³⁵U, Pu, and C on a 60 g scale using a graphite electrode.
2. Solution treatment of the arc melted ingot for 24 h at 1600°C.
3. Crushing of the ingot in a WC vibratory mill, followed by screening of the resulting powder to -62 µ.
4. Blending of several powder batches.

5. Elimination of excess carbon by reaction with H_2 at $850^\circ C$.
6. Cold compaction at 20 tsi into pellets without the use of binders or sintering aids.
7. Sintering the pellets in Ar at $1800^\circ C$.
8. Characterization of the pellets by linear dimensioning, weighing, metallography, x-ray diffraction analysis, chemical analysis (including determination of U, Pu, C, N, O), spectrochemical analysis for trace impurities, electron microprobe analysis, and radiography for detection of possible internal cracks.

B. Results During FY 1968

A total of 1012 pellets have been produced by the above process. Results of the characterization of randomly selected samples from the different lots are shown in Tables I and II.

The following conclusions can be drawn from these results:

1. It is possible to prepare pure single phase (U,Pu)C pellets by this process.
2. Single phase $U_{0.8}Pu_{0.2}C$ exists as a slightly substoichiometric material. The monocarbide C/(U + Pu) ratio of 0.97 ± 0.01 is readily obtained by reaction of excess C with H_2 .
3. The concentrations of U and Pu can be controlled to better than 0.80 ± 0.01 g-atom/mole and 0.20 ± 0.1 g-atom/mole carbide, respectively.
4. The O and N concentrations can be maintained at 0.007 ± 0.003 g-atom/mole and 0.005 ± 0.002 g-atom/mole, respectively.
5. The lattice parameter of the single phase monocarbide is $4.9649 \pm 0.0004 \text{ \AA}$.
6. The density of a large number of pellets

Table I
Characterization of $U_x Pu_y C_z$ Pellets

Lot	X	Y	Z	O	N	Diam	Density % T.D.	Lattice Parameter $\text{\AA}$	Pellet Microstructures
1	0.794	0.206	0.97	0.008	0.009	0.261	91	4.9655	MC, I
2	0.800	0.200	0.98	----	----	0.260	91	4.9654	MC, I
3	0.797	0.203	0.94	----	----	0.264	90	-----	MC, I
4	0.795	0.205	0.98	0.007	0.003	0.266	85	4.9654	MC
5	0.800	0.200	0.97	----	----	0.260	90	4.9655	MC
6	0.798	0.202	0.99	0.004	0.005	0.264	88	4.9651	MC, I
7	0.798	0.202	0.98	----	----	0.266	(85)	-----	MC, I
8	0.796	0.204	0.96	0.015	0.001	0.264	89	4.9636	MC
9	0.797	0.203	0.95	0.011	0.008	0.266	(88)	4.9651	MC, I
10	0.793	0.207	0.99	----	----	0.265	(88)	4.9650	MC, I
11	0.796	0.204	0.99	0.009	0.005	0.266	(88)	4.9656	MC, I
12	0.796	0.204	0.99	0.004	0.007	0.263	(90)	4.9645	MC
13	0.795	0.205	0.97	0.005	0.009	0.264	91	4.9652	MC
14	0.796	0.204	0.97	0.003	0.005	0.263	(90)	4.9645	MC
15	0.800	0.200	0.97	0.005	0.006	0.265	(91)	4.9648	MC
16	0.797	0.203	0.97	----	----	0.265	(91)	4.9643	MC
17	0.798	0.202	0.98	----	----	0.263	(90)		MC
18	0.798	0.202	0.97	0.009	----	0.264	(88)		MC
19	0.797	0.203	0.98	0.008	0.003	0.263	89		MC
20	0.795	0.205	0.95	0.009	----	0.261	89		MC
21	0.793	0.207	0.96	0.003	0.003	0.263	92		MC
22	0.792	0.208	0.97	0.004	0.004	0.263	91		MC
Av.	0.796	0.204	0.97	0.007	0.005	0.264	90	4.9649	
	± 0.007	± 0.002	± 0.01	± 0.003	± 0.002	± 0.002	± 1	± 0.0004	

Note: I indicates < 0.5 v/o impurity phase
Densities in () are mechanically measured

Table II
Average Spectrochemical Analysis of
(U,Pu)C Pellets
concentration expressed in ppm

Li < 1	Co < 5
Be < 1	Ni < 24
B < 1	Cu 40
Na < 2	Zn < 10
Mg < 5	Sr < 5
Al < 10	Zr < 100
Si 132	Nb < 50
P < 50	Mo < 10
Ca < 5	Cd < 10
Ti < 50	Sn < 2
V < 5	Ba < 10
Cr < 10	W 20
Mn 3	Pb < 2
Fe 68	Ri < 2

from different lots can be reproducibly controlled at $90 \pm 1\%$ T. D. In so doing, the as-sintered diameter of the pellet is maintained at 0.264 ± 0.002 in.

During the year, 211 (U,Pu)C pellets were supplied for compatibility experiments, and 119 pellets were supplied for EBR-II irradiations. Ten single phase UC pellets were also supplied for use as insulator plugs in the EBR-II capsule loading. The present inventory of single phase monocarbide pellets numbers 658. No effort was allocated for preparation of nitride pellets for compatibility testing during this period.

III. LOADING FACILITY FOR TEST CAPSULES (D. N. Dunning)

A. General

A prerequisite to a compatibility program involving (U,Pu)C and sodium is a satisfactory capsule loading and bonding facility. There is little point to obtaining well-characterized materials for testing if these materials are contaminated before they are placed in test. Sodium and (U,Pu)C are sufficiently reactive that all operations must be performed either in vacuum or in a high-quality inert atmosphere. A loading facility for handling these materials has been operational during the last half of the year, though it is not yet complete. An inert-atmosphere glovebox to facilitate handling

fuel pellets prior to their insertion into capsules must still be installed; in addition, an inert gas cleanup system must be incorporated into the facility. Most of the components for these units are on hand.

B. Results During FY 1968

All loading operations are done in evacuable gloveboxes using high-purity helium as the cover gas. The present procedure provides helium with less than 10 ppm total impurities, as measured by a tungsten hot wire meter, at the start of a cycle of operation; typically, 18 ppm total impurities are present at the completion of an operations cycle. Figure 1 is a general laboratory view showing two inert boxes,

Fig. 1. Capsule loading facility.

a sodium supply loop, and associated instrumentation. There are three stations in the system; (1) fuel loading, (2) sodium purification, casting, extrusion, and loading, and (3) capsule closure welding. The present procedure is to load fuel pellets and sodium in the same box, because the evacuable fuel loading and inspection box has not been incorporated into the system. The sodium loading box and closure welding box are kept "alpha cold," so care must be taken not to contaminate the box during loading operations.

The sodium purification loop and sodium loading box are operating satisfactorily. The sodium supply loop runs at a bulk sodium temperature of 175°C and a cold trap temperature of 130°C . The initial work in the sodium loading box was done utilizing a pump-down and back-flush procedure. However, an inert gas purification recirculation unit has been installed on the box and final checkout is in progress. The pump-down and back-flush method of operation has

produced test capsules of satisfactory quality, but it places restrictions on the time and type of work done in the gloveboxes.

A new two-section, evacuable inert atmosphere glovebox for fuel pellet loading and inspection has been assembled and is awaiting delivery of an inert gas cleanup system. This box provides both "alpha hot" and "alpha cold" sections in the same box. A loading procedure has been developed that eliminates transfer of contamination from the fuel loading facility to the sodium loading and final closure welding stations.

Bonding of the clad and fuel pellets with sodium is accomplished by heating to 600°C to promote wetting followed by a 300°C treatment with a magnetostrictive device operating against the capsule bottom. Destructive and nondestructive tests have not revealed any defects in the annular sodium volume after this treatment.

All of the required capsules for the currently scheduled tests were loaded and bonded. The capsules ranged in length from 3 in. to 39 in. and contained from 3 to 53 (U,Pu)C fuel pellets and 1 to 10 g of sodium.

IV. CARBIDE FUEL COMPATIBILITY STUDIES (F. B. Litton, L. A. Geoffrion, J. H. Bender)

A. General

The objectives of this program are to study the interactions among single-phase mixed uranium-plutonium carbide, a sodium bond, and potential cladding materials, i.e., to investigate the technology related to sodium-bonded fuel elements. There are two approaches to the experimental work. One approach is to determine the reactions occurring between $(U_{0.8}Pu_{0.2})C$ and potential cladding materials, using Type 316 stainless steel and a high-strength vanadium-base alloy as the first and second choices of cladding material, respectively. A second concurrent set of experiments is designed to study the mechanism of carbon transport through sodium, the effect of impurities such as oxygen, and the carburizing potential of sodium in mutual contact with carbides and the preferred cladding materials.

Capsules containing sodium-bonded, single-phase (U,Pu)C are tested in sodium loops at 750°C for periods up to 10,000 h. High-purity, thoroughly characterized sodium is used for the studies. Fuels

of known composition, produced by methods developed by the Ceramic Plutonium Fuel Materials (807) program at LASL, are used in all tests. Most of the testing is performed on single-phase (U,Pu)C fuel in which the Pu/U ratio is maintained at 0.2, but some experiments are being carried out on material containing a second phase (either metallic or carbon-rich). Other experiments are being carried out on stoichiometric and hyperstoichiometric UC to determine the effect of plutonium addition on the behavior of the carbide fuel.

B. Results During FY 1968

1. Removal of Sodium Bond from Sintered (U,Pu)C Fuel Pellets¹

In the early stages of this program it became apparent that a suitable technique for the removal of the sodium bond after test (one that would not disturb the structure of the fuel pellets) was required. The techniques considered were distillation, dissolution in high-purity organic reactants, mercury amalgamation, and dissolution in liquid ammonia. Evaluation of the latter two techniques has been deferred while work was completed on distillation and dissolution techniques.

In the dissolution techniques, the sodium bond was removed from the fuel pellets by reaction with butyl and ethyl alcohols, and with ethyl alcohol containing 5 vol. % of distilled water. In the distillation technique, the sodium bond was removed from the fuel pellets by distilling the sodium under a vacuum of 5×10^{-6} torr at a temperature of 475°C. Both techniques required 3 to 7 h for sodium removal.

The structure of sintered (U,Pu)C was studied by metallography after removing the sodium bond by dissolution and distillation. Porosity was determined by the method of two-dimensional, systematic, point count. Fuel porosity after sodium removal was compared to porosity of unbonded, "as-received" pellets. The data on porosity were obtained from at least three pellets for each technique and are presented in Table III.

Low-temperature vacuum distillation is the preferred method for removing sodium from sodium-bonded fuel capsules since this technique has no appreciable effect on either the size or shape of the pores. Both pore size and shape are changed by dissolution techniques. Butanol has less effect on the micro-

Table III

Effect of Sodium Removal Techniques on the Porosity of (U,Pu)C Pellets ($\sim 90\%$ T.D.)

Technique	Average Porosity (%)	Maximum Porosity (%)	Maximum Pore Size (μ)
None (Unbonded pellets)	10.1	11.0	16.6
Ethanol	12.5	13.0	21.8
Butanol	11.7	12.2	16.2
Distillation	8.5	10.0	12.9
Ethanol + 5% H ₂ O	19.7	23.3	33.3

structure than ethanol, although both produce a rounding of the pore edges.

2. Compatibility of Clad with Sodium-Bonded Carbide Fuel

An isometric drawing of the capsule types used for studying the compatibility of sodium-bonded carbide fuel is shown in Fig. 2. Type "A" capsules (0.30-in. o.d. by 0.10-in. wall by 3-in. long) are loaded with three (U,Pu)C fuel pellets (0.265-in. diam by 0.25-in. long) and one length of extruded sodium rod (0.24-in. diam by 1-in. long). After the closure weld is made, the capsules are sodium bonded using the procedure outlined in Section III (Capsule Loading Facility). They are then tested in hot-trapped, isothermal sodium loops. Provision is made to invert the test capsules at the end of the test period (prior to cooling them) to separate the sodium in the bond for subsequent analysis. Each of the isothermal loops is equipped with a vacuum distillation assembly for oxygen analysis of the loop sodium.

Type "B" capsules are loaded and bonded using techniques similar to those used for Type "A" capsules. In addition, they are sealed in welded stainless steel cans. Tests on Type "B" capsules are conducted in inert gas furnaces.

Three Type "A" capsules were tested at 650°C for 1000 h and three additional capsules were tested at 750°C for 1000 h. The capsules contained (U,Pu)C characterized as essentially single-phase material. After tests, the capsules were inverted at temperature to separate the bonding sodium from the fuel. Residual sodium was removed from the pellets by vacuum distillation at 500°C.

Results of analysis of the bond sodium from

WELDED SECONDARY CONTAINMENT CAPSULE

DUPLEX CAPSULE

3 INCH TEST CAPSULE

TYPE "A"

1 GRAM Na

5 GRAMS Na

(U,Pu)C

TYPE "B"

Fig. 2. Isometric view of two types of capsules used in compatibility studies.

these capsules for fuel constituents are shown in Table IV.

Table IV

Analyses of Bond Sodium from 1000 h Tests

Capsule	Test Temp. (°C)	Concentration, ppm		
		U	Pu	C
D-1600	650	60	2.9	Insufficient sample
D-1601	650	2400	350	Insufficient sample
Composite from three capsules	750	6	0.8	42

The wide variation in U and Pu concentrations obtained from the different capsules indicates that these elements were probably present as particulate matter. However, the U/Pu ratios differ from that of the carbide fuel, so these particulates were not simple pieces of the mixed carbide fuel.

Samples of the Type 316 stainless steel cladding

from each capsule were examined by metallographic, electron microprobe, and microhardness techniques. There was no evidence that reaction had occurred between clad and fuel. A sample of the cladding from a capsule tested at 750°C was prepared for ^3He activation analysis, but this was not completed during this reporting period.

Metallographic examination of the fuel pellets tested at 650°C revealed no significant change from their initial characteristics. However, a widening of the grain boundaries at the sodium contact surfaces was noted in the pellets tested at 750°C. This is shown in Fig. 3.

Fig. 3. Typical structure of pellets tested at 750°C at the sodium contact surface. Electro-etched, 300X.

Type "B" 316 stainless steel capsules containing (U,Pu)C pellets were tested to obtain compatibility and sodium bond analytical data. Pellets containing excess carbon and excess heavy metal, as well as single-phase material, were tested to determine if variations in fuel composition affected compatibility. The larger amount of bond sodium in these capsules (compared to Type "A" capsules) allowed more detailed analyses to be run. Pre-test chemical compositions of pellets in these capsules are shown in Table V.

These capsules were tested at 750°, 650°, and 550°C for 1000 h. Chemical analyses revealed that the carbon content of the bond sodium, which was 10 ppm before test, increased to 20-70 ppm during

Table V
Characterization of (U,Pu)C Pellets
Tested in Type "B" Capsules

Fuel Type	Major Impurity (ppm)	(% T.D.)	Metallography
Excess C	Si, 250	88.5	Needle-like second phase
Stoichiometric	W, >1000	90-95	Essentially single phase
	Si, 450		
Excess heavy metal	W, >1000	93.0	Metal phase present
	Si, 540		
	Al, 165		

the tests. No other significant change in impurity content of the sodium was detected.

Specimens from the Type 316 stainless steel capsules were subjected to metallographic and electron microprobe examination after test. Those capsules containing fuel with a needle-like second phase showed carburization at test temperatures of 650° and 750°C. This is shown in Fig. 4.

Fig. 4. Type 316 stainless steel clad showing carburization of sodium contact surface after 1000 h at 750°C. 300X.

Microprobe analysis showed that the dark reaction layer at the inner surface of the capsule was enriched in carbon relative to the adjacent matrix. A scan perpendicular to the surface indicated carbon diffusion into the stainless steel to a depth of approximately 100 microns. Grain boundary enrichment of carbon was not observed. No significant differences

in chromium, iron, nickel, and molybdenum x-ray intensities as a function of proximity to the surface of the steel were observed.

The capsules containing fuels of essentially single phase and hypostoichiometric compositions also showed carburization. Electron microprobe examination of these capsules (750°, 650°, and 550°C test temperatures) showed a wide range of carbon x-ray intensities along the contact surfaces and varied depths of carbon penetration. The scans perpendicular to the surfaces indicated no carbon diffusion to depths exceeding 300 microns. No significant differences in chromium, iron, nickel, and molybdenum x-ray intensities as a function of proximity to the surfaces were detected.

Control capsules that contained no fuel pellets were also tested at 550°, 650°, and 750°C. These capsules exhibited localized carburization. Analyses of the sodium in these control capsules revealed that the carbon concentration, which was originally approximately 10 ppm, decreased to < 10 ppm. (The final carbon concentrations could not be determined more precisely because 10 ppm is the detection limit for carbon in sodium). This unexpected carburization of control capsules complicates the interpretation of the experimental results. However, the capsules containing fuel with excess carbon were carburized significantly more than were the control capsules.

Compatibility tests were also performed with uranium carbide containing 4.8 and 5.2 a/o carbon. The purpose of these tests was to determine the effect of plutonium content of the fuel on compatibility with Type 316 stainless steel. Capsules containing sodium-bonded UC pellets were heated at 750° and 650°C for 1000 h.

Metallographic examination showed that the pellets of the two compositions had essentially the same structure, consisting of the di- and sesquicarbide phases distributed in the monocarbide matrix. Extensive carburization of the stainless steel capsules - considerably more than was experienced in any of the tests with (U,Pu)C fuels - occurred during test. Electron microprobe scans of the clad contact surfaces indicated a depletion of chromium and molybdenum and an enrichment of iron, nickel, and carbon. The depths of the affected zones were a maximum of 500 microns at 750°C and 300 microns at

650°C.

X-ray examination of the uranium carbide pellet containing 5.2 a/o C showed a carbon depleted zone at the surface consisting of mono- and sesquicarbide phases. This is shown in Fig. 5. The depletion of

Fig. 5. Surface of 5.2 a/o C uranium carbide pellet after 1000 h at 750°C. 300X.

the dicarbide phase confirmed previous information that the sesqui- and monocarbide phases are more stable than dicarbide in a sodium/Type 316 stainless steel environment.²

Additional compatibility tests in a thermal gradient loop are planned for EBR-II prototype fuel pins. This loop, shown in Fig. 6, is constructed of Type 304 stainless steel; it is designed for a sodium inlet temperature of 700°C and an outlet temperature of 400°C over a 2-3/4-in. i.d. by 20-in.-long test section. The loop contains approximately 1.5 gal of zirconium-gettered sodium, which is circulated at a rate of approximately 0.5 gal/min. Heat is supplied by 1.5 kW immersion heaters at the test section inlet and removed by air cooling. The thermal-gradient loop is equipped with a distillation sampler for oxygen analysis of the sodium.

3. Corrosion Study

The behavior of selected cladding materials in zirconium-gettered sodium is being investigated as a function of temperature. Groups of six one-half in. square specimens each of vanadium alloys, stainless steels, and other refractory metals and alloys were

Fig. 6. Thermal gradient sodium loop.

immersed in sodium in a hot-trapped forced-convection loop. (Specimen and sodium analyses have been given in LA-3820-MS and LA-3880-MS.) Tests were run at 550°, 650°, and 750°C for 1000 h. Results of these tests are shown in Table VI.

Films were detected on the vanadium alloys tested at 650°C, but the amounts were insufficient for x-ray diffraction analysis. The vanadium alloys tested at 750°C were covered with a light tan film resembling rutile, which is composed largely of titanium-rich mononitride. Inasmuch as the sodium had been analyzed to contain < 5 ppm nitrogen, the data suggest transfer of nitrogen from the stainless steel loop.

Specimens of Type 304 stainless steel, Type 316L stainless steel, V-20Ti, and V-15Ti-7.5Cr, tested at both 650° and 750°C, were subjected to electron microprobe examination to determine whether a depletion of any constituents occurred near the surface of the specimen. The only significant change in composition that was detected was a depletion of titanium to a depth of 30 microns in the V-20Ti sample tested at 650°C.

V. VENTED (U,Pu)C EXPERIMENTS (J. C. Clifford, J. H. Bender)

A. General

Sodium and single-phase (U,Pu)C are being contacted in a small forced-convection sodium system for periods of 1000 h and longer at 700°C. The experiments are limited to determining the out-of-pile stability of single-phase (U,Pu)C in flowing sodium in support of studies of fission product release from the irradiated material. (Section IV, Project 801). The tests employ fuel pellets and capsules of the

Table VI
Corrosion of Materials in Hot-Trapped Sodium (1000 h)

Material	Annealing Temp (°C), 1 h	Weight Change* (mg/cm ²)		
		550°C Test	650°C Test	750°C Test
V	900	- 0.37	- 0.023	+ 0.25
V-10Ti	900	+ 0.11	- 0.029	+ 0.47
V-20Ti	900	--	+ 0.044	+ 0.44
V-40Ti	900	+ 0.09	+ 0.108	+ 0.39
V-15Ti-7.5Cr	850	+ 0.04	+ 0.241	+ 0.83
Zr	850	--	--	+ 0.54
Nb	850	--	--	+ 0.07
Nb-1Zr	1350	- 0.12	--	+ 0.021
Nb-10W	1350	- 0.05	--	- 0.006
Type 304 SS	1000	None	- 0.037	- 0.23
Type 316L SS	1000	None	- 0.040	--

*Average of six one-half in. square specimens.

same materials and dimensions as those used in the compatibility program (Section IV Project 808 Type "A" capsules) except that one or both end caps are absent from the capsules. With only the lower end cap in place, fuel is isolated from the flowing sodium in the loop by a 2-in. column of static sodium. When neither end cap is used, system sodium flows in the gap between pellets and tube wall. Capsules are tested in sets of three, and each set consists of two flow-through and one static-bond capsule. Upon completion of a test, residual sodium is removed from the capsules by vacuum distillation, and pellets and capsules are examined by metallographic and electron beam microprobe techniques.

B. Results During FY 1968

Tests of 1000-h and 2000-h duration have been completed, and a 4000-h test will be completed during July. Capsules removed after 1000 h exhibited no features by which they could be distinguished from control materials, except for the presence of sodium in the pellets' internal voids. Midway during a 2000-h exposure, the loop developed a serious sodium leak and was badly contaminated with air. The loop was repaired and cleaned, and the test was completed without further incident. No oxygen analyses were conducted on loop sodium prior to the failure so the length of time during which the oxygen concentration was above normal, and the oxygen levels attained, are unknown. Because all results were suspect, a second 2000-h test was conducted. This test also was affected by oxygen-contaminated sodium and produced essentially the same phenomena seen after the loop failure.

All capsules tested in the accidentally contaminated sodium were affected by impurities in the sodium, but the effects were much more pronounced in the flow-through capsules. Figure 7 shows a longitudinal section of a pellet from a flow-through capsule. Extensive cracking has taken place adjacent to the surfaces, and what appears to be an acicular precipitate is visible in a small volume along the cylindrical surface of the pellets (Fig. 8). Microprobe examination and x-ray diffraction measurements of this material have failed to detect any phase other than the monocarbide. A section from the Type 316 stainless steel wall of the same flow-through capsule is shown in Fig. 9 to illus-

Fig. 7. (U,Pu)C pellet from a flow-through capsule after 2000 h in 700°C sodium containing oxygen. 4X.

Fig. 8. Surface region of the (U,Pu)C pellet shown in Fig. 7. An acicular phase is visible. Electrolytic etch, 300X.

trate the changes taking place at localized regions in the fuel section of flow-through capsules. The capsule's inner surface exhibits a white layer approximately 8 μ thick and, adjacent to this, a band in which carbide precipitation has occurred. The white layer is depleted in chromium and rich in carbon, while the band containing carbide precipitates shows no evidence (microprobe) that redistribution

Fig. 9. Wall section in the fueled region of a flow-through capsule (Type 316 stainless steel) after 2000 h in 700°C sodium containing oxygen. Chromium has been removed from a layer along the inside surface and carbide precipitation has occurred in the adjacent band. Electrolytic etch, 300X.

of the alloy major constituents has occurred. Carbon enrichment could be detected to a maximum depth of $\sim 80 \mu$, or 1/3 of the wall thickness. Although alpha contamination was observed on all capsules, plutonium and uranium could not be detected in the clad.

Aside from the occasional presence of an acicular phase, fuel removed from static bond capsules appeared similar to that shown in Fig. 10. (The light phase appearing at grain boundaries is a Pu- and Si-rich impurity present in the "as-received" material.) Stainless steel from the fueled region of the static bond capsules exhibited spotty carbide precipitation, but no chromium-depleted surface zone was found.

Differences between flow-through and static bond capsules appear to be differences of degree rather than of kind and probably arise from the fact that ingress of impurities and egress of reaction products are diffusion limited in the static bond configuration, while a more direct link is provided between system sodium and fuel in the flow-through capsules.

After both 2000-h tests, uranium and plutonium were recovered from the zirconium hot traps, indi-

Fig. 10. (U,Pu)C pellet from a static bond capsule after 2000 h in 700°C, oxygen-contaminated sodium. The light grain boundary phase is a silicon-rich impurity present in the "as-received" material. Electrolytic etch, 300X.

cating that some fuel had been lost from the capsules. However, no reliable estimates of fuel loss can be made because uranium and plutonium were badly segregated in the traps and because the traps have been demonstrated to be poorer collectors of uranium and plutonium than the stainless steel surfaces of the loop.

After the second 2000-h test, system sodium was analyzed for several elements, including the principal constituents of the fuel and stainless steel. Aside from the presence of plutonium after test, at a level less than 0.1 ppm, no significant changes were noted. No evidence could be found to indicate that fuel particulates were present in the sodium.

Although no reliable oxygen concentration could be established during the second test, the level would appear to be relatively low. The stainless steel racks and the outside surfaces of the capsules (Fig. 9) did not appear to have been attacked, and microprobe analyses failed to show any Cr, Ni, or Mo depletion in the vicinity of these surfaces. Published information indicates that chromium and nickel depletion can occur at the surfaces of Type 316 stainless steel after 2000 h in sodium containing as little as 12 ppm oxygen,³ although the ratio of

stainless steel surface to sodium volume and the sodium velocity will have some effect on the oxygen concentration and contact time required to cause depletion.

VI. POST-TEST EXAMINATION (J. H. Bender)

A. General

Identification of different phases and precipitates in (U,Pu)C fuel and clads and determination of the changes that these materials undergo during testing are essential to the compatibility testing program. Metallographic examination is one of the chief diagnostic tools for this investigation. It is often necessary to develop and standardize new techniques for use in metallographic examination of test materials. Procedures for the identification of the phases that may be present in sintered (U,Pu)C (metallic, dicarbide, and sesquicarbide) have been developed. Delineation of Pu-Si metallic inclusions in the (U,Pu)C matrix is also possible.

Interest in the physical appearance (macro- and microstructure) of the sodium bond has led to initiation of a study to develop a metallographic polishing technique for metallic sodium. Selected information on the process is given below.

B. Results During FY 1968

A metallographic procedure that distinguishes between the metallic, dicarbide, and sesquicarbide phases and precipitates of Pu-Si agglomerates in sintered (U,Pu)C fuel has been developed, standardized, and proven effective by cross-check with electron microprobe analyses. The technique is a step-wise procedure consisting of stain-etching, microhardness testing, and preferential etching.

1. Sample Preparation

The (U,Pu)C fuel pellets (0.265-in. diam by 0.25-in. long) are sectioned longitudinally and vacuum-impregnation mounted in epoxy resin. The mounted sections are wet-ground on SiC papers through 600 grit with lapping oil as the lubricant. Polishing is performed by hand and with automatic equipment on synthetic napless lap coverings using 15 μ , 6 μ , and 1 μ diamond paste with silicone oil as the extender and lubricant. The sample mounts are ultrasonically cleaned with methyl chloroform between each preparative step. Because of hydrolysis prob-

lems¹ with (U,Pu)C specimens, the grinding, polishing, and cleaning liquids were analyzed for their water content, and molecular sieves were placed in the lubricant containers to absorb the small amount of water present.

2. Etching and Microhardness Techniques

The prepared samples are electrolytically etched with 1:1:1 lactic, nitric, and acetic acids (2.5 V dc, 9 sec, touch probe) to distinguish grain boundaries and precipitates.

The differentiation of the metallic, dicarbide, and sesquicarbide phases by optical means utilizing distinctive grain and precipitate shapes proved effective only with the dicarbide phase, which appears as needle-shaped precipitates within the grains, as shown in Fig. 11.

Fig. 11. Hyperstoichiometric (U,Pu)C. Matrix = MC, needle phase = MC₂. Electro-etched, 300X.

Diamond point microhardness testing of the precipitates and the surrounding matrix proved valid in detecting the metallic phase; i.e., the metallic phase has lower hardness numbers than the matrix. Precipitates with higher hardness numbers than the matrix have been determined by analysis to be sesquicarbides or metallic agglomerates containing plutonium and silicon. The microhardnesses of these types of precipitates are all approximately the same.

A preferential etch for Pu-Si inclusions (1:1:3 hydrofluoric acid, nitric acid, and methanol),⁴ swab-applied after the electro-etch and hardness testing,

colors the Pu-Si precipitates, removes all coloration of the matrix grains, and leaves the metallic or sesquicarbide phases white.

3. Qualitative Metallographic Procedure⁵

a. The sample of (U,Pu)C is electro-etched to distinguish grain boundaries, porosity, and precipitates. Figures 12 and 13 are typical examples of hypo- and hyperstoichiometric (U,Pu)C.

Fig. 12. Hypostoichiometric (U,Pu)C. Electro-etched, 300X.

Fig. 13. Hyperstoichiometric (U,Pu)C. Electro-etched, 300X.

b. The microhardnesses of precipitates and matrix grains are measured to distinguish between the metallic phase and harder phases (M_2C_3) or metallic precipitates containing plutonium and silicon.

c. Samples are then re-etched with the Pu-Si preferential etch. If a precipitate or a segment of it develops a color, Pu-Si inclusions are present; lack of color indicates that the precipitate is sesquicarbide. Figure 14 is typical of an agglomerate containing metallic plutonium and silicon. Figure 15 exhibits precipitates of the sesquicarbide phase in a double-etched sample.

Fig. 14. Hypostoichiometric (U,Pu)C. Precipitate shaded areas = Pu-Si agglomerates, precipitate white areas = M. Pu-Si etch, 400X.

4. A Technique for the Metallographic Examination of Metallic Sodium

Work has been initiated on the development of a technique for the examination of bonding sodium from test capsules. In the preliminary tests, extruded metallic sodium was mounted in a low-melting alloy, and the mount was deep-frozen with liquid nitrogen. The specimen was ground with SiC using kerosene as the lubricant. A portable helium chamber with an optical glass viewport has been constructed for transport and photomicrography of the mounted sodium. Polishing and etching of the as-ground sodium is under study and will be facilitated by the completion of an inert atmosphere metallographic glovebox now

Fig. 15. Hyperstoichiometric (U,Pu)C. White precipitates = M_2C_3 . Pu-Si etch, 400X.

being assembled.

Preliminary results have been sufficiently encouraging to warrant additional development of this procedure. It is anticipated that, if a satisfactory technique for polishing sodium can be developed, cross sections of sodium-bonded test capsules can be mounted and examined.

VII. EBR-II *IRRADIATION TESTING (J. O. Barner)

A. General

The purpose of these irradiations is to evaluate candidate fuel/sodium/clad systems for the LMFBR program. In the reference design, pellets of single-phase (U,Pu)C are separated by a sodium bond from a cladding of Type 316 stainless steel or vanadium alloy. Seven fuel-element tests are planned in the initial group of a continuing series of EBR-II irradiation experiments.

B. Results During FY 1968

The capsules are to be irradiated under the following conditions:

1. Lineal power: 29.15 to 30.20 kW/ft (max).
2. Fuel composition: $(U_{0.8}Pu_{0.2})C$, (single-phase, sintered, fully enriched).
3. Fuel density: 90% of theoretical.
4. Smear density: 80%
5. Clad size: 0.300 in. o.d. x 0.010 in. wall.

6. Fuel size: 0.265 in. diam x 0.25 in. high pellets.
7. Clad type: 316 SS.
8. Maximum clad temperature: 1250°F.
9. Maximum fuel centerline temperature: 2130°F.
10. Burnup: 0.22 to 0.66 g fissioned per cm^3 .

Procedures for loading the EBR-II capsules were determined by loading a mockup capsule. After completion of nondestructive testing on the mockup, the first of the planned irradiation capsules (designated LASL-42) was loaded and bonded. During nondestructive testing, chips of fuel were found in the sodium bond. These chips were sufficient grounds for rejection of the capsule for the initial set of irradiation experiments in EBR-II.

A second capsule (designated LASL-42B) was loaded, bonded, and nondestructively tested. No chips were found in the capsule and eddy-current tests indicated satisfactory bonds. The capsule, which has been accepted for insertion in EBR-II, is available at EBR-II for insertion in the X039 subassembly. However, the insertion is dependent upon acceptance of the remainder of the capsules (non-LASL) in the X039 subassembly.

A pellet measuring machine has been built and installed in an inert atmosphere glovebox. The machine was built to measure dimensions of the fuel pellets used in the next six EBR-II irradiation capsules. These six capsules will be loaded with fuel during the first quarter of FY 1969.

A mockup of the EBR-II capsules was irradiated in the Omega West Reactor for 113 h. The experiment was designated OWREX-10. Table VII lists comparisons between OWREX-10 and LASL-42B. The maximum burnup at the fuel surface was ~ 5900 MWD/T.

OWREX-10 has been destructively analyzed in the hot cells. All welds and hold-down devices operated satisfactorily. The pellets were recovered intact with no apparent cracks or chipping. The pellets were later inadvertently exposed to air and water vapor while bonding sodium was being removed with butyl alcohol, and they disintegrated. No carburization of the Type 316 stainless steel or of the Type 316 stainless steel pellets immediately adjacent to the fuel was observed. A small amount of ^{133}Xe was found in the pin gas plenum and small amounts of ^{131}I , ^{140}La , and ^{137}Cs were found in the bonding sodium. The OWREX-10 experiment indicated that there

Table VII

Physical, Dimensional and Operating Characteristics of OWREX-10 and LASL-42B

	OWREX-10	LASL-42B
Lower blanket	316 SS	^{238}U
Fuel (U enrichment 93%)	$(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}$	$(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}$
Upper blanket	316 SS	^{238}U
Fuel hold-down	Nb	Nb
Bonds and reservoir	Na	Na
Inner pin	316 SS	316 SS
Outer capsule	304 SS	304 SS
Pin centering device	316 SS	316 SS
Pin hold-down spring	308 SS	308 SS
All weld design	Identical	
All hold-down design	Identical	
Lower blanket length, in.	0.750	1.000
Fuel length, in.	0.750	13.250
Upper blanket length, in.	0.250	0.250
Sodium reservoir length, in.	2.50	5.25
Fuel hold-down spring, in.	9.25	22.01
Inner pin length, in.	10.973	36.637
Total capsule length, in.	12.313	39.80
Fuel diameter, in.	0.265	0.265
Inner pin o.d., i.d., in.	0.300 x 0.280	0.300 x 0.280
Outer capsule, o.d., i.d., in.	0.375 x 0.335	0.375 x 0.335
Average heating rate, kW/ft	~ 24	25.85
Maximum heating rate, kW/ft	~ 24	30.20
Maximum mean outer capsule temperature, °F	1038	1067
Maximum mean inner pin temperature, °F	1250	1200
Max inner pin heat flux, Btu/h-ft ²	1.53×10^6	1.29×10^6
Max fuel centerline temperature, °F	~ 1950	~ 2130

are no serious mechanical design errors in the design or construction procedures of the EBR-II capsules.

VIII. GAMMA SCANNING AND RELATED STUDIES

(D. M. Holm, J. L. Parker, W. M. Sanders,
B. M. Moore, H. M. Ruess, B. J. Barnes)

A. General

Gamma scanning is a nondestructive technique for obtaining information on the distribution of fission products and activation products in fuel elements. During the past fiscal year, a new advanced semi-conductor detector system was constructed, and equipment was constructed for determining gamma-ray spectra of short-lived fission products

from fast fission of plutonium. ^3He activation has also been studied as a method of determining the concentration and distribution of impurities in stainless steel.

B. Results During FY 1968

1. Semiconductor Anticoincidence Detector System

A commercially produced 20-cc Ge(Li) detector has been mounted in a Dewar and is operating satisfactorily. Table VIII shows the Ge(Li) characteristics, and Fig. 16 shows a typical spectrum from an uncollimated ^{60}Co source now obtainable with this detector. Figure 17 shows a plot of a typical ^{137}Cs spectrum taken with this detector and a large NaI

Table VIII
Ge(Li) Characteristics
(at 1.33 MeV FWHM)

	Vendor's Mounting	LASL Mounting
Relative peak efficiency compared to a 3 x 3-in. NaI detector	≈ 3.0%	≈ 3.0%
System resolution	3.7 keV	3.1 KeV
Peak-to-Compton ratio	12:1	13.4:1

Fig. 16. Typical spectrum from an uncollimated ^{60}Co source taken with 20-cc Ge(Li) detector.

Fig. 17. Typical ^{137}Cs spectrum from 20-cc Ge(Li) detector using anticoincidence techniques with a concentric large NaI detector. The resolution is 3.59 kW FWHM, and the peak-to-Compton ratio is 75.

annulus (see Project 801) in anticoincidence. The resolution for ^{137}Cs is 3.59 kW FWHM, and the peak-to-Compton is 75.

2. Gamma Scanning of EBR-II Driver Fuel Pins

Three EBR-II driver fuel pins were gamma scan-

ned to determine the distribution of fission products and activation products. The Ge(Li) anticoincidence gamma-ray spectrometer was used, and the spectra were unfolded to determine the spatial distributions of the isotopes. The existing scanners and cave were successfully modified to accommodate the EBR-II fuel, which is larger than specimens normally handled in this LASL facility.

Reduction of the scanning data from these fuel pins is essentially complete. (Most of the details have been reported previously,⁶ but they are given again here for clarity in summarizing the work.) Table IX summarizes the pertinent information on the scans. Axial scans were made with a horizontal slit

Table IX
Gamma Scans of EBR-II Driver Fuel Pins

Pin No.*	Type of Scan	Collimator	No. of Spectra Measured
4	Axial	Horizontal slit	74
4	Diametrical at 15.700 in.	Pinhole	25
3	Diametrical at 10.040 in.	Pinhole	9
3	Diametrical at 16.040 in.	Pinhole	10
3	Axial	Horizontal slit	90
3	Diametrical at 10.040 in.	Vertical slit	28
3	Diametrical at 3.740 in.	Vertical slit	36
1	Diametrical at 15.980	Vertical slit	30
1	Axial	Horizontal slit	93
1	Axial	Horizontal slit	32
1	Axial	Horizontal slit	44
1	Diametrical at 10.000 in.	Vertical slit	40

*LASL identification:

LASL No.	EBR-II No.
4	4087-53
3	4088-100
1	4015-56

collimator 0.020 in. high, 1/2 in. wide, and 8 in. long. Diametrical scans were made perpendicular to the axial scans with a 0.031-in. diam pinhole collimator and a vertical slit collimator 1/2 in. high, 0.004 in. wide, and 8 in. long. The diametrical scans were made at approximately the midplane of the fuel (10-in. position) and 6 in. above and below the midplane.

From spectra taken at different positions, 22 gamma-ray lines were analyzed. Table X lists the energies and sources of these lines.

Table X
Gamma-Ray Energies Observed in EBR-II
Driver Fuel Pins

Gamma-Ray Energy (keV)	Isotope	Reaction
2186	^{144}Pr	Fission
1490	^{144}Pr	"
1332	^{60}Co	$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$
1173	^{60}Co	"
1050	^{106}Rh	Fission
834	^{54}Mn	$^{54}\text{Fe}(n,p)^{54}\text{Mn}$
810	^{58}Co	$^{58}\text{Ni}(n,p)^{58}\text{Co}$
765	^{95}Nb	Fission
757	^{95}Zr	"
724	^{95}Zr	"
695	^{144}Pr	"
662	^{137}Cs	"
620	^{106}Rh	"
512	^{106}Rh	"
512	^{58}Co	$^{58}\text{Ni}(n,p)^{58}\text{Co}$
497	^{103}Ru	Fission
144.7	^{141}Ce	"
133.5	^{144}Ce	"
116	Unidentified	Unidentified
112	"	"
100	"	"
97	"	"

Two diametrical scans at the midplane of Pin #2 were made to illustrate the difference in the quality of the data taken with a pinhole and with a vertical slit collimator. Figure 18 shows the distribution of the stainless steel activation product ^{54}Mn with the two different collimators. It is apparent that the poorer response of the pinhole collimator does not permit an adequate description of the distribution of the ^{54}Mn , whereas the vertical slit data give a good measure of the distribution of the ^{54}Mn . Figure 19 shows three sets of data for the diametrical distribution of ^{95}Nb . The Δ 's are the calculated activities, normalized to the center of the fuel, which should be observed when using an infinitely narrow slit that is perfectly aligned with the axis of a 0.154-in.-diam fuel element. The

Fig. 18. Diametrical distribution of ^{54}Mn at the midplane of Pin #2, as determined with slit and pinhole collimators.

Fig. 19. Comparison of scans for ^{95}Nb taken with a 0.031-in.-diam pinhole collimator ($\bullet$) and a 0.004-in.-wide slit ($\blacksquare$). For comparison, calculated values for an infinitely narrow slit are shown by the triangles (Δ).

calculation assumes 1% burnup of PuO_2 , a fuel density of 18 g/cc, and a uniform distribution of ^{95}Nb throughout the element. Since the calculated distribution is very nearly that observed with the vertical slit, there was apparently no fission product migration, and the small difference between the slit scan and the calculated scan is due to the finite width of the slit (0.004 in.). The pinhole scan was not normalized, and it gives much poorer representation of the distribution. This is to be expected because of the greater horizontal dimension (0.031 in.) as compared to the slit (0.004 in.).

All fission products had similar distributions, and no evidence of migration was observed. Axial

buckling is evident; the activities at the center of the pin were about 30% greater than at the top and bottom.

The most interesting observations to date are with regard to the effects of neutron energy on the distributions of nuclear reaction products. The fission rate in the center plane was about 30% higher than at the ends of the fuel; however, in this region, the fast neutron activation products of stainless steel increased to nearly 3 times the values at the ends. The concentration of ^{60}Co , a thermal neutron activation product, had its maxima in the inert or blanket portions of the fuel pin; no ^{60}Co was detected in the fueled region of the capsule.

3. Gamma-Ray Spectra of Short-Lived Fission Products from Fast Fission of Plutonium

Information on the gamma-ray spectra from short-lived fission products from fast fission of plutonium is limited when compared to the data available on uranium fission. To obtain this basic data, a program for studying fission product gamma-ray spectra following the fast neutron induced fission of plutonium is underway. An unshielded uranium metal critical assembly (Hydro)⁷ serves as a source of neutrons for irradiating the plutonium.

Foil measurements have been run on the Hydro critical assembly to determine its spectral indices. These average cross section ratios were obtained to give an approximate characterization of Hydro's neutron spectrum. Preliminary values obtained for the spectral index, $\sigma_f(^{235}\text{U})/\sigma_f(^{238}\text{U})$, indicate that the leakage spectrum from the assembly is quite fast, as is shown in Table XI. As can be seen from

Table XI
Spectral Indices

	$\sigma_f(^{235}\text{U})/\sigma_f(^{238}\text{U})$
Leakage neutrons on top of Hydro	7.6
Hydro leakage neutrons at ^{239}Pu foils	8.5
Neutrons from FLATTOP ⁸	6.8
^{235}U fission spectrum	4.2
Typical fast reactor ⁹	13.3

Table XI, the effective neutron energy in the Hydro appears to lie between that of the ^{235}U neutron fission spectrum and the neutron spectrum for a typi-

cal fast reactor.

Equipment for the experiments has been built and tested during the past year¹⁰ and preliminary foil irradiations have been made. No analyzed data are available yet.

4. ^3He Activation of Stainless Steel

The concentration and distribution of carbon in stainless steel can markedly affect its properties as a containment material for reactor fuels. ^3He activation is a method by which the concentration and distribution of carbon in stainless steel can be nondestructively determined.

An experiment was performed which shows that ^3He activation in conjunction with autoradiography will give good measurements of both the concentration and the concentration gradient of carbon in stainless steel. (The work was reported earlier in detail.¹⁰) Other important conclusions are that spatial resolution of about 0.001 in. can be obtained in determining carbon gradients in stainless steel; and that NBT-2 track plates have a sensitivity about 10 times greater than NBT plates in the autoradiography step.

IX. SODIUM-BOND HEAT-TRANSFER STUDIES (J. O. Barner, K. Meier)

A. General

The purpose of this project is to evaluate methods for determining the effects of fuel-pin defects on heat-transfer properties of the sodium bond. Such defects could arise in a number of ways. For example, a void in the sodium bond could: (1) be present before insertion in the reactor, (2) come from dewetting of the pellet due to change in composition as fission products are formed, (3) form from a hot spot on the pellet and consequent local vaporization of the sodium, and/or (4) be produced from desorbed or fission-product gases. Of these, probably the most serious defect would be the presence of fission-gas bubbles in the bond region.

There appear to be three methods of obtaining the high heat fluxes necessary for "defect analysis": (1) in-pile experiments, (2) out-of-pile experiments utilizing a central, high-heat-flux heater, (3) out-of-pile experiments utilizing an induction heat source with the heat flow direction reversed. These three methods are all receiving consideration for use in sodium-bond heat-transfer studies.

B. Results During FY 1968

As a preliminary step toward developing instrumentation for studying the effects of small defects in bonding sodium, a qualitative investigation of bubbles in thin sheets of liquid was carried out.¹⁰ Next, calculations were made to permit estimates of the local temperature perturbations which might be caused by the presence of bond defects in typical LMFBR fuel pins (at heat fluxes of 2×10^5 and 1×10^6 Btu/h-ft²).¹⁰ It was concluded that for the higher heat flux case, the perturbation should be detectable and measurable.

The feasibility of scanning clad temperatures (in an out-of-pile experiment) with small sheathed thermocouples was investigated. If sufficiently fine spatial resolution can be achieved, the size and location of bubbles in bond sodium can be sensed by temperature measurement on the coolant side of the clad. Calculations to determine the expected thermocouple output under the conditions of high heat flux and with the thermocouple in the coolant sodium indicated that the thermocouple output produced by the temperature peak at the edge of a bubble would be about 50% of the normal temperature differential through the clad alone.

Design of a system for use in flowing sodium with a bond heat flux of 10^6 Btu/h-ft² was started. Several methods of generating the heat flux were investigated. The first method used induction heating on an "inverted" fuel element; i.e., the clad annular fuel would be cooled by sodium flow through the center of the element. It was planned that a series of thermocouples be mounted on a rotating rod in the center of flowing coolant and arranged to contact the clad of the "inverted" element. A crude mockup of the concept, electrically heated and air cooled, gave promising results. The mockup was rotated by a lathe and temperature differences of 3°C caused by heat loss to the lathe chuck jaws could be detected.

After further study, it was decided that a rod resistance heater could be built which was about the same diameter as a typical LMFBR fuel element. The "inverted" technique was discarded, because it was felt that the proper geometry would yield better results. In the configuration now being considered, the heater will slip inside a uranium carbide tube which is sodium bonded to a stainless steel clad.

A stainless steel heater with a beryllium oxide insulator tube was designed. However, difficulties were encountered in obtaining the BeO tubes in the sizes and with the tolerances required. A graphite rod heater with a boron nitride insulator was designed and is being fabricated. Fabrication of the UC tube has also begun.

Preliminary design of the test section has been completed. The section is 5 in. long and will contain 40 thermocouples which will rotate around the fuel element. Slip rings will be used to transmit the thermocouple signals from the rotating section to an analog to digital data acquisition system. An existing sodium coolant loop has been modified to accept the test apparatus. A power supply has been obtained and the necessary operating and recording instruments are being fabricated.

X. ANALYTICAL CHEMISTRY

A. General

Specific analytical techniques have been developed and evaluated to cope with the problems encountered in the investigation of fuel-clad compatibility and in the general development of sodium technology. While the results of many of these special analyses are given in several sections of the report in Projects 801 and 808, the analytical techniques themselves have not been described. A brief summary of some of the techniques, and the problems to which they were applied, is given below.

B. Results During FY 1968

1. Spectrophotometric Determination of Trace Amounts of Uranium in Sodium (A.L. Henicksman)

In the study of corrosion by molten sodium metal, it became necessary to determine 1 to 5 ppm of uranium in sodium metal that had been exposed to UC or (U,Pu)C in stainless steel capsules. To determine uranium at this dilution, a very sensitive reagent is required such as Arsenazo III, with a reported molar extinction coefficient of 120,000. In a strongly acid medium the reagent is also reported to be quite selective, with known interference only from zirconium, hafnium, thorium, and plutonium(IV). The procedure is quite simple, involving reduction of uranium(VI) to uranium(IV) with zinc metal and reaction of the uranium(IV) in 6N HCl medium with an excess of Arsenazo III. At this acidity only the

1:3 complex is formed, and its absorbance is measured at 670 mμ. It was found experimentally that the method is satisfactory, although the molar extinction coefficient calculated from this work is substantially less than that claimed.

The remaining problem was to determine if the impurities likely to be present would interfere with the uranium measurement. Neither the elements in Type 316 stainless steel nor plutonium(IV) were found to interfere, but large amounts of sodium are detrimental and have to be removed. This is accomplished by adsorbing the $\text{UO}_2(\text{NO}_3)_4$ complex from an 8M HNO_3 medium onto a Dowex 1 anion exchange column.

The determination of uranium in known solutions containing 1 to 5 μg of uranium with equal amounts of plutonium, 1 gram of sodium, and 1 mg of stainless steel metals, showed that the precision of the method in the 1 μg range is better than 10%, and it is about 5% in the 5 μg range.

2. Investigation of Distillation Residues from the Vacuum Distillation of Metallic Sodium (K. S. Bergstresser)

Equipment was designed and fabricated to test methods for measuring carbon at the 1 ppm level in sodium, and to investigate the nature of residues remaining following vacuum distillation of metallic sodium. Fabrication of the equipment has gone forward at a slower than anticipated rate, and the experimental work has not been started. An inert-atmosphere enclosure to house the vacuum distillation equipment was put into operation, and the O_2 and H_2O in the argon atmosphere have been reduced to less than 1 ppm and 4 ppm, respectively. It is anticipated that continued operation of the inert system will gradually reduce the moisture level to 1 ppm. A 5 kW induction heater to power the vacuum distillation apparatus was installed, and other ancillary equipment made ready. The equipment for measuring impurities in sodium was assembled, filled with sodium, and tested. Final assembly of this major component with the inert system was made late in the year; the entire complex is now operational and is undergoing initial testing.

3. Spectrochemical Analysis of Sodium (O. R. Simi, C. J. Martell, R. T. Phelps)

An existing method for the analysis of sodium was modified by adapting an electrode-sample preparation reported by WAPD.¹¹ The modified method

involves dissolution of the sodium in ethanol, conversion to NaCl, evaporation to dryness, mixing with SP-2 graphite powder, and exciting with a dc arc. As done previously, the concentrations of impurities are evaluated semi-quantitatively by visual comparison of spectra. The improved limits of detection for various impurity elements are listed in Table XII. The method should be applicable to hot cell use for analysis of irradiated samples.

Table XII

Tentative Limits of Detection for Impurity Elements in Sodium by Spectrochemical Analysis

Element	ppm	Element	ppm
Li	0.8	Cu	3
Be	0.8	Zn	300
B	3	Ga	3
Mg	0.8	Sr	0.8
Al	3	Y	3
Si	3	Mo	3
K	3	Rh	3
Ca	0.8	Ag	0.8
Ti	3	Cd	3
V	0.8	In	3
Cr	3	Sn	3
Mn	0.8	Ba	0.8
Fe	0.8	Au	3
Co	3	Pb	3
Ni	3	Bi	3

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PROJECT 811
REACTOR PHYSICS

Person in Charge: D. B. Hall
Principal Investigator: G. H. Best

I. INTRODUCTION

Basic to the evaluation of fast breeder concepts and proposals are the analytical techniques and physical data used in the analyses. Valid comparisons between different concepts and proposals depend on minimization of differences in results due to the methods of analysis. To this end, the Los Alamos Scientific Laboratory is cooperating with other AEC laboratories and contractors in the development of evaluated cross-section data and associated processing codes. This work is coordinated by the Cross Section Evaluation Working Group (CSEWG), which is made up of representatives of the various organizations. In addition, the Laboratory is working on the development and maintenance of digital computer programs pertinent to the nuclear analysis of fast breeder concepts. Finally, the Laboratory is evaluating the performance characteristics of various fast breeder reactor concepts.

II. CROSS-SECTION PROCUREMENT, EVALUATION AND TESTING (M. E. Battat, D. J. Dudziak, R. J. LaBauve)

A. General

Accurate predictions of reactor design parameters, such as critical mass, sodium worth, and spectral response, require the development and maintenance of up-to-date basic microscopic nuclear data files. To meet this need, a national cooperative program is in progress to prepare an evaluated nuclear data file (ENDF/B) and associated processing codes.

Figure 1 summarizes the manner in which the processing codes fit in with ENDF/B and the LASL reactor calculational program. Most of these codes are now operational at LASL. Short descriptions of the processing codes follow:

CRECT - corrects ENDF/B tape (BNL)

DAMMET - combines and alters modes of ENDF/B tape (BNL)

ETOE - prepares ENDF/B data for MC² (APDA)

WLIB - puts a mathematical function on a tape that is subsequently used by MC² in resonance calculations (ANL)

MC² - generates multigroup cross sections (ANL)

B. Data Testing

Data for ⁶Li and ⁷Li in the ENDF/B format were submitted to Brookhaven National Laboratory for incorporation in the second version of ENDF/B. For version two, certain sections of the data for version one were altered, combined, or omitted to conform to the limitations of the associated processing codes. The second version of ENDF/B was distributed internationally during the latter part of 1967.

Calculations were performed for three selected critical experiments, using multigroup constants derived from the Category I ENDF/B library data. The experiments selected for study were:

1. a bare plutonium-metal assembly - JEZEBEL
2. a uranium-reflected ²³⁵U metal assembly - TOPSY
3. a dilute plutonium-fueled assembly surrounded by a depleted uranium reflector - ZPR-3 Assembly 48.

For all three systems, critical masses and central reactivity worths were computed; in addition, central activation ratios were calculated for ZPR-3 Assembly 48. Calculations were compared with experiment and with results obtained from the UKAEA and LRL neutron data contained in the LASL library. Results are summarized in Tables I through VI. This work was presented at the Second Conference on Neutron Cross Sections and Technology, held March 4-7, 1968, in Washington, D. C.

Fig. 1 Relationships of ENDF/B processing codes.

Calculational results submitted by other laboratories for ZPR-3 Assembly 48 were examined. A discrepancy of about 2.5% $\Delta k/k$ was found between results obtained by LASL and ANL for the same configuration. The multigroup neutron cross sections obtained from the ANL versions of ETOE and MC² were compared with ours to determine the reason for this discrepancy.

The difference in k_{eff} resulted from the use of the MC² fine-group option in the LASL calculations and the use of the ultrafine-group option in the ANL calculations. With updated versions of ETOE and MC², we ran an ultrafine-group problem for ZPR-3 Assembly 48. For the ultrafine-group option, the LASL and ANL results differed by about 0.5% in k_{eff} .

The difference in k_{eff} between the fine-group and ultrafine-group results was largely due to differences in the capture cross sections for ²³⁸U

in the neutron energy range between 300 eV and 5 keV. For the ZPR-3 Assembly 48 spectrum, the difference in this energy range is surprising. In order to ascertain whether this difference is obtained with other versions of MC², we have asked the National Neutron Cross Section Center if they could perform both the fine-group and ultrafine-group problems for the assembly under study, using the codes at their installation. Results of this study will be presented to the Data Testing Subcommittee of the CSEWG.

C. Shielding

In a meeting of the Shielding Subcommittee on July 6 and 7, 1967, this Laboratory assumed responsibility for examining hydrogen and deuterium data and for translating M. Drake's (Gulf General Atomic) neutron and photon data for calcium into the ENDF/B format.

TABLE I

CALCULATED AND MEASURED CENTRAL SPECTRA
Percent of Total Flux - ENDF/B Cross Sections

E _{lower}	ϕ calculated			ϕ experiment ZPR3/48*
	JEZEBEL	TOPSY	ZPR3/48	
6.065 MeV	2.36	1.23	0.42	
3.679	9.04	5.72	1.71	
2.231	16.27	12.29	3.81	
1.353	18.73	16.22	5.47	
0.821	17.73	16.60	7.31	
0.498	14.37	15.77	9.90	10.85
0.302	9.95	13.27	11.94	11.36
0.183	5.69	8.87	12.01	10.85
0.111	3.04	5.14	10.15	10.31
67.4 keV	1.75	2.74	8.88	8.97
40.9		1.31	7.20	7.13
24.8	0.86	0.65	6.77	5.83
15.0		0.13	5.64	4.76
9.12		0.04	3.42	3.85
5.53	0.19		2.08	2.80
3.35			1.40	1.82
2.03			0.42	1.27
1.23			0.85	
748 eV			0.43	
454			0.14	
214			0.05	

* Normalized as follows:

Sum of measured fluxes = sum of corresponding
calculated fluxes

TABLE II

CALCULATED AND EXPERIMENTAL CRITICAL MASSES
ENDF/B CROSS SECTIONS

JEZEBEL Pu contains 4.5% ²⁴⁰Pu.
TOPSY U is enriched to 94.1% ²³⁵U.

System	Calculated (kg)	Experiment (kg)
JEZEBEL	15.65 Pu	16.28 Pu
TOPSY	15.9 U	17.4 U
ZPR-3/48	339 ²³⁹ Pu*	272 ²³⁹ Pu**

* Calculated homogeneous sphere

$$(R_{\text{core}} = 49.78 \text{ cm}) = 337.1 \text{ kg}$$

$$\text{Homogeneous cylinder} = 337.1/0.927 = 363.6$$

$$\text{Heterogeneous cylinder} = 363.6 - 25.0 = 338.6$$

$$k_{\text{eff}} = 0.975 \text{ for } R_{\text{core}} = 47.42 \text{ cm}$$

** Heterogeneous cylindrical mass.

TABLE III

JEZEBEL - CENTRAL REACTIVITY WORTHS
cents/mole

Material	ENDF/B	UKAEA	LRL	Experiment
Fe	-27.2	-22.2		-21.5
Ni	-60.1	-54.6		-48.0
²³⁵ U	929.	821.	798.	804.
²³⁸ U	87.	103.	98.	114.
²³⁹ Pu	1763.	1557.	1591.	1592.
²⁴⁰ Pu	1091.	983.	855.	1038.

TABLE IV

TOPSY - CENTRAL REACTIVITY WORTHS
cents/mole

Material	ENDF/B	UKAEA	LRL	Experiment
⁶ Li	-70.2	-72.8		-130.4
⁷ Li	0.004	3.0		7.9
Be	9.1	8.9		9.2
Fe	-2.4	-2.7		-2.2
Mo	-6.7		-5.8	-3.5
²³⁵ U	212.7	216.8	207.3	208.4
²³⁸ U	25.4	21.5	28.7	26.7
²³⁹ Pu	392.5	396.4	403.4	402.6
²⁴⁰ Pu	221.	210.	168.	286 ± 14

TABLE V

ZPR-3 ASSEMBLY 48 - CENTRAL REACTIVITY WORTHS
cents/mole

Material	ENDF/B	UKAEA	LRL	Experiment*
C	-0.21	-0.04	-0.21	-0.017
Na	-0.19	-0.07		-0.046
Cr	-0.279			-0.149
Fe	-0.287	-0.18		-0.204
Ni	-0.443	-0.32		-0.325
Mo	-1.78		-0.49	-1.27
²³⁵ U	26.8	23.3	23.9	24.1
²³⁸ U	-2.02	-1.87	-1.56	-1.80
²³⁹ Pu	35.4	31.9	35.0	32.2
²⁴⁰ Pu	6.56	2.94	-7.0	5.87

* Values were converted from central perturbation
cross sections to cents/mole.

TABLE VI
ZPR-3 ASSEMBLY 48
CENTRAL ACTIVATION RATIOS RELATIVE TO ^{235}U FISSION
ENDF/B CROSS SECTIONS
(1.0-cm radius central region)

Type	Calculated	Experiment
^{238}U fission	0.0332	0.0307
^{238}U (n, γ)	0.158	0.138
^{239}Pu fission	0.960	0.976
^{240}Pu fission	0.248	0.243

An evaluation of neutron interaction and photon production cross sections for sodium, magnesium, chlorine, potassium, and calcium was recently completed by Drake,¹ and the data were presented in an extension of the United Kingdom (UK) data file format.² As part of the LASL effort on the CSEWG, the sodium data were translated to the extended ENDF/B format (extended to include photon data³), and a copy of these data was sent to the National Neutron Cross Section Center (NNCSC) at BNL, where they propose to use the data as a test set for extending the checking code CHECKER to include the photon production data and data for inelastic scattering to discrete levels. The data will then be plotted by the NNCSC, where possible, for comparison with the sodium evaluation presently on the ENDF/B file. A review of the two sets of sodium data will be performed by LASL. The ENDF/B version of Drake's sodium data is also being sent to ORNL for review. The calcium data will be translated into the extended ENDF/B format when the final version of the data is available in the extended UK format.

The translations were performed by two LASL codes written for this purpose: LUTE, which translates the photon data, and LATEX, which translates neutron data and makes a complete ENDF/B tape. Both codes, along with flow diagrams, are being sent to ORNL to assist in constructing a general UK $\leftrightarrow$ ENDF/B translation code. Some parts of the UK $\leftrightarrow$ ENDF/B translation could not practically be automated, such as the general file 1 data in ENDF/B, which has no counterpart in the UK data file. Also, the photon production data from inelastic scattering were entered in ENDF/B by hand,

using the transition probability option which is available only in ENDF/B format.

The translation of Drake's sodium data is the first set of photon production data in the ENDF/B format, which will be useful for debugging the data retrieval codes for photon data. A code is now being written at LASL to extract photon production matrices for use with photon transport codes. The code, called LAPH, will compute pointwise (in energy) photon production cross sections and average them over N arbitrary neutron energy groups, for G arbitrary photon energy groups. The resulting $N \times G$ matrix can then be used in conjunction with neutron-group flux vectors to prepare the spatially dependent photon source term for photon transport codes such as QAD, MCG, or DTF-IV. Figure 2 is a schematic diagram of the code.

Translation of calcium data from the UK to ENDF/B format began but was stopped because of format uncertainties. The data in UK format have the (n,p) continuum gamma-ray production included in the cross section for continuum gamma rays from inelastic scattering. Also, since the specification of formats for (n,p₀), (n,p₁), ..., (n,p_k) reactions

Fig. 2 Schematic diagram of LAPH code. This code extracts photon production matrices from ENDF/B data for use with photon transport codes.

(along with other format recommendations) is presently under review by the Shielding Subcommittee of the CSEWG, the translation is being held in abeyance pending the outcome of this review.

III. REACTOR ANALYSIS METHODS AND CONCEPT EVALUATIONS

A. General

In fast reactor analysis and evaluation, computer programs must be updated continually to utilize advances in computer technology. These advances also make possible the extension of existing calculational techniques and the development of new computational methods. Research areas have included during this fiscal year input-output data preparation, computer programs to solve the nonseparable space-time, multigroup neutronics equations, numerical techniques for improving transport and diffusion calculations, numerical methods for evaluating heat deposition in fast reactor shields, fission product yields from ^{239}Pu fast fission, preparation and maintenance of code packages, and evaluation of blanket design parameters.

B. Output Data Preparation (D. J. Dudziak)

The plotting code TRAZAR was revised to plot (as an option) on a graph field defined by tick marks rather than grid lines and to use large letters for labeling the coordinates.

C. Space-Time Reactor Kinetics Codes

1. Synthesis Method (J. C. Vigil). The space-time synthesis method which results in the multimode equations was programmed for the CDC-6600 computer. The code consists of two separate programs, PARAS and ANCONM. PARAS computes the parameters which appear in the multimode equations by using fluxes and currents for various trial functions computed with the DTF-IV code. These parameters are then input to the ANCONM code, which solves the multimode equations by continuous analytic continuation and performs the space-time synthesis by combining the trial functions with the solutions to the multimode equations.

The code is presently limited to one space dimension in any geometry, step reactivity perturbations (in microscopic cross sections and/or atom densities), with no reactivity feedback. Any num-

ber of delayed neutron groups is allowed. PARAS also computes the parameters required by the conventional point kinetics equations.

One test problem has been run, with encouraging results. Comparisons with point kinetics, the WIGL2 code,⁴ and the GAKIN code⁵ are planned.

The General Atomic version of the WIGL2 code, which was written for use on the UNIVAC-1108 computer, was compiled on the CDC-6600 computer. Results from a sample problem run on the CDC 6600 agreed completely with the UNIVAC results.

WIGL2 is a one-dimensional (slab, cylinder, or sphere), two-group, time-dependent diffusion theory code with zero, one, or six delayed neutron groups. The program includes nonboiling heat transfer and feedback is available for temperature changes, control rod motion, and xenon buildup. Transients are excited by prescribed changes in inlet coolant temperature, coolant flow rate, or rod position.

The GAKIN code⁵ was compiled on the CDC-6600 computer. GAKIN is a one-dimensional multigroup diffusion theory kinetics code which incorporates the following features:

- a. Solutions for slab, cylindrical, or spherical geometry.
 - b. Arbitrary number of neutron energy groups.
 - c. Arbitrary number of regions and space points.
 - d. Optional inclusion of xenon poisoning.
 - e. Time-dependent cross sections.
 - f. Optional inclusion of external sources.
 - g. Arbitrary number of delayed neutron groups.
- GAKIN is an extension of the WIGL2 code to the multigroup case, except it does not include thermal feedback.

2. Multienergy-Group Method (G. C. Hopkins)

Preliminary comparison runs have been made with the monoenergetic transient analysis code ANCON⁶ and its multigroup equivalent, ANCONMG. Data representing \$1.50 and \$0.65 reactivity insertions were prepared by ONEDAC for input to ANCON and by PARAM for input to ANCONMG. The analysis employed UHTREX data, a step reactivity insertion and two feedback lumps (fuel and moderator). When delayed neutrons were included, the Keepin 6-group parameters⁷ were used. Results are shown in Table VII.

TABLE VII
COMPARISON OF TRANSIENT RESULTS
ANCON AND ANCONMG

Program	No. Groups	Delayed Neutrons Included	Feedback Included	Peak Power (MW)	Time to Peak Power		(T _f) _{max} (°K)	Time to (T _f) _{max}	
					Transient (sec)	CP (sec)		Transient (sec)	CP (sec)
<u>\$1.50 Reactivity Insertion</u>									
ANCON		X	X	56.99	3.413	6.249	900.0	26.05	9.592
ANCONMG	1	X	X	56.84	3.409	0.869	900.0	25.26	2.472
ANCONMG	2	X	X	57.00	3.412	457.8	906.5	25.58	3366
ANCON			X	28.92	1.295	10.10	352.7	1.971	15.03
ANCONMG	1		X	29.29	1.312	0.953	352.7	1.974	1.412
ANCONMG	2		X	24.67	1.265	90.1	344.7	1.972	139.8
ANCON		X		0.25 ^a	2.140	7.777			
ANCONMG	1	X		↓	2.139	1.122			
ANCONMG	2	X			2.140	227.2			
ANCON				1.95 x 10 ^{5a}	1.833	15.41			
ANCONMG	1			↓	1.832	0.895			
ANCONMG	2				1.821	69.59			
<u>\$0.65 Reactivity Insertion</u>									
ANCON		X	X	1.318	41.57	5.512	570.7	130.53	9.640
ANCONMG	1	X	X	1.367	42.71	0.918	570.7	131.15	3.833
ANCONMG	2	X	X	b					
ANCON			X	5.42	2.665	9.123	319.6	4.106	13.56
ANCONMG	1		X	5.65	2.735	1.241	319.6	4.115	1.837
ANCONMG	2		X	4.73	2.668	183.7	315.8	4.129	282.2
ANCON		X		6.0 x 10 ^{-6a}	2.102	1.701			
ANCONMG	1	X		↓	2.101	0.347			
ANCONMG	2	X			2.101	224.3			
ANCON				1.6 x 10 ^{13a}	7.133	26.23			
ANCONMG	1			↓	7.134	1.529			
ANCONMG	2				7.174	264.1			

^a Calculation arbitrarily stopped at this power level.

^b Peak power not reached after 60.2 min CP time. Extrapolated CP time to peak power = 93.2 min.

Although ANCONMG central processor (CP) times were shorter than ANCON CP times for equivalent 1-group problems, direct comparisons between the actual peak powers and maximum fuel temperatures are prohibitively expensive in CP time for 2-group problems that include delayed neutrons. A quicker insight may be gained about multigroup behavior trends, however, from a comparison of the time profiles of the leading edge of the power peak for larger reactivity insertions.

A study was conducted on numerical methods other than continuous analytic continuation. Both the Runge-Kutta and Milne Central Difference Predictor-Corrector methods were tried. However, for stable numerical results to be obtained, the time step size had to be shortened to the point where the resulting CP times were 1.5 to 2.0 times as long as those encountered with ANCONMG.

D. Numerical Techniques for Improving Transport and Diffusion Calculations (B. M. Carmichael)

By synthesis techniques, the number of parameters can be formally reduced in calculational problems. For example, time-dependent one-dimensional solutions to neutron kinetics problems can be obtained by synthesizing the separate space and time solutions, or two-dimensional static solutions to neutron transport problems can be obtained by combining the separate solutions for each of the two space dimensions. In either of these applications, the synthesis method would reduce computing times by more than an order of magnitude. Preliminary equations have been formulated for applying synthesis techniques to multigroup transport and diffusion theory.

E. Heat Deposition in Fast Reactor Shields (M. E. Battat, D. J. Dudziak)

1. Shield Design Techniques. In order to minimize the computation time required in shield design analyses, acceleration techniques are being investigated. Converged fluxes from a CRAM⁹ two-dimensional, 16-group diffusion calculation were used as an input guess for a similar S_4 calculation with the DDK code. A simplified model of the MPBE¹⁰, a typical fast reactor shielding problem, was used for both calculations. The accelerated DDK problem took 140 min on the IBM 7094, a fraction of what would be required for a crude initial flux guess (e.g., a uniform spatial distribution over the core of a fission neutron spectrum). For identical physical specifications, the CRAM and DDK problems gave a k_{eff} of 1.000 and 1.039, respectively. When the core height of the DDK model was adjusted to give a k_{eff} of 1.000, the regional neutron economies and flux spatial distributions agreed well with the CRAM results.

In addition, starting fluxes have been obtained from an S_2 calculation and from a DTF-IV one-dimensional S_4 calculation with a cosine axial distribution. Using these starting fluxes, running times for a two-dimensional S_4 calculation for a small, experimental fast reactor system were comparable to those achieved with starting fluxes from CRAM. Regardless of the starting flux used, the converged eigenvalues (k_{eff}) were the same for all the S_4 calculations. Present investigations are aimed toward determining the effect, if any, of the starting flux on calculated fluxes in outlying shield regions, as well as on the neutron economy in such regions. Computer-time savings from the accelerating techniques vary with the system size, the spectrum, and the core-to-total-system relative areas.

2. ^{239}Pu Fission Product Energy Release (M. E. Battat, D. J. Dudziak, H. R. Hicks). By

use of currently available experimental and calculated fission product yields from ^{239}Pu fast fission, the Lockheed Fission Product Inventory Code, FPIC,¹¹ has been expanded to include the capability of calculating fission product decay powers for ^{239}Pu fast fission. The revised code, FPIC/U-Pu, is operational on the CDC-6600 computer, and the

required nuclide data and operating instructions are reported in Ref. 12.

Summation calculations of beta, gamma, and total decay powers from ^{235}U thermal fission and from ^{239}Pu fast fission were compared for both an instantaneous burst and infinite irradiation. Shutdown times ranged from 10^{-10} to 10^9 sec, and significant ($\geq 10\%$) differences occur principally for very short and very long shutdown times. In order to determine changes in energy release caused by updating of the fission product yields and decay constants, the decay powers from ^{235}U thermal fission were compared with previous studies¹³⁻¹⁵ for an instantaneous burst and for infinite irradiation, and good agreement was found over the applicable shutdown times. Calculations of beta, gamma, and total fission product decay powers from ^{239}Pu fast fission for a specific irradiation history in the Dounreay Fast Reactor were then compared with the corresponding experimental measurements by K. Johnston¹⁶ of AWRE, as well as with ^{235}U thermal fission calculations. For gamma and total decay powers, the ^{239}Pu fast fission calculations generally agreed better with the experiment, whereas for beta decay power, the ^{235}U thermal fission calculations were generally better. Similar conclusions were drawn from comparisons of instantaneous burst FPIC/U-Pu calculations with the corresponding analytical fits derived from the experimental data. Plots of these comparisons are shown in Figs. 3, 4, and 5.

F. Preparation and Maintenance of Code Packages

1. THMOD (B. M. Carmichael, J. S. Philbin)

The code THMOD is being developed for collapsing a set of fine-group cross sections into a set of broad-group cross sections by a Lagrangian flux weighting technique. Given any system described by linear operator equations, an adjoint solution can be defined, together with a Lagrangian functional whose stationary property is equivalent to the equations of the system.¹⁷ A Lagrangian function can, therefore, be formulated for the transport equation. For simplicity, an infinite medium and isotropic scattering were assumed.

Formulas have been derived which can be applied to both macroscopic and microscopic cross sections.

Fig. 3 Fission product beta decay powers following an instantaneous burst of fissions.

In all instances, the collapsing formulas reduce to the regular-flux weighting formulas when the adjoint fluxes are constant.

These Lagrangian functional weighting techniques have been applied to a 59-group set of thermal cross sections. Down-scattering from high energies was treated as a source term to the top thermal energy groups. The values of the collapsed thermal cross sections were not appreciably different from values derived by regular-flux weighting techniques (THERM 1 code). The reason for this is that the adjoint flux is very nearly a constant over the thermal range. For collapsing outside the thermal range, however, the adjoint flux is not, in general, constant. In finite medium problems, it is expected that the Lagrangian-functional weighted cross sections will preserve the eigenvalue more accurately than the conventional regular-flux-weighted cross sections.

2. Homogenized Cell Cross-Section Code (B. M. Carmichael, R. L. Cubitt).

A code (MDTR) using some of the standard DTF-IV subroutines⁸ has been developed to compute homogenized cell cross sections. This code has the advantage that for input it uses the cell DTF-IV input deck intact and requires only the addition of the cell fluxes. This code will be enlarged to accommodate perturbation calculations and to obtain reactor performance figures, such as reaction rates for breeding ratio and specific power.

3. One-Dimensional Perturbation Code (B. M. Carmichael, R. L. Cubitt).

The one-dimensional version of the DAC perturbation code, DAC1, is being written in the same format as the one-dimensional S_n code DTF-IV.⁸ Accordingly, the input format is the same as in DTF-IV, the variable dimension scheme from DTF-IV is used, and the options in DTF-IV applicable to perturbation theory are preserved.

Fig. 4 Fission product gamma decay powers following an instantaneous burst of fissions.

Input for DAC1 consists of the unmodified input deck to DTF-IV, flux dumps from regular and adjoint DTF-IV k-eigenvalue problems for the nuclear system under study, and specification of perturbations.

The entire code has been written; the input section, the calculation of the effective delayed neutron fraction, the neutron lifetime calculation, and the buckling perturbation option have been debugged. The calculation of the delayed neutron fraction has been generalized to permit calculation of an arbitrary mixture of delayed neutron emitters.

The buckling perturbation was added recently. In DTF-IV, the buckling parameters introduce fictitious absorption in the one-dimensional calculation which accounts approximately for neutron leakage in directions transverse to the specified dimension. The buckling corrections are calculated from the extrapolated heights or radii in the directions transverse to those stipulated in the DTF-IV input.

DAC1 calculates the reactivity resulting from a perturbation of the extrapolated dimensions.

The remaining perturbation sections of the code are being debugged. These routines will provide reactivity estimates for arbitrary perturbations of the atom densities, dimensions, and microscopic cross sections of the nuclear system.

4. Cell-Averaged Cross-Section Code (J. C. Vigil).

A computer program, EFFXS, has been written for the CDC-6600 computer to compute cell-averaged cross sections. The code can be used for any cell in one-dimensional geometry (slab, cylinder, or sphere), an arbitrary number of energy groups, and an arbitrary cross-section table length. Input to the program includes DTF-IV⁸ problem data input plus point group fluxes from the DTF-IV calculation.

Fig. 5 Fission product total decay powers following an instantaneous burst of fissions.

5. Calculation of Central Reactivity Worths (M. E. Battat). Certain inconsistencies

have been noted in the results of calculations to determine the central reactivity worth of ^{239}Pu in JEZEBEL. As an example, the finite-sample (0.7268-cm radius) worth calculated by the DTF-IV code⁸ (eigenvalue differences method) was slightly larger than the small-sample (0.1454-cm radius) worth calculated by the DAC code (perturbation method). Experimentally, the finite-sample worth is about 8% less than the small-sample worth.

To investigate this anomaly, the original DTF-IV S_8 calculations were repeated with finer mesh spacing (10 instead of 5) in the sample region; in addition, the problems were rerun with the S_{16} option. A summary of the DTF-IV and DAC problems with the S_8 and S_{16} options is given in Table VIII. Although the analysis of the results is not yet complete, it can be seen that the ^{239}Pu worth was reduced by 2.5% in going from S_8 to S_{16} ; however,

TABLE VIII
 ^{239}Pu CENTRAL WORTH IN JEZEBEL

Problem	Theory	S_n	k_{eff}	Core Radius (cm)	Material in Center	$\Delta k/g\text{-atom}$
DTF-IV						
01058	REG	8	critical	6.2807	Fuel	
021868	REG	16		6.3023		
01048	ADJ	8		6.2807		
021968	ADJ	16		6.3023		
01038	REG	8		6.3044	Void	
022168	REG	16		6.3250		
12287	ADJ	8		6.3044		
022268	ADJ	16		6.3250		
12317	REG	8		6.3044	^{239}Pu	0.03090
022368	REG	16		6.3250		0.03014
11197	ADJ	8	1.003959	6.3044		0.03090
022468	ADJ	16	1.003860	6.3250		0.03013
DAC (small sample)						
01048		8		6.2807	Fuel	0.03122
01058		16		6.3023		0.03119
021868						
021968						
DAC (0.7268 sample)						
12287		8		6.3044	Void	0.02869
12317		16		6.3250		0.02870
022268						
022368						

the critical mass was increased by 1%. In contrast, the DAC results did not seem to change significantly in going from S_8 to S_{16} . Examination of the data is still in progress.

G. Blanket Design Studies (M. E. Battat, R. L. Cubitt, G. L. Ragan). S_4 cell calculations (infinite cylinders) have been performed to evaluate the effects of varying blanket ^{239}Pu enrichments on breeding ratios, blanket multiplication, and other parameters of interest. The systems which were studied had 30-cm-thick blankets with ^{239}Pu :total-heavy-atom ratios from 0.02 to 0.06; the core radius was either 20 or 30 cm. Both metal (U-Pu-Zr) and oxide blankets were investigated.

With U-Pu-Th alloy as core fuel, preliminary calculations have been made to determine the effects of varying plutonium concentrations in the blanket. Both metal (U-Pu-Zr) and oxide (UO_2) blanket materials were studied. For comparison, a few problems have also been run for a core fuel composed of coated particles in the uranium matrix and a uranium metal blanket.

Calculations were made with the DTF-IV neutron transport code⁸ in the S_4 approximation and the 16-group Hansen-Roach cross-section set. The geometry assumed was an infinite cylinder with either a 10- or 20-cm-radius core surrounded by a 30-cm-thick blanket. A reflective outer-boundary condition was specified, i.e., no radial leakage. For selected blanket ^{239}Pu concentrations in the 2 to 5% (of total heavy atoms) range, problems were run in which criticality was achieved by adjusting the core ^{239}Pu concentration. This adjustment was made subject to the constraint that the sum of the heavy atoms -- plutonium, uranium, thorium, and fission products -- remained constant. The fact that, in some cases, the resulting relative concentrations of uranium, plutonium, and thorium might not constitute a practical fuel was not considered.

With regard to fraction of fissions which occur in ^{238}U , blanket multiplication, and blanket power fraction, metal blankets seem more promising than oxide blankets. However, the oxide blanket does give more favorable sodium voiding effects.

Similar calculations were made for a core consisting of coated particles in a uranium matrix

surrounded by a metal uranium blanket. Insofar as blanket performance and breeding ratios are concerned, the coated-particle fuel is more attractive than either the metal- or oxide-blanket systems. However, the core sodium void worth for the coated-particle system is more positive than that for either the metal- or oxide-blanket configurations with U-Pu-Th as core fuel.

IV. COOPERATIVE ARRANGEMENTS

W. H. Hannum is at the United Kingdom Atomic Energy Research Establishment at Winfrith, England. His reports covering approximately the fiscal year have been distributed.

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PROJECT 822

EXAMINATION OF FAST REACTOR FUELS

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I. INTRODUCTION

This project is directed toward the examination and comparison of the effects of neutron irradiation on LMFBR Program fuel materials. Irradiated materials will be examined as requested by the Fuels and Materials Branch of DRD & T.

Another important phase is the development of an analytical chemistry program designed to assure the high-quality well-characterized fuel required by the LMFBR/FFTF Program. In close cooperation with PNL, an analytical program has been developed which has the following objectives:

1. To evaluate the present capabilities of potential fuel producers for making the analytical measurements on FFTF fuel that are necessary to assure the uniformly high quality fuel required by the LMFBR/FFTF Program.
2. To provide technical guidance to fuel producers, as may be required, to assure these capabilities are established at the level required by FFTF reactor fuel specifications.
3. To establish and conduct a monitoring program that will assure continuing technical competence of fuel producers for the analysis of FFTF fuel at the level required by fuel specifications.

II. FUEL CAPSULE HANDLING CAPABILITY (P. J. Peterson)

A shielded cask has been designed for shipping irradiated capsules (in a vertical position) from EBR-II to LASL for post-irradiation examination. The cavity of the cask, which is 6 in. diam x 46 in. long, is provided with a removable Al container for holding the capsules. A wall thickness of ~6.5 in. of depleted U provides the required shielding. The cask is adequate for handling at least 19 capsules, each containing 159 g fissile material ($^{235}\text{U}_{0.8}$ - $^{239}\text{Pu}_{0.2}$) irradiated to 100,000 MWD/T and cooled for 30 days. The design of the cask is compatible with handling operations at the TAN Facility in Idaho. Engineering analyses indicate that the cask will withstand the hypothetical accidents (drop, fire, puncture and immersion) as set forth in Chapter 0529 of the AEC Manual. At the conclusion of review of this design by personnel from ANL and PNL, drawings will be submitted to the AEC for approval. Results of the engineering analyses, radiation attenuation calculations and calculations for dissipating the fission product decay heat will be submitted with the drawings.

Procedures and equipment have been developed and tested for carrying out the following operations remotely: unloading and loading the cask; removal of the Al insert; and transferring the capsules into a shielded alpha-box. Handling procedures and equipment were designed to maintain the capsule in a vertical position. Enough latitude exists in the equipment to accommodate a variety of shipping casks and experimental fuel capsules.

An existing cask was modified to permit on-site transportation to other facilities for gamma scanning and x-ray radiography.

III. INERT ATMOSPHERE BOXES

(G. R. Brewer, M. D. Keehn, R. F. Velkinburg)

In order to handle Na-bonded fuel capsules and fuel materials reactive with air, an inert atmosphere capability within some of the alpha-boxes is being provided. It is desirable to keep H_2O and O_2 concentrations as low as possible, with < 1 ppm being an ideal condition.

The design of alpha-boxes, previously used with air atmospheres, was modified to provide much lower leak rates. A recirculating Ar purification unit capable of processing ~ 100 SCFM has been received, installed and tested. Although several design deficiencies have been observed, the purification unit appears satisfactory for providing purified Ar for the disassembly cell. Instruments for determining purity, Moisture Monitor and Oxygen Analyzer, were installed and appeared to operate satisfactorily. In tests on a typical alpha box, in which no manipulators were installed, readings as low as 4 ppm O_2 and 0.5 ppm H_2O were obtained with the purification unit installed. With manipulators in place and operating, the concentrations of O_2 and H_2O are certain to be much higher than observed during the test. It appears reasonable, however, to attain a level of 25 ppm $O_2 + H_2O$ under operating conditions. A sealing system has been devised to maintain a secondary inert atmosphere within the booting.

The alpha-box for Cell 14, where the fuel element testing, disassembly, etc. are carried out, has been He leak checked, installed and aligned. Service connections have been completed, and additional runs will be made when the Ar purification unit and controls are completed. It is anticipated that the equipment for this cell will be installed and operable by about September 1, 1968.

Present planning schedules indicate that the inert metallography system (two alpha-boxes and the metallograph containment box) will be available in January 1969. A recirculating Ar purification unit has been ordered for this purpose. The two alpha-boxes for the grinding, polishing and other operations are being outfitted with the standard

service and transfer devices.

IV. IN-CELL EQUIPMENT

(G. R. Brewer, E. L. Ekberg, C. E. Frantz, M. W. McCloskey, F. H. Newbury, P. J. Peterson, D. S. Shaffer, A. E. Tafoya, T. Romanik, J. R. Trujillo)

To accommodate irradiated fuel elements of different sizes and shapes it was necessary to modify existing equipment to perform those tests for which capabilities already existed. The presence of Na, the requirement for inert atmosphere and the variety of post-irradiation tests to be conducted necessitated the development of new equipment and techniques. Among some of the accomplishments during this period are those listed below:

Inert Gas System for Transfer Containers

Equipment was developed to first evacuate containers to $< 200\mu$ and then pressurize to 1 psi of Ar before attaching to the box transfer system. Such a scheme minimizes the introduction of O_2 into the containment box.

Removal of Cladding from Fuel

Satisfactory tests were run with the stripping fixture on unirradiated material. A single test on an irradiated ($\sim 1\%$ burnup) EBR-II rod of driver fuel (swelled) was unsatisfactory since the clad tended to break into short pieces as it was removed. Tests on other irradiated cladding will be carried out as part of the continued development on this problem.

A slitting saw was fabricated for removing cladding from fuel which has swelled or reacted with the clad.

The fuel from two irradiated (1% burnup) and three unirradiated EBR-II driver fuel rods was successfully removed intact by heating the rod in a specially designed vacuum furnace to $175^\circ C$. Pressure was applied to the top of the fuel by pushing a long rod through an O-ring seal. The clad had been previously removed above and below the fuel. Removal of the fuel intact permitted: taking continuous diametral measurements on the full length fuel pin; viewing of the entire length of an intact pin; and preserving the cladding for such measurements as tensile test and tube burst.

Dimensioning Equipment

Equipment for taking dimensions of both capsules and pellets has been fabricated and tested. Sensitivities

of ~ 0.0002 in. are possible on diametral measurements of the capsule, and on diameter and length of the pellets. The pellet dimensioner will also indicate bulged and dished ends as well as perpendicularity of the pellets.

The profilometer was used in obtaining: bow measurements on irradiated EBR-II driver fuel rods and diameter measurements on both the rods and pins.

Fission Gas Sampling

A system for obtaining pressure and void volume measurements in addition to the capability of obtaining a fission gas sample will be available for the inert atmosphere disassembly box. The system is similar in design to that used successfully for sampling fission gas from the EBR-II rods.

Gamma Scanning

The existing facility and equipment will continue to be used until the newly-designed mechanical equipment can be installed at the DP West Hot Cells. When this operation is completed, the existing electronics, counters, etc. will be used at DP on an as-required basis.

It is planned over the next two years to acquire additional electronic equipment for establishing a complete gamma scanning capability at DP West.

Na Removal

The unit for distilling Na from the fuel pellets has been completed. A special holder for the pellets was constructed to serve the following functions: permit viewing of top, bottom and sides; store the pellets in holes for identification; and serve as the holder during distillation.

Removal of Na from sections of cladding will be performed either by distillation or reaction with Dowanol EB or other suitable solvent. Removal by the latter technique would be carried out in an area where the solvent would be compatible with the alpha-box atmosphere.

Pellet Density Measurements

Additional development of the immersion method for obtaining densities was necessary to achieve an accuracy of 0.1% on a fuel pellet of $1/4$ in. diam x $1/4$ in. long and to correct immersion weights which are in error because of thermal convection caused by radioactive decay heat. The analytical balance used in this study has

an accuracy of ± 0.2 milligrams.

Density measurements of a $1/4 \times 1/4$ in. stainless steel pellet utilizing water had a standard deviation of about 0.4% which does not meet the requirement. Mercury was tried as the immersion liquid, but reproducible weighings in Hg could not be obtained. This was attributed to surface tension effects; and consequently, experimentation with Hg has been discontinued.

When using bromobenzene as the immersion liquid, standard deviation of the density of a $1/4 \times 1/4$ in. stainless steel pellet was about 0.16%. This is the best result obtained to date. Procedures to insure the absolute accuracy of density determinations utilizing bromobenzene are in progress.

Errors introduced into immersion weights in bromobenzene because of radioactive decay heat are being studied using pellets containing small electric heaters. A "true" immersion weight is determined while the heater is off; then the immersion weight is determined with a measured power input. The difference in weights is a correction factor. For a half watt power input the weight correction is about 6 milligrams. This investigation will continue in an attempt to find suitable methods for accurately determining densities of thermally hot, irradiated fuels.

V. DIFFERENTIAL THERMAL ANALYSIS (D. B. Court)

Apparatus for determining differential thermal analysis on U-Pu compounds at LASL has been discussed previously.¹ Utilizing the basic design of this apparatus, a capability for obtaining DTA measurements on irradiated fuels was developed.

All of the equipment for this analysis has been designed, fabricated and tested. Installation of the equipment in the alpha-box is essentially completed. With no major difficulties foreseen to wiring in the induction heater and completing the recirculating chilled water piping, the entire system should be operable about August 15, 1968.

VI. HEAT CONTENT MEASUREMENT (C. E. Frantz)

A need exists for heat content measurements of fast reactor fuels at temperatures of about 1000 to 2500°C. For this reason an investigation was made into the isothermal drop calorimeter as used by the Ceramic Plutonium Fuel Material Program,² alternatives were also considered. A decision was made to design and build the isothermal drop calorimeter similar to that shown in the report referenced above, but incorporating the following changes: instead of immersing the calorimeter container in a constant temperature bath, a jacket would be built around the calorimeter container through which water would be circulated from a constant temperature bath; and a tungsten mesh heating element and tantalum radiation shields would be used in the furnace. Other minor modifications would be incorporated as required for remote assembly and operation.

The isothermal calorimeter and furnace are designed. The calorimeter is fabricated and undergoing testing. There have been numerous difficulties encountered in fabricating the furnace which should be completed by August 15, 1968.

Services for the calorimeter which have been designed, purchased, fabricated, and installed are: power supply and power leads for the furnace, vacuum pumps and vacuum lines, special dropping and retrieving devices for the specimen capsules, and control and instrument consoles.

A remotely operated welding rig is required to seal the calorimeter specimens in tungsten capsules. The welding rig includes a heliarc welding power supply, controls, and an inert chamber containing a welding fixture. The chamber, welding fixture, and controls are designed and built; and a power supply is available. An Ar and He gas system is partially installed.

The use of optical pyrometry for obtaining temperature measurements of furnaces located within hot cells appeared to offer decided advantages over thermocouple methods. Measurements must be made through the hot cell windows or through a periscope system. Sufficient experimental data were accumulated to indicate

that the most accurate measurements were obtained by viewing directly through the windows. After applying the appropriate corrections to the readings, errors in the measurements are in the order of 0.2-0.5%.

VII. HOT CELL METALLOGRAPHY (K. A. Johnson, M. W. McCloskey)

Metallographic capabilities have been improved to the point where 12 samples per day can be mounted and polished. The limit on specimen examination now will be the number and types of tests or operations that are required on the polished specimens, i.e., hardness, microphotography, autoradiography, etc.

A vacuum potting chamber has also been installed and tested. The capability to pot specimens under vacuum will greatly help in mounting cracked, porous, or thin specimens.

A holder for checking the quality of polish of specimens while still in the specimen mount holder has been installed and tested. This attachment allows the use of the hardness tester microscope for interim examination before removing the 6 finished specimens from the mount holder.

VIII. ANALYTICAL CHEMISTRY

Hot Cell Applications of Methods of Analysis

The principal objective was to develop a capability to do various quantitative analyses in a hot cell on irradiated fuels. Most of the work involved selection of methods to be used, and chemical and mechanical modifications, if necessary, so that each step in the procedure could be executed with manipulators. These included the following:

Dissolution of Uranium Fuels Containing Ru (U Fissium) (J. W. Dahlby)

Several samples of unirradiated U-fissium alloy were dissolved in a $\text{HCl-HNO}_3\text{-HClO}_4$ mixture in a dissolver designed for hot cell use. The apparatus consists of a closed dissolver pot connected to a water-cooled NaOH trap to collect volatile Ru. Samples ranging between 0.5 and 1 g were dissolved without visible residue remaining, and the recovery of Ru was 100%. The dissolver was installed in a hot cell and applied successfully

to dissolution of irradiated fuel alloys.

The Determination of Free (Uncombined) Carbon
in Irradiated Carbide Fuels
(T. K. Marshall)

In adapting a method (Rpt. LA-3603, 1966) for remote manipulation, a compact system for igniting the separated free C was fabricated and tested. The system consisted of a fused-silica furnace tube, having a fused-silica pedestal to hold the ceramic filtering crucible during ignition, connected to a Ni furnace tube filled with CuO (to oxidize CO to CO₂). Each furnace tube was wrapped with a Nichrome wire heating element. Separation of the free C from carbide samples was done by selective dissolution of metal carbides in either HCl or HNO₃, and filtration of the solution through a ceramic filtering crucible which retained the insoluble (free)C. Ignition of the free C in O₂ at 1000°C, absorption of the CO₂ formed on an Ascarite trap, and weighing of the trap completed the analysis. Twelve portions of a UC sample were analyzed for total and free C to test the apparatus. Average values of 9.32% total C and 0.91% free C were obtained. The relative standard deviation of 6.6% calculated from these measurements reflected the heterogeneity of the C distribution in the UC as well as the reproducibility of the method. The apparatus also was tested by determination of total C in sucrose. The C found was equal to the calculated amounts added (as sucrose) and the relative standard deviation was only 0.5%.

Operation of the furnace using manipulators was found to be satisfactory, and installation in the hot cell has started.

Determination of Oxygen in Irradiated Fuels
(C. S. MacDougall, W. Hutchinson)

A furnace consisting of a fused-silica water-cooled tube heated by induction was designed for inert-gas-fusion measurement of O₂ in irradiated fuels and tested under simulated hot cell conditions. Plans for installation of the furnace in a hot cell were made, and installation of a 25 KW induction heater and other ancillary equipment was partially completed. Some delays are anticipated because an inert atmosphere enclosure for sample preparation is not completed.

Determination of Nb, Pd, and Rh in Fissium
Fuel Alloys

(R. G. Bryan, W. G. Baughman, E. A. Hakkila,
G. R. Waterbury)

X-ray fluorescence and spectrophotometric methods were developed or adapted to measure Nb, Pd, and Rh in U fissium fuel alloys. The x-ray fluorescence method for measuring Nb coupled a solvent extraction separation with x-ray fluorescence measurement of the Nb using Y as an internal standard. The solvent system for the separation was H₂SO₄-HF-hexone. Following corrections for Mo and U interference, the relative standard deviation of the method was about 10% in measuring 50 ppm of Nb. In the x-ray method developed for measuring Pd and Rh, Y was added as the internal standard and the Pd, Rh, Y, and Ir, added as a carrier, were separated from the U and other fissium elements by hydroxide precipitation prior to x-ray fluorescence measurement of the Pd and Rh. The precision (1 σ) was approximately 2 relative percent in measuring Pd and 4 relative percent in measuring Rh at concentrations between 0.05 and 0.5%.

A spectrophotometric method [Anal. Chem. 30, 1007 (1958)] for determining Nb was modified to eliminate interference from Mo. The HCl solution of the U fissium alloy was washed repeatedly with equilibrated hexone to remove the Mo before HF was added and the Nb extracted. The spectrophotometric measurement of Nb as the Nb-hydroquinone complex had a precision (1 σ) of approximately 2 relative percent. Spectrophotometric measurement of Pd as the 2-nitrosonaphtholate complex was made following separation of the complex by extraction from weakly acid (pH 2) solution of the U fissium into toluene. The precision (1 σ) of the method in measuring Pd concentrations between 0.1 and 0.3% was about 2 relative percent. Adsorption of U and some alloying elements from 8M HCl onto anion exchange resin was used to separate Rh prior to its reduction with SnCl₂ and spectrophotometric measurement as the reduced Rh chloro complex. The relative standard deviation of this method was approximately 3%.

Successful application of the spectrophotometric methods was made to determination of Pd and Rh in

irradiated and non-irradiated U fissium, and of Nb in non-irradiated alloys. The x-ray fluorescence methods were applied only to analysis of non-irradiated alloys. The results obtained by both methods for each element were in good agreement.

Spectrochemical Analyses
(O. R. Simi, R. T. Phelps)

A hot cell specially designed for emission spectrochemical analysis of irradiated materials was tested by analyzing an irradiated fuel (EBR II). The design of the cell permits all manipulations of the sample, including excitation in an arcing box, to be done by remote handling. The light emitted by sample during excitation is brought to the spectrograph, which is located outside the cell, by a system of front-surfaced mirrors and lenses and a quartz window in the cell wall.

Studies with stand-in unirradiated UC_2 showed that a carrier-distillation technique could be used to analyze irradiated U or Pu fuel by remote manipulation in the hot cell. The sample is cut or crushed, ignited, mixed with 4% Ga_2O_3 as a carrier, and excited with a d.-c. arc either in air or in a controlled atmosphere of O_2 -30% Ar. Concentrations of the impurity elements are determined either semi-quantitatively by visual comparison of spectra or quantitatively by photometry of the spectrograms. The method was found applicable to the following elements (lower limits of detection are indicated) up to a limit of about 300 ppm: Be and B, 0.3; Mn and Cu, 0.6; Mg and Sn, 2; Cr, 3; Al, Si, Fe, Ni, Mo, Pb and Bi, 6; Zn, Cd and Ba, 20; P, Ca, V and Sr, 30.

First use of the hot cell to analyze irradiated material was successfully performed with samples of three EBR-II fuel pins (U-25% Mo-2% Ru-0.3% Rh-0.2% Pd) which had undergone 1.3% burn-up. The operations, all remotized, were performed as planned and previously tested, without any difficulty.

The method used to analyze Na is being adapted to hot cell operation. It involves dissolving the sample in butanol, converting to NaCl by adding hydrochloric acid, evaporating to dryness, mixing with graphite powder, and exciting by a d.-c. arc. Concentrations are evaluated semi-quantitatively by visual comparison of spectra. The

limits of detection (ppm) obtained with standards arced in the hot cell are listed as follows: Be, Ca, V, Cr, Mn, Fe, Sr, Mo, Ag and Sn, 0.8; Mg, Al, Si, Ti, Ni, Cu, Pb and Bi, 3; B and Co, 8; Cd and Ba, 30; Zn, 300. Other elements such as Li, K, Y, Rh, In and Au will be added to the list.

A method to analyze Type-300 stainless steel for the characteristic metal constituents has been adapted to use by remote manipulation in the hot cell. It consists of taking filings of the sample, adding 2 mg of the filings to a platform-type L-3748 graphite electrode and completely consuming the electrode charge by d.-c. arc. By using photometry to evaluate the spectrogram and the major constituent Fe as an internal standard, the following elements are measured, usually, with 10% relative standard deviation: Cr, Ni, Mn, Si, Mo, Nb and Ti. Al, Co, Cu and V are evaluated semi-quantitatively by visual comparison of spectra. First irradiated stainless steel analyzed in the hot cell was cladding of Type-304 material removed from EBR-II fuel rods.

Development of additional in-cell spectrochemical analysis capabilities included techniques for the analysis of fuel pins, fuel-rod spacer wire, cladding, and sodium bond of EBR II Fuel Rods. The results of these analyses are discussed elsewhere.

New Equipment

(a) Micro Sampling. An ultrasonic "impact grinder" manufactured by Raytheon was selected and purchased for hot cell sampling of irradiated fuels. Cores as small as 0.015 inch in diameter reputedly can be obtained, thus enabling chemical analyses, x-ray diffraction, and microprobe examination to be made on a small and pinpointed section of the sample. Out-of-cell testing will be started upon receipt of some auxiliary equipment.

(b) Shielded Microprobe. An instrument manufactured by the Materials Analysis Company was examined at the Company's plant and has been purchased. Designed to adequately shield 0.3 curies of 2 mev beta gamma radiation it appears adequate for our needs. The instrument includes a portable shielded cask for transfer of the sample prepared in the hot cell to the instrument

itself. This cask, when in position so that a sample transfer can be made into the instrument where examination is made, becomes a part of the shield of the instrument, and remains in place until the sample is removed.

A delivery date of October 1, 1968, is anticipated.

(c) Microliter Pipets. Hot cell tests were made of commercial, self-filling, disposable micropipets. Repeated measurements of weighing, filling, and reweighing these pipets indicated an overall reproducibility (1 σ) of < 1 relative percent for pipetting volumes of 1 and 100 μ l. This precision is quite acceptable for hot cell applications.

IX. EXAMINATION OF UNIRRADIATED FUELS

Thermal Conductivity (K. W. R. Johnson)

A 3M, Model TC-200 comparative type thermal conductivity apparatus is being modified to permit measurements on Pu materials. For these comparative type measurements a temperature gradient is imposed between the top and bottom surfaces of a thermal conductivity stack which consists of an unknown specimen sandwiched between two meter bars of known thermal conductivity. Surrounding the stack are guard heaters which are adjusted to match the temperature profile of the stack. Thermocouples in the stack and guard indicate when matched, steady state conditions have been achieved and the temperature drop across the specimen and meter bars. If the stack is of uniform diameter, the thermocouples are equally spaced in each compartment of the stack and no heat is transferred to or from the guard, then the product of the thermal conductivity and temperature drop should be equal for each component and the thermal conductivity of the specimen can be calculated.

Calibration

To prepare for thermal conductivity measurements a group of 11 Pt, Pt-10% Rh thermocouples were calibrated using U. S. Bureau of Standards freezing point standards. Measured freezing points varied linearly from +0.2° at 231.9° to -0.4° at 1083.3°C.

The initial calibration measurement was made with commercially supplied 1 in. diam Inconel 702 meter bars and an Inconel 702 specimen 1 in. diam x 1 in. long. In the range 101° - 750°C the measured thermal conductivities were within 2% of the recommended values⁽³⁾ whereas at 1212°C the measured values were 12% low.

In the next series of calibration measurements consideration was given to:

- a. Specimen size-homogeneous specimens 1/2 in. diam x 1/2 in. long could be more readily fabricated than larger specimens; and
- b. Insulation-bubble alumina, normally used between guard and stack would probably react with many Pu fuel specimens at elevated temperatures.

Accordingly a 1/2 in. diam meter-specimen-meter assembly was fabricated and radiation shields consisting of horizontally spaced Ta discs were substituted for the ceramic insulation.

With 1/2 in. long specimens the guard and specimen thermocouples were in dissimilar planes hence guard temperatures were established by graphical analysis of the temperature profile of the stack.

Preliminary measurements made at $<10^{-3}$ torr indicated that the attainment of matched, steady state conditions was impossible in the existing equipment because of heat conduction down the walls of the guard tube. An atmosphere of pure Ar was therefore used in all subsequent measurements. Various guard temperature profiles were used to establish the conditions at which absolute error and measurement deviations were minimal. The results of these measurements are shown in Table I. It can be seen that by adjusting guard heaters to minimize the temperature gradient at the specimen-meter bar interface, both accuracy and deviation were within the 10% limit specified for the instrument.

Plastic Deformation (M. Tokar)

Measurements of the compressive creep behavior of the uranium-plutonium ceramic fuels are a requisite in predicting the mechanical behavior of these materials

Table I
The Thermal Conductivity of a 1/2-in. Dia. x 1/2-in. Long
Inconel 702 Specimen

Experimental Conditions	Temperature (°C)	Measured Thermal Conductivity (cal./sec.cm.°C)	Measurement Deviation (%)	Absolute Accuracy (% Error)
Matched Guard	303	0.0331	4.8	13.6
Linear Guard	314	0.0347	1.2	9.8
	474	0.0423	2.2	6.2
	704	0.0523	4.8	7.6
	761	0.0539	9.9	7.0
	848	0.0718	14.8	3.2
Minimum	663	0.0579	6.6	5.8
Interfacial ΔT	881	0.0746	8.8	4.8

under reactor operating conditions. Equipment for obtaining such measurements has been installed in an inert glove box. The apparatus is a modification of a design now in use on UC-graphite composites.⁽⁴⁾ In this apparatus cylindrical specimens, about 1/2 in. diam x 1/2 in. long, are subjected to compressive loads (8000 psi max) at elevated temperatures (1800°C max) under vacuum or inert atmosphere. During the creep test the specimen is held in a graphite die, which is heated by an induction coil, powered by a 15 KVA motor-generator. The compressive load is applied by a hydraulic ram, which passes through an O-ring in the floor of the inert box and another O-ring in the bottom of the water-cooled stainless-steel vacuum chamber containing the graphite susceptor and heating coil. The graphite die-susceptor rests on a stack of pyrolytic graphite insulating disks atop the hydraulic ram. The load is transferred to the specimen through graphite push-rods at each end. In order to prevent changes in stoichiometry in the specimens due to carbon pick-up from the graphite push-rods, B₄C disks, 30 mils thick, are placed between the ends of the specimen and the graphite rods. The assembly is completed by a stack of pyrolytic graphite disks placed above the susceptor, between it and the top of the vacuum can.

The amount of deformation of the specimen is determined from measurements of its dimensions before and after the creep test. These measurements are, at present, made with a micrometer calibrated to 0.0001 inch. The measurements are, of necessity, made while the specimen is at ambient temperature. Errors due to

recovery are minimized by cooling the specimen under load.

The typical creep test is conducted at constant load-constant temperature. The simplest way to treat data from such a test is to plot % deformation vs time for a given load and temperature. Such a plot consists of two main sections termed "primary" and "secondary" creep. During primary creep, the rate of creep decelerates until a constant rate is approached. The second stage of creep is the strain that occurs at a constant rate, usually termed the "minimum creep rate." The minimum creep rate ($\dot{\epsilon}$) can be described by an equation of the form

$$\dot{\epsilon} = A \sigma^n \exp(-Q/RT) \quad (1)$$

where σ is the creep stress, A and n are constants, and Q/RT is the Arrhenius term. The exponent n can be determined from the slope of a $\dot{\epsilon}$ vs log σ for constant T. The activation energy, Q, is determined from the usual Arrhenius plot. Hence, all the unknowns in equation (1) can readily be determined. Solution of equation (1) is highly desirable since it yields information on the possible rate-controlling mechanism of creep in the material of interest as well as provides useful engineering data.

Since plastic deformation, particularly under creep conditions, is highly structure sensitive, a major portion of this investigation must be concerned with the determination of the effects of microstructural variables on the creep rate. Porosity, grain size, amount, and distribution of secondary phases--all have effects which will depend on the rate-controlling mechanism of creep for the given material.

Before committing the creep-testing apparatus to use with plutonium materials, a preliminary testing program has been undertaken on UC. Compressive creep data on UC are available in the literature,⁽⁵⁻⁷⁾ thus making it possible to check the results obtained on the new apparatus with data obtained elsewhere. So far, the data is in good agreement. For example, a specimen of UC, tested at 6000 psi, 1300°C had (after 57 hours) a minimum creep rate of 1.45×10^{-4} /hr as compared to

1.6×10^{-4} /hr reported by Norreys.⁽⁵⁾

Hot Hardness
(A. L. Gonzales)

The hot hardness equipment has been installed in the glove box. As soon as all vacuum system leaks have been located and sealed, the system will be tested with UC and $U_{0.8}Pu_{0.2}C$.

Vacuum Cathodic Etcher
(K. A. Johnson and A. L. Gonzales)

This instrument is located in the same enclosure as the hot hardness unit, and will be ready for use at the same time.

X. EXAMINATION OF EBR-II DRIVER FUELS
(K. A. Johnson, J. W. Schulte, G. R. Waterbury)

The Division of Reactor Development and Technology requested that LASL extensively investigate 6 irradiated EBR-II Driver Fuel Rods. Three unirradiated rods were received on December 21 for check-out of equipment and techniques. Additional rods, 2 unirradiated and 6 irradiated, were received on January 5, 1968. The capabilities which LASL had developed in support of the LMFBR program as well as previous projects were used to obtain meaningful measurements on these rods. The results obtained during this examination are given below.

Fuel Element

A. Measurements of Physical Properties

B. Stereo-viewing and Macro-photography

All six irradiated and five unirradiated elements were visually examined. The only notable feature on both irradiated and unirradiated elements was a slight discoloration (golden brown) on all the elements. The elements with the most prominent stain SL 42-17 (irradiated) and SL 49-60 (unirradiated) were selected for an attempt to identify the stain by chemical analyses.

C. Chemical Analyses of Surface Material in Discolored Areas on Stainless Steel Clad and Wires

Discolored surface areas on spacer wires or clad of three fuel elements were leached in succession with alcohol-acetone and then twice with a dilute $HCl-HNO_3$ solution. The first acid leach removed the discoloration and the second dissolved some of the substrate material to provide a reference solution. The total quantities of material found in each of the first two leaches of each sample were small, ranging from 0.8 to 44.4 μg . Emission spectrochemical determinations showed that iron, chromium, and nickel, which are constituents of the stainless steel, were the main solutes in the acid leach solutions. Submicrogram quantities were found of surface contaminants such as Cu, Y, Pb, Mn, Al, and Ca. Oxygen, which might contribute to the surface discoloration, could not be measured because of the nature of the sample, it was difficult to evaluate the significance of the

Table II

Measured Physical Properties

Element	Radiation, ¹ R/hr at 1 m	Weight, g	Max. Surface Temp., °C ²	Dimensions in inches		Length ($\pm 1/32$ in)	Bow, ³ in.
				Max.	Min.		
4015-56 (Irrad.)	28	84.82	30.6	0.1750	0.1744	18 1/10	0.080
SL 38-16 (Irrad.)	29	84.64	29.2	0.1754	0.1750	18 1/16	0.035
4088-100 (Irrad.)	30	84.49	29.9	0.1749	0.1743	18 1/16	0.018
4087-53 (Irrad.)	32.5	84.80	29.6	0.1746	0.1742	18 1/16	0.011
4057-84 (Irrad.)	26	84.07	30.7	0.1736	0.1732	18 1/16	0.038
SL 42-17 (Irrad.)	28	84.42	30.0	0.1752	0.1748	18 3/32	0.019
SL 49-60	--	84.81	--	--	--	18 1/16	--
0459-14	--	83.54	--	--	--	18 1/16	--
0121 H-05	--	--	--	0.1735	0.1729	--	0.014
0121 H-23	--	--	--	0.1739	0.1735	--	0.055
0121 H-27	--	--	--	0.1735	0.1728	--	0.027

¹Swipes showed no α contamination and 4-50 mr/hr β - γ contamination.

²Temperature of hot cell was 29.0°C.

³Bow measurements are to ± 0.005 in., but flexibility of the fuel elements makes the tolerance accuracy doubtful. Some bow may have been induced by handling.

metallic contaminants which might have been introduced onto the surface during the many handling operations.

D. Gamma Scanning
(D. M. Holm, K-1)

A detailed report of the results obtained from gamma scanning three irradiated EBR-II rods is listed in Project 808 of this Annual Report.

E. Nondestructive Tests
(Group GMX-1)

1. Beta-Gamma Autoradiographs

The six irradiated elements were autoradiographed; the dark images obtained were then x-ray radiographed at a low energy level. The resulting radiographs were traced with a microdensitometer. The maximum change in film density of the fuel element images was about 2.2%.

This method is not particularly productive of information as applied to this particular type of fuel element.

2. Eddy Current Measurements

Eddy current measurements were made on the elements at a frequency of 250 K Hz with the results as shown in Table III. The values in Table III have not yet been correlated with any particular features of the element; however, low conductivity indications may show Na voids.

Table III
Locations of Conductivity Changes

Element	Distance from Top of Fuel Element, in Inches ± 0.2 Inches						
4015-56(Irrad.)	4.6*	5.8	11.5	13.5			
SL38-16(Irrad.)	1.1	1.75	3.9*	6.6	7.75	12.1*	
	13.2	13.8	14.4*	15.0*	15.5	15.75	16.4
4088-100(Irrad.)	1.13	2.6	3.6	6.6	14.2	14.3	
	14.9	16.2					
4087-53(Irrad.)	4.5	5.9	9.4	13.5			
4057-84(Irrad.)	2.6	6.3	9.25	11.8	12.4	13.9	14.3
SL42-17(Irrad.)	2.0*	3.7	9.3*	10.1 to	11.0*	11.75	12.3
	12.8	16.1					
0121H-05	4.5	6.9	7.7	11.3 to	11.7	12.4 to	12.9
	13.4 to	13.9					
0121H-23	2.1	3.0	3.4 to 3.7	6 to 7.5	10.5		
0121H-27	5.3	6.2	10.5 to 10.9	15.2			

* High conductivity points, all others are low conductivity points.

3. X-ray Radiography

Results of radiographic inspection of 9 elements are as follows:

Element	
4015-56(Irrad.)	Five voids, 10 to 30 mils diam located in the fuel pin between 1 and 2 inches from the bottom of the capsule
SL38-16(Irrad.)	No voids detected.
4088-100(Irrad.)	Two voids in the fuel pin, about 10 mils diam, 5.2 and 5.6 inches from the top end of the element.
4087-53(Irrad.)	No voids detected.
4057-84(Irrad.)	No voids detected.
SL42-17(Irrad.)	No voids detected.
0121H-05	Voids in the fuel pin from the top to 6.8 inches from the bottom, all in center of pin.
0121H-23	Possible incomplete fusion in weld at top end. Voids all along the center of the fuel pin.
0121H-27	No voids detected.

4. Sodium Level Measurements

Sodium levels in the elements, as measured from the top of each element, were determined to be as follows:

Table IV

Measured Sodium Levels, in Inches

Element	By X-ray Radiography	By Eddy Current ± 0.125 in.
4015-56(Irrad.)	1.03	1.00
SL38-16(Irrad.)	0.84	0.75
4088-100(Irrad.)	2.55	2.75
4087-53(Irrad.)	1.82	1.75
4057-84(Irrad.)	2.45	2.25
SL42-17(Irrad.)	1.45	1.13
0121H-05*	2.81	
0121H-23*	2.40	
0121H-27*	2.81	

* These elements were rejected by ANL because the Na levels did not conform to specifications.

5. Infrared Radiometry

One unirradiated element was inspected by this method, and indications are that this technique may be useful in detecting Na levels.

Components

A. Clad

1. Chemical Analysis

The bottom tip and one section (wall) of clad from three unirradiated and three irradiated fuel elements were analyzed spectrochemically for several metals, and the unirradiated samples also were analyzed by a micro-combustion method for C (Table V). The C values were within the maximum specified in the composition requirements of ASTM-A-240-63 for type 304 L stainless steel and in the Product Specification for the EBR-II Driver Fuel Elements, FCF-1. The concentrations of the metallic constituents, with the exception of Cr, also were within the specified limits. The values for Cr in the clad of element 4087-53 and 4057-84 were approximately 4 percent high, which is equivalent to one standard deviation of the analytical method.

2. Autoradiography and Metallography

Alpha and beta-gamma autoradiographs were made using exposures of up to 16 hrs. These autoradiographs of irradiated clad (top, middle, and bottom sections) showed no detectable images.

Table V
Chemical Analyses of Cladding

	C, ppm	Cr, %	Mn, %	Concentrations					Cu, %	Mo, %
				Ni, %	Si, %	V, %				
4088-100 (Irrad.)										
Tip	-	20	1.0	10.0	1.0	0.04		0.1	0.08	
Wall	-	17.5	1.5	11.5	1.0	0.03		0.1	0.07	
4087-53 (Irrad.)										
Tip	-	24	1.5	8.0	0.9	0.05		0.1	0.05	
Wall	-	23	2.0	9.5	0.5	0.06		0.1	< 0.05	
SL42-17 (Irrad.)										
Tip	-	20.5	1.0	10.5	1.2	0.04		0.1	< 0.05	
4057-84 (Irrad.)										
Wall	-	25	1.5	9.0	0.6	0.05		0.1	< 0.05	
SL49-60										
Tip	60	17.5	0.80	11.0	0.7	0.05		0.1	0.05	
Wall	80	17.5	0.85	11.5	0.7	0.05		0.1	0.10	
121H-05										
Tip	65	19.0	1.4	11.0	0.3	0.05		0.1	< 0.05	
Wall	180	20.5	1.3	10.0	0.7	0.05		0.1	0.10	
121H-27										
Tip	50	19.0	1.3	11.0	0.3	0.05		0.1	< 0.05	
Wall	105	18.5	1.1	11.0	0.7	0.05		0.1	0.10	
Specifications ^a	300	18 to	2.0	8 to	1.0	-		-	-	
	Max.	20	Max.	12	Max					

^aASTM-A-240-63, composition requirements for 304-L stainless steel.

A transverse section of the clad tubing is shown in Fig. 1. This microstructure is very typical of all the tube material. Figures 2 and 3 illustrate the welds at the top and bottom, respectively. These are also typical of the microstructures in this area of all the elements.

On the irradiated clad there was no detected change in microstructure from that of the unirradiated clad.

Fig. 1. Transverse section of clad tubing from element SL42-17, showing i.d. edge of tube. Electrolytically etched. 500X.

Fig. 2. Top weld between clad (lower section in photograph) and the restrainer in element 0121H-27. Electrolytically etched. 500X.

Fig. 3. Bottom weld between clad and bottom plug. Electrolytically etched. 100X.

3. Tensile Tests

Results of tensile tests on sections of clad are given in Table VI.

Table VI
Tensile Test Results

Clad from Element	Clad Length, in.	Head Speed, in./min	Yield Point*	Ultimate Point*
4088-100 (Irrad.)	5	0.5	444 lb	492 lb
4087-53 (Irrad.)	5	0.5	426 lb	519 lb
4057-84 (Irrad.)	5	0.5	357 lb	495 lb
SL49-60	3-1/2	0.05 to 0.5	162 lb	462 lb
0121H-05	6	0.5	225 lb	444 lb
0121H-27	3-1/2	0.5	225 lb	432 lb

* Strengths are reported direct, not as psi.

The above results indicate an increase in both yield and ultimate strengths in the clad as a result of the irradiation.

B. Fuel Pins

1. Stereo-Viewing and Macro-Photography

Three unirradiated and three irradiated fuel pins were examined; the only notable feature was a few shallow depressions on the irradiated rod 4087-53. These depressions may have been produced during the removal of the fuel from the clad, as evidenced by flakes found in the Na and the disassembly equipment.

2. Measurements

Table VII
Measured Physical Properties

Element	Weight g	Immersion Density, g/cc ± 0.16%		Diameter, in. ± 0.002 in.		Length, in. ± 0.030 in.
		Near Top	Near Bottom	Max.	Min.	
4088-100 (Irrad.)	64.95	17.40	17.48	0.1478 ^a	0.1450	13.56
4087-53 (Irrad.)	64.90	15.77	16.63	0.1530	0.1488	13.81 ^b
4057-84 (Irrad.)	64.97	-	-	0.1470	0.1455	13.56
SL42-17 (Irrad.)	-	17.42	15.84	0.1570	0.1460	-
SL49-60	-	18.06	18.03	-	-	-
0121H-05	-	17.91	17.97	-	-	-
0121H-27	63.79 ^c	17.95	17.94	0.1438	0.1413	-

^aDiameter of pre-irradiation pin is ~ 0.144 in.

^bPre-irradiation length of this fuel pin was 13.499 in.

^cWeight of this fuel pin, as reported by ANL Idaho, was 63.81 g.

The weight of fuel pin 4087-53 is 0.16 g lower than the pre-irradiation weight (65.06 g), as reported by ANL Idaho. This difference may be attributed to the dislodging of small chips during the removal of fuel from clad.

Surface temperatures measured for two irradiated fuel pins were within 1°C of the hot cell temperature (31°C).

Eddy current inspection of irradiated pins detected decreasing conductivity from the top to the bottom with slight local variations (4057-84 Irrad.). The minimum was approximately two inches from the bottom. On pin 4087-53 (Irrad.) the conductivity was lower on the ends and higher in the middle. The d.c. resistivity was also measured as follows:

Top	--	2.005×10^{-6} ohm/in.
Middle	--	2.624×10^{-6} "
Bottom	--	1.683×10^{-6} "

These measurements are roughly related to the pin diameters. 4057-84 is larger at the top and 4087-53 is larger in the middle.

The average hardnesses in DPHN (100 g load) obtained on pin SL 49-60 were as follows: matrix--650-750; inclusions ~ 1200.

3. Chemical, Isotopic, and Radiochemical Analyses

Concentrations of some alloying elements and impurities were determined in three unirradiated and three irradiated fuel pins by spectrophotometric, radiochemical, and x-ray fluorescence methods, and the isotopic composition of the U in two pins was measured mass spectrometrically. These determinations were made on aliquots of solutions prepared by dissolving 1-g samples taken from the top, middle, and bottom of the fuel pins. Solid samples from the middle of each rod were analyzed by an inert gas fusion method for O₂ and a microcombustion method for C. The results obtained (Tables VIII and IX) are within the concentration ranges listed in Product Specification for the EBR-II Driver Fuel Elements, FCF-1, with the exception of the slightly high concentrations of 2.76% for Mo and 2.19% for Ru in the top sample of fuel pin SL-49-60, the slightly high

concentration of 2.67% for Mo in the bottom sample of fuel pin 4088-100, and the slightly low values for Zr in pins 0121H-05 and 0121H-27. Emission spectrographic determinations of impurities in the samples from the middle of each pin (Table X) showed that the impurity concentrations were less than the specified maximum concentrations except for Fe in element 4088-100 and Si in elements 0121H-05, 0121H-27, and 4088-100. The isotopic compositions of the U in the remaining three irradiated fuel pins and one unirradiated fuel pin are being measured mass spectrometrically.

Radiochemical measurements of five fission product elements were performed on two sections of fuel pin 4087-53. The first section had a diameter of 0.1525 in. and was taken from a region of maximum swelling. The second section had a diameter of 0.1488 in. and was taken from a region having a minimum swelling. The results (Table XI) showed that the concentration of each fission product element in the section having the larger diameter was greater than in the section having the smaller diameter. As the relative fission product concentrations are indicative of relative burn-up in the two samples examined, there appears to be a positive correlation between burn-up and diameter or swelling. Calculation of actual burn-up cannot be made from these data because of lack of details of irradiation history.

4. Metallography

Typical microstructures of the top, middle, and bottom of unirradiated fuel are shown in Figs. 4, 5, and 6. As can be seen, the microstructure is relatively uniform from top to bottom. Figure 7 illustrates the etch patterns formed on the larger inclusions in the fuel.

Typical microstructure of irradiated fuel is shown in Figs. 8 and 9. The microstructure consists of an even distribution of inclusions in a matrix which is a very fine mixture of U allotropes. The small amount of observed porosity in the irradiated fuel is little different from that found in the unirradiated fuel.

Table VIII

Chemical Analyses of Unirradiated Fuel Pins

Element	Specified Concentration ^a	Concentrations								
		Pin SL49-60			Pin 0121H-05			Pin 0121H-27		
		Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Mo	2.46 ± 0.17%	2.76%	2.49%	2.51%	2.33%	2.33%	2.33%	2.32%	2.32%	2.33%
Ru	1.96 ± 0.16%	2.19%	1.97%	1.96%	2.00%	1.99%	2.00%	2.01%	2.00%	2.01%
Rh	0.28 ± 0.05%	0.29%	0.27%	0.27%	0.28%	0.28%	0.29%	0.29%	0.28%	0.29%
Pd	0.19 ± 0.04%	0.21%	0.20%	0.19%	0.19%	0.20%	0.19%	0.19%	0.19%	0.19%
Zr	0.10 ± 0.03%	0.079%	0.068%	0.069%	0.057%	0.053%	0.056%	0.055%	0.054%	0.056%
Nb	0.01 ± 0.006%	0.0053%	0.0050%	0.0040%	0.0053%	0.0056%	0.0062%	0.0048%	0.0053%	0.0050%
Th	< 100 ppm	7 ppm	9 ppm	9 ppm	1.5 ppm	4.2 ppm	3.5 ppm	5.3 ppm	1.0 ppm	1.6 ppm
Pu	---	9.6 ppm	10 ppm	9.6 ppm	< 1 ppm	< 1 ppm	< 1.1 ppm	< 1 ppm	< 1 ppm	< 1 ppm
O	< 200 ppm		80 ppm			90 ppm			110 ppm	
C	< 400 ppm		165 ppm			400 ppm			530 ppm	
N			25 ppm			7 ppm			6 ppm	
U	95.0 ± 1.0%	95.3%	95.3%	94.7%	95.4%	95.4%	95.3%	94.9%	95.3%	95.3%
²³⁵ U	52.18 ± 0.50%	51.99%	51.99%	52.28%	52.09%					
²³⁴ U										
²³⁴ U	47.82 ± 0.50%	48.00%	48.00%	47.72%	47.91%					
²³⁶ U										
²³⁴ U	< 1.0%	< 1.0%	< 1.0%	< 1.0%	< 1.0%					
²³⁶ U										

^aProduct Specifications for the EBR-II Driver Fuel Elements, FCF-1.

Table IX

Chemical Analyses of Irradiated Fuel Pins

Element	Specified Concentration ^a	Concentrations								
		Pin #4087-53			Pin #4088-100			Pin #SL42-17		
		Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Mo	2.46 ± 0.17%	2.48%	2.66%	2.49%	2.45%	2.48%	2.67%	2.44%	2.47%	2.51%
Ru	1.96 ± 0.16%	1.97%	2.04%	1.93%	1.96%	1.94%	1.95%	2.00%	2.01%	2.03
Rh	0.28 ± 0.05%	0.29%	0.32%	0.27%	0.28%	0.30%	0.32%	0.29%	0.30%	0.30%
Pd	0.19 ± 0.04%	0.18%	0.20%	0.19%	0.18%	0.19%	0.19%	0.20%	0.21%	0.20%
Pu	---	440	140	360	185	215	315	570	680	430
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
U	95.0 ± 1.0%	95.1%	94.8%	95.8%	95.5%	94.6%	95.1%	94.8%	94.8%	95.3%

Table X

Emission Spectrographic Analyses of Fuel Pins

Element	Concentrations, ppm						
	Al	Be	B	Cr	Fe	Ni	Si
SL49-60	35	< 0.4	2	12	125	50	120
0121H-05	65	< 0.4	9	16	200	50	680
0121H-27	65	< 0.4	9	16	180	50	650
4087-53 (irrad.)	20	< 0.4	2.5	20	280	150	200
4088-100 (irrad.)	40	< 0.4	5	60	350	100	380
SL42-17 (irrad.)	30	< 0.4	1.2	25	150	150	100
Specifications ^a (Maximum concentration)	300	100	100	300	300	200	300

^aProduct specifications for the EBR-II Driver Fuel Elements, FCF-1.

Table XI

Isotope	Concentration, d/min/mg. ²³⁵ U	
	Section 3F, diameter 0.1455 in.	Section 7F, diameter 0.1525 in.
⁹⁰ Sr	1.02 x 10 ⁸	1.06 x 10 ⁸
¹³⁷ Cs	1.19 x 10 ⁸	1.25 x 10 ⁸
¹⁵⁵ Eu	5.47 x 10 ⁶	5.94 x 10 ⁶
¹⁴⁴ Ce	2.40 x 10 ⁹	2.48 x 10 ⁹
⁹⁵ Zr	3.96 x 10 ⁹	4.23 x 10 ⁹

Fig. 4. Fuel near top of pin 0121H-27. 500X

Fig. 6. Fuel near bottom of pin 0121H-27. 500X

Fig. 5. Fuel near middle of pin 0121H-27. 500X

Fig. 7. Fuel from 0121H-27. Note etch patterns on larger inclusions. 1750X

Fig. 8. Typical microstructure from the middle of fuel pin 4087-53 (Irrad.) Electrolytically etched. 500 X

Fig. 9. Typical microstructure from the bottom of fuel pin 4087-53 (Irrad.) Electrolytically etched. 500X

C. Sodium

1. Chemical Analyses

Metallic impurities in the Na from five fuel elements were determined by an emission spectrographic method. The samples were obtained either by leaching the Na with Dowanol or butanol from the top section of the clad or by removing a small sample of metallic Na with a spatula. Hydrochloric acid was added to each sample and the butanol or Dowanol was evaporated to prepare the samples for analysis. The results (Table XII) showed that Ca was the only impurity for which the concentration was consistently at or above the specified maximum. The data also showed that the impurity concentrations in the Na removed mechanically from the one element (0121H-27) were lower than found in the butanol or Dowanol solutions of the Na. The higher impurity concentrations for the leached samples could be the result of contamination from foreign material either on the clad or introduced during the leaching operation. Unfortunately, mechanical removal of Na samples from the irradiated elements was not possible, but great care was exercised in cleaning the outside of the cladding prior to leaching of the Na.

In addition to the measurement of metallic impurities, a portion of the Dowanol solution of the sodium from each irradiated element was analyzed semi-quantitatively for cyanide by a colorimetric method. The small samples available were inadequate to permit highly sensitive measurements of the cyanide (Table XII), but none was found in the three samples analyzed.

D. Fission Gas Analyses

(E. D. Loughran)

Sampling was done in the customary manner by piercing the gas space above the Na and allowing the gas to expand into a sample collector of known volume. Void volume within the rod was not determined; therefore, the gas pressure within the rod was not obtained.

Results of the analyses obtained by mass spectrometry are listed in Table XIII.

Table XII
Concentrations of Impurities in Sodium

Element	Specified Maximum, ppm ^a	Concentrations, ppm, in La Leached from					
		0121H-27 ^b	SL49-60	0121H-27	0121H-05	4087-53 ^c	SL42-17 ^c
Ag	20	< 0.8	< 0.8	5	0.8	< 0.8	0.8
Au	30	< 3	60	< 12	< 12	< 12	< 12
B	5	< 3	12	< 8	< 8	< 8	< 8
Ca	10	10	200	100	150	30	300
Cd	20	< 3	3	< 30	< 30	< 30	< 25
In	30	< 3	< 3	< 3	< 3	< 3	< 3
K	1000	125	120	150	150	150	150
Li	20	< 0.8	< 0.8	< 3	< 3	< 3	< 3
CN ⁻	-	-	-	-	-	< 25	< 50
							< 125

^aProduct Specifications for the EBR-II Driver Fuel Elements, FCF-1.

^bNa removed from element mechanically with a spatula.

^cIrradiated elements.

Table XIII
Fission Gas Analyses

Element	H ₂	He	Percent By Volume			Other	Kr ^a	Xe ^a
			N ₂	O ₂	Ar			
SL38-16	trace	0.29	0.55	0.13	77.1	--	3.89	18.04
4057-84	0.04	0.29	0.36	0.10	96.7	0.04	0.43	2.06
SL42-17	0.18	0.37	2.2 ^b	0.55 ^b	95.2	--	0.27	1.23

^aIt is possible to obtain the percentages of the various Kr and Xe isotopes

^bSignificant but undetermined quantities of these components were introduced during sampling on the mass spectrometer

XI. LMFBR/FFTF FUELS DEVELOPMENT ANALYTICAL QUALITY ASSURANCE AND CONTROL PROGRAM (PNL DESIGNATION: TASK G-2)

(C. F. Metz, R. G. Bryan, C. S. MacDougall,
J. Dalby, G. Nelson, O. R. Simi)

On March 1, 1968, LASL was requested to assume responsibility for the technical direction of an analytical quality assurance and control program oriented to ensure a uniformly high quality, well characterized fuel for the FFTF reactor. PNL, who had already initiated such a program, has designated it as Task G-2.

A major factor in the production of high quality, well characterized FFTF fuel is technical competence of correspondingly high quality for the required chemical analysis. To assure this caliber of technical competence, LASL and PNL, in close cooperation, have developed a

program having the following objectives:

1. To determine the present extent of the analytical capabilities of potential producers of FFTF fuel.
2. To provide technical guidance and evaluation to assure these capabilities are established at the level required by FFTF fuel specifications.
3. To set up and conduct a monitoring program to assure continuing adequate analytical capabilities of fuel producers at the level required by FFTF fuel specifications.

In close cooperation with PNL, a statistically planned analytical program has been initiated which has as its first phase the short term objectives of, (a) determining the extent and quality of the present day analytical capabilities of potential fuel producers, (b) examining the degree of adequacy of analytical methods currently in use, and (c) determining the immediate needs for analytical standards.

In order to be compatible with the time schedule for fuel procurement, it was necessary to initiate the analytical program as soon as possible. For this reason, and also because of the lack of primary chemical standards, the first phase of the analytical program was initiated using as an analysis material sintered pellets of UO₂-PuO₂

previously prepared by PNL and designated Lot ME-21. Although limited analytical information on this material existed, it seemed likely that considerable information might result from various measurements by several laboratories. In particular, the precision of the methods used by the several laboratories could be determined if the analyses were done according to a statistically controlled plan.

The potential fuel producers participating in this plan are AI, ARHCO, B & W, GE, NFS, NUMEC, and UNC.

The analyses being made by these organizations, each making as many as his capabilities permit, are listed below in order of their priorities.

1. U and Pu Assay
2. Isotopic, both U and Pu
3. O/M Ratio
4. Spectrographic Impurities
5. Total Gas Content
6. Halogen Content (Cl and F)
7. Carbon and Nitrogen Contents
8. Density
9. Water Content
10. Homogeneity and Solid Solution

The original target date of July 1, 1968, has not been met by any of the participating laboratories. Their statements of progress indicate their data will be available by August 1. Upon acquisition of the data, LASL will make a statistical study which will be used as a basis for evaluation of each participants capabilities, evaluation of the methods used and recommendations for future work. These evaluations will be limited on scope because the analysis material is not a well-characterized primary standard.

In anticipation of future requirements, work has started at LASL on a high purity, UO_2 -25% PuO_2 material to be used as a primary standard for U and Pu assay. This primary standard will be used for methods calibrations. A secondary, or working standard of similar material is being prepared by PNL. High purity plutonium metal is being supplied by LASL which will be used in this material. Plans have been made for PNL to prepare

three standards for O/M ratio, each having a significantly different value. LASL will provide the PuO_2 for these materials. Plans are being made by LASL to prepare spectrographic standards although specifications for spectrographic impurities will need to be set up before these standards can be completed.

Studies in progress at LASL on the effect of matrix composition on the sensitivity of the spectrographic method for determining impurities in UO_2 - PuO_2 materials indicate that for some elements a significant difference is observed.

Incomplete studies at LASL of two independent methods for determining O/M ratio are aimed at establishing the reliability of both methods.

Repeated assays for U and Pu on ME-21 sintered pellets by controlled potential coulometric methods showed relative standard deviation of 0.32% for the U and 0.10% for the Pu. Lack of a well characterized standard precludes knowledge of the accuracy of these methods. Comparison with a "home made" standard, however, indicates there is no measureable bias in the methods.

XII. REQUESTS FROM DRDT

A cooperative study with Gulf General Atomics personnel was started in an effort to determine the cause of failure in element C-05-05 from the Peach Bottom Reactor. Representative pieces from the failed fuel element are scheduled for delivery to LASL on about July 17, 1968, at which time the examination will be started.

A feasibility report was prepared relative to the disassembly and examination of a fuel element from AI. This fuel element, which was irradiated at Chalk River, contained W-doped pellets and was an experiment designed to provide information on fuel swelling. Since the fuel element was 11 1/2 ft long, two hot cells (6 ft x 6 ft) would have been required for the disassembly. Because of commitments to other programs, the two cells where this operation would have been done were not available until May 1969.

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PROJECT 824

FAST REACTOR METALLIC FUEL STUDIES

Persons in Charge: R. D. Baker
D. B. Hall
Principal Investigators: W. J. Maraman
R. H. Perkins

I. INTRODUCTION

The objective of this program is the development of metal fuels for fast reactor application. Much of the primary effort is placed on preparation and fabrication development of the U-Pu-Zr alloys. Supporting effort is directed toward areas of physics and system evaluation and determining the physical and chemical properties of the fuel.

Irradiation testing is an essential part of the evaluation of a potential fuel alloy for fast reactor application. A knowledge of its intrinsic swelling rate as a function of alloy composition, metallurgical history, irradiation temperature, and total burnup must be obtained. The fission gas release rates and the limits of lattice-retained gas as a function of the above parameters are also required. In addition, the compatibility of fuels and claddings during irradiation at temperatures of interest to the LMFBR program must be determined.

II. FUEL PREPARATION AND FABRICATION (D. R. Harbur)

A. General

The initial goals of this project are to prepare high-purity, homogeneous U-15Pu-10Zr to U-15Pu-15Zr alloys, to fabricate these alloys into fuel pins of the EBR-II size, and to fully characterize these pins. The major effort has been directed toward the preparation of a high-purity, homogeneous alloy. Several fabrication methods have been considered; design and procurement of equipment for the more promising of these methods have been initiated.

B. Results During FY 1968

Two methods are being evaluated for the preparation of high-purity, homogeneous U-15Pu-10Zr to U-15Pu-15Zr alloys: induction melting in conventional crucibles and induction melting in "cold crucibles." Induction melting of the alloying materials inside a graphite crucible with a nonreactive coating offers the advantage of being able to prepare and cast homogeneous alloys in a one-step operation. Induction melting in a "cold crucible" eliminates the need of finding a nonreactive crucible coating for the preparation of the alloy.

Homogeneous ternary alloys have been prepared at 1400°C in less than 10 min by mechanically stirring the melt which consists of plutonium and a pre-alloyed U-Zr binary. The binary was prepared from high-purity uranium and crystal-bar zirconium using repeated arc meltings. (The oxygen content was held at 70 ppm by weight.) The homogeneity of these ternary alloys has been determined chemically by analysis of samples from the top and bottom of chill-cast rods. The degree of alloy segregation during the relatively slow cooling of rods cast into hot molds is being investigated.

The reaction of crucible materials and crucible coatings with the ternary U-15Pu-12.7Zr alloy at 1400°C for short times is being studied. The most promising crucible coating which has been found so far is a colloidal suspension of Y_2O_3 which can be easily sprayed onto a graphite or tantalum surface with argon gas. (The oxygen content of alloys prepared in a crucible coated with Y_2O_3 is around 500 ppm.) Colloidal ZrO_2 coatings are no more

reactive, but at present their adhesive strength is not good enough to prevent attack on the underlying crucible. Flame-sprayed coatings of these two oxides have also held up well during tests. In one casting utilizing a tantalum stirrer and stopper rod coated with colloidal Y_2O_3 , the stirrer and stopper rod were not wetted by the melt. The tantalum content of the casting was 62 ppm. A quantitative evaluation of NbC coatings is being conducted. Flame-sprayed coatings of tungsten and molybdenum and coatings of Fiberfrax cement all showed poor corrosion resistance to the melt. Oxidized tantalum and BN crucibles were also attacked by the ternary alloy. Flame-sprayed TaC coatings and CeS crucibles were entirely wetted by the melt. The oxygen content of the alloy prepared in the CeS crucible was only 190 ppm, but the cerium content was 3000 ppm.

In the cold crucible technique the ternary alloy is prepared by melting and stirring inside a water-cooled metallic crucible. When using this method there is always a frozen alloy skin next to the water-cooled crucible which prevents pickup of impurities from the crucible. Homogeneous U-15Zr alloys have been prepared on the wall of a horizontally-positioned, water-cooled copper heat concentrator. (The concentration of copper in the binary was 6 to 13 ppm by weight.) A heat concentrator unit has been installed in a plutonium glovebox, and several 65-g batches of U-15Pu-12.7Zr alloy have been prepared. These ternary alloys have a minimum zirconium variation from top to bottom of 2% due to a zone refining effect associated with the liquid-to-solid interface within the alloy button. New heat concentrator designs are being tested to improve the homogeneity within the alloy button and to increase the volume of metal contained. A 50 kW radiofrequency unit which has been ordered will double the power available for this operation. An alternate method being studied involves the partial levitation and stirring of a 500-g (or larger) charge in a thin, water-cooled tantalum cone. In this case the charge is heated by the output from a motor-generator set. (This approach offers the added possibility of being able to cast the alloy directly.) Carefully selected stocks of characterized feed materials have been

obtained for all these studies.

Since it may not be feasible to gravity-cast rods to the EBR-II size, both extrusion and swaging are to be investigated. The design and fabrication of a high-temperature extrusion die and press have been completed, and the equipment is now being installed in a plutonium glovebox. Several mockup extrusions have been made on the U-10Zr and U-15Zr binaries. These binaries are gamma extrudable by conventional techniques using a graphite die and punch at a temperature of 925°C and a pressure of 10,000 psi, with an extrusion ratio of 7 to 1. The U-15Zr binary has also been extruded at 800°C in a Dynapak high-speed extrusion machine at an extrusion ratio of 11 to 1. Since the as-cast U-15Zr alloy cannot be swaged below 500°C, a high-temperature swaging machine has been purchased to reduce the extruded rods to the EBR-II size. The temperature at which the extruded binary rods can be swaged is under investigation.

III. IRRADIATION EFFECTS STUDIES

(J. A. Horak, R. L. Cubitt, L. B. Lundberg)

A. General

All long-term irradiations of metal fuels to date have had the effects of thermal cycling (due to reactor shutdowns and changes in power level) imposed upon the effects due to irradiation. Some of the detrimental effects to the fuel caused by this thermal cycling are:

1. The internal stresses produced by the volume changes associated with the alpha-gamma phase transformation in uranium-base alloys could be the source of microcracking in these alloys.
2. Upon cooling, as alpha grains nucleate and grow from the existing gamma grains, the fission products (those that are insoluble and/or above their solubility limits) are swept ahead of the new alpha grains and end up in the alpha grain boundaries. The reverse process occurs on heating. The agglomeration of these elements produces a brittle and/or weak phase (usually intermetallic) resulting in a decrease in the mechanical strength and ductility of the fuel. This phase could exhibit a lower corrosion resistance to hot sodium than the parent fuel.

3. Possibly even more important is the relocation of fission gases during thermal cycling; the agglomeration of fission gases during repeated phase transformations could very well be responsible for the extensive swelling and cracking observed in many of the fuel alloys irradiated to date.

It is evident that thermal cycling of unirradiated material does not provide the information necessary to separate the effects due to irradiation from those due to combined irradiation and thermal cycling.

One of the prime objectives of this program is to determine the effects of irradiation in the absence of thermal cycling. Irradiations will be conducted in the Omega West Reactor where there are instrumented facilities capable of maintaining the irradiation temperature within 5°C of the setpoint at fuel/clad interface temperatures up to at least 700°C, with or without reactor power. Parallel experiments will involve thermal cycling to accurately assess the effects of thermal cycling during irradiation on the properties to be studied.

B. Results During FY 1968

An irradiation assembly has been designed and is being fabricated; it will allow simultaneous irradiation of 3 to 6 fuel specimens, 36 sets of compatibility specimens, and 3 tensile specimens. Each fuel specimen (2 in. long by 0.144-in. diam) is located in the center of a 3-in.-long Type 304 stainless steel tube. Sodium fills the annulus between the fuel and stainless steel. The tubing size is selected so that the tube does not interfere with the intrinsic swelling of the fuel. Stainless steel end-plugs are employed for positioning the fuel in the center of the tube, positioning the tube in the sodium-filled irradiation capsule, and retaining the fission gases in the plenum above the fuel. Three of the fuel specimens occupy the lower level of the irradiation capsule.

The compatibility specimens are in the form of 0.144-in.-diam by 1/8-in.-thick wafers. Kirkendall markers of tungsten wire are placed at each fuel/clad interface. Twelve alternate wafers of fuel and clad are contained in a closed molybdenum holder with sodium present for heat transfer. Three of these assemblies occupy the midplane of the irra-

diation capsule.

The tensile specimens of candidate cladding alloys are 1-in. gauge length by 0.250-in. diam. These are immersed in hot sodium at the upper level of the irradiation capsule. These specimens, as well as the tubes around the fuel pins, will be postirradiation tested at the same temperature at which they were irradiated.

Postirradiation examination of the fuel will include volume and density measurements, optical and electron metallography, microprobe analysis, and determination of lattice-retained gas. The sodium in the tube will be analyzed for fission products and fuel content, and the fission gas content in the plenum will be measured. The tube will then be tensile- or burst-tested at the irradiation temperature and examined metallographically. Examination of compatibility specimens will include microprobe analysis to determine the diffusion of cladding atoms into the fuel and fuel atoms into the cladding alloy and optical metallography for observation of Kirkendall markers and reaction zones. The sodium will be analyzed for fuel and clad constituents, and the molybdenum tube will be subjected to mechanical testing if it does not adhere to the wafers.

Initial emphasis is on U-5Fs and U-15Pu-11Zr fuels with Types 304 and 316 stainless steel clads. These materials have been received and are being characterized and assembled for irradiation. The first fuel irradiation will include U-5Fs at 650°C center temperature, U-5Fs + 304 SS, U-5Fs + 316 SS, U-5Fs + Fe, U-5Fs + Ni, and U-5Fs + Cr diffusion couples at 600°C and 304 SS tensile specimens at 600°C. The samples will be irradiated for approximately 30 days to demonstrate operation of the constant temperature facility. Subsequent irradiations will include U-5Fs and U-Pu-Zr at increasing temperatures in 50°C increments for increasing irradiation times up to 1 yr.

Preliminary measurements of the flux profile and neutron energy spectra in one of the Omega West Reactor experimental facilities have been made. The results are shown in Table I. The flux remains at the level shown from 2 in. below the experimental capsule to 6 in. above the capsule; hence, the fuel, diffusion couples, and tensile specimens experience the same neutron environments.

Table I
Neutron Dosimetry and Spectral Measurements
in the Omega West Reactor

Detector	Reaction	$\bar{\sigma}_E$ (barns)	E	$\phi \left(\frac{10^{13} \text{ neutrons}}{\text{cm}^2 \cdot \text{sec}} \right)$
Al-0.11Co	$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	36	< 0.5 eV	8
Al-0.11Co (Cd shield)	$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	75	> 0.5 eV	0.5
Ni	$^{58}\text{Ni}(n,p)^{58}\text{Co}$	0.4	4.5 MeV	0.06
Fe	$^{54}\text{Fe}(n,p)^{54}\text{Mn}$	0.3	4 MeV	0.06

The flux and spectra measurements are necessary to determine if the average neutron energy in the facility can be increased significantly by use of a neutron converter. Calculations indicate that the present average energy of the neutrons producing fission in the Omega West Reactor is 0.04 eV; this results in a power generation of 990 W/pin. A 0.025-in.-thick ^{235}U converter in the irradiation capsule would raise the neutron energy to 0.3 eV, but only 270 W/pin of power would be produced. With a 0.025-in.-thick ^{239}Pu converter the neutron energy would be increased to 70 eV, but only 120 W/pin of power would be produced. Hence, it appears that the loss of power (fission rate) accompanying the use of a converter would be so large that burnup data of interest could not be obtained in a reasonable test time.

PROJECT 901

OTHER ADVANCED SYSTEMS - RESEARCH AND DEVELOPMENT

Person In Charge: D. B. Hall
Principal Investigators: G. H. Best
E. O. Swickard

1. AQUEOUS NEUTRON SOURCE

A. General

During the last year general studies have been made on two different concepts of aqueous reactors which may be useful as neutron sources. One is the Liquid Excursion Pulsed Reactor (LEPR) and the other is the Liquid Jet Super Flux Reactor or KING.¹ The fuel in either case might be aqueous, enriched UO_2SO_4 , possibly containing other constituents to improve the stability of the fuel. The intensity of the pulse in the LEPR might vaporize most or all of the water in the fuel. There is a question of whether or not the condensate would return readily to its initial composition for the next pulse. Both reactors could have problems of corrosion and erosion. The KING would produce a steady neutron flux but would probably operate at a lower temperature than the Homogeneous Reactors of Oak Ridge National Laboratory.² There could be a problem of precipitating UO_4 together with a hazard of local overheating or difficult control in the KING:

A precipitation of UO_4 also could occur with the LEPR depending on the chosen operating conditions. Radiolytic hydrogen and oxygen from either reactor would be recombined using a platinum catalyst.

B. Results During FY 1968

1. Fuel Chemistry (B. J. Thamer, R. Wilhelm)

Regarding the LEPR concept, an experiment was conducted with a solution of 3.12 M UO_2SO_4 to test

its thermal stability (out-of-pile) to an energy burst of about 5×10^6 J/liter. One reason for choosing the concentrated solution for this experiment was to improve the visual observation of decomposition if it should occur. The energy density was one of interest according to various calculations on LEPR configurations.¹ The high energy density required, and a desire to minimize interactions with other materials led to the use of one microliter of solution that was heated by a laser beam. The sample had been sealed under air in a quartz capillary. It was heated with about 80% efficiency by a 6-J, giant pulse from a ruby laser. The laser beam was made to converge on the sample by means of a lens. The pulse lasted 15 nsec. Since UO_2SO_4 could not absorb light efficiently at this laser's frequency (6943 Å), the solution had been doped to enhance absorption. The vaporized and condensed solution was centrifuged to one end of the capillary for comparison with its original state. Qualitative observations indicated no decomposition of the solution.

Regarding the radiolytic production of H_2O_2 in a KING, some measurements were made on the solubility of total peroxide as a function of UO_2SO_4 concentration. The solution had 0.50 M excess H_2SO_4 in each case because it was anticipated that added acid would be required to repress the reaction shown in Eq. 1. The results are those of Table I. The last column gives estimates of the permissible energy density per transit of the fuel.

TABLE I

H_2O_2 Solubilities and Corresponding Fission-Pulse Densities (H_2SO_4 molarity = 0.50; temperature, 24°C)

UO_2SO_4 Molarity	H_2O_2 Solubility, Molar	G^a	J/cm ³ -pass ^b
0.864	0.0062 ± 0.0004	1.1	54.
0.432	0.0088 ± 0.0004	1.3	65.
0.200	0.013 ± 0.001	1.5	83.

^a G = No. of molecules of H_2O_2 produced per 100 eV of reactor energy.⁴

^bCalculated from J/cm³-pass = (H_2O_2 solubility)/0.000104 G.⁴

through the critical region of the KING. Exceeding these values would risk the precipitation of UO_4 . Of course the values given are for 24°C, but they are not believed to vary rapidly with temperature.⁵ Although the fuel might contain ferric, cupric, or other salts to decompose H_2O_2 , such decomposition would probably be slight during a 0.02-0.04 second transit time through the critical region. However, it is hoped that virtually all of the H_2O_2 could be made to decompose in the 10-20 seconds delay between successive passages through the critical region. It is probable that the values in the second and fourth columns of Table I could be increased by raising the concentration of excess H_2SO_4 . However, this might increase the corrosiveness of the fuel toward some cladding materials.

A proof-of-principle version of the KING concept can be tested at 20°-50°C.⁶ Some studies are under way to determine how rapidly radiolytic H_2O_2 would decompose after passage of the solution through the critical region of a non-recirculating test version of the concept. The applicable equation is:

The rate of the decomposition obeys an equation of the form

$$\frac{d[H_2O_2]}{dt} = -k[H_2O_2]^n \quad (3)$$

where k and n are usually constants for a given temperature and otherwise constant composition. The data of Table II were obtained with 0.003-0.006 M

TABLE II

First-Order Decomposition Constant for H_2O_2
(0.319 M UO_2SO_4 + 0.50 M H_2SO_4 +
0.793 g/liter of Cu^{+2} , 25°C)

No. g/liter of Fe^{+3}	$k(h^{-1})$
0.006	0.031
0.096	0.23
1.536	1.75
5.585 (= 0.1 M)	4.17

added H_2O_2 and a Fe^{+3} - Cu^{+2} promoter combination for catalysis. The order n was found to be 1.0 in each case. The dependence of the rate on the Fe^{+3} concentration is stronger than the one-half power that has been found elsewhere with the optimum Cu^{+2} concentration.⁷ This proof-of-principle version of the KING might operate at about ten pulses per day, thus allowing a time t of 40-60 min between pulses.⁶ If this time is constant, it can be shown that the maximum molarity of total peroxide, i.e., $[H_2O_2]_{max}$ is:

$$[H_2O_2]_{max} = [H_2O_2]_0 / (1 - \exp(-kt)) \quad (4)$$

where $[H_2O_2]_0$ is the peroxide concentration produced in one pulse and peroxide production from β and γ radiation is neglected. Using a value of $t = 0.75$ h and the highest value of k from Table II gives $[H_2O_2]_{max} = 1.046 [H_2O_2]_0$, i.e., only slightly more than $[H_2O_2]_0$. The data of Table II at 25°C may be extended to higher temperatures.

2. Neutronic Calculations (M. E. Battat)

During the year, preliminary neutronic calculations have been made as part of the overall investigation of the high-flux potential of the KING concept. It was verified that those aqueous solutions which seem suitable from the chemical standpoint are apparently also satisfactory from the neutronic point of view. Details of these calculations were reported previously.⁸ The most interesting conclusion is that systems with fluxes in the range 10^{16} - 10^{17} n/sec-cm² may be feasible.

II. HIGH TEMPERATURE NEUTRON DETECTOR TEST (E. O. Swickard, J. L. Bacastow)

A. General

Two high temperature neutron detectors were

purchased from each of three manufacturers for evaluation. The detectors have ^{235}U coated electrodes with integral, mineral-insulated cables. Purchase specifications required that both the detector and cable operate at 600°C . The test objective was the determination of the effect of temperature on the following: (1) pulse height distribution; (2) neutron counting sensitivity; (3) detector and cable resistance; (4) detector and cable capacitance; and (5) detector and cable noise.

Detectors with their integral signal cables were installed in four 17-ft high furnaces that contain a helium atmosphere at a few psig. Electrical heaters on the outside of the furnace tube were wired so that those in the detector region and those in the cable region are independently controllable.

The integral cable was connected to a suitable preamp, an amplifier, a scaler, and a 400-channel pulse height analyzer. Counts were taken with and without a neutron source just outside furnace insulation. Measurements were made at ambient temperature, 100, 200, 300, 400, 500, 600, 625, and 650°C .

B. Results During FY 1968

All experimental work for evaluation was completed during the current year, and data analysis continues. Some details of the detectors' performance were presented in earlier quarterly reports.^{8,9} The general observations which were made may be summarized as follows:

1. The dc leakage current of the chamber-and-cable assembly increased by factors of 10^3 - 10^4 as the temperature of the unit was raised from room temperature to 600°C .

2. Five of the six detectors tested were operable at a temperature of 600°C ; two functioned at 650°C .

3. The maximum voltage at which the detectors could be operated with a usable signal-to-noise ratio decreased as the temperature was raised. The maximum voltage which could be satisfactorily employed at 600°C was in some cases less than the minimum operating voltage specified by the manufacturer. In all cases, it was less by factors of 2 to 4 than the upper limit of voltage recommended by

the manufacturer.

4. After exposure to 600°C for 1000 h, only one of the five still-usable detectors was capable at room temperature operation at the maximum voltage recommended by the manufacturer.

When analysis (now 90% complete) of all the data has been finished, the effect of temperature on pulse height distribution, neutron sensitivity, and signal to noise ratio, can be evaluated. The results will be presented in a topical report whose preparation is now in progress.

III. EQUATION OF STATE OF REACTOR FUELS (B. C. Goplen)

A. General

Fast reactor accident analysis could be made more realistic if data on the equation of state for fuel materials at high temperatures were available. Currently such information is obtained by extrapolation of available low temperature data using an assumed model. Results of such an extrapolation are dependent on the model used and there is little to indicate which model is a correct representation.

Shock transient time measurements have been used to calculate the material equation of state for high pressures and low temperatures. By testing material (fuel) of reduced density, this technique may yield data applicable at temperatures and pressures of interest in reactor accident analysis.

A program is underway to investigate the feasibility of (1) fabricating reactor fuel samples with a range of densities down to about one-fourth normal density, and (2) making shock transient time measurements on a series of different density materials to find if the method will yield equation of state in the range of interest.

B. Results During FY 1968

Small UO_2 samples have been made having densities 10.34, 6.38, and 2.91 g/cm^3 . Shock transient times for these samples were measured in high explosive experiments and the Hugoniot for the material has been calculated. Normalization of the Hugoniot requires the preparation and shooting of much larger samples. The large samples of 6.38 g/cm^3 density have been prepared and shot and fabrication of 2.91 g/cm^3 density large samples is almost complete.

Making low density samples from the next

material to be tested, UC, is much more difficult than fabricating those of UO_2 . Sample densities less than about 60% of crystalline require porous particles as starting material. Means of producing such porous particles is under investigation.

All data on uranium compounds from these experiments is automatically classified "Secret RD," and therefore, no results can be described in this unclassified report. Declassification of data for temperatures and pressures in the ranges pertinent to reactor safety analysis is in progress.

IV. GENERAL APPLICATION OF 3He ACTIVATION ANALYSIS (D. M. Holm, B. K. Barnes)

A. General

Certain specific application of 3He activation analysis to reactor materials has been reported under Project 808. During the past year, other studies peripherally related to reactor programs, but also of interest from other points of view, have also been performed. Results of an investigation of the impurity content of lithium-drifted germanium detectors are reported here. Interest in this application arose because it appeared that the drifting properties of the germanium crystal

were affected by the concentration and distribution of impurities such as oxygen and carbon. By means of ion-channeling phenomena, the location of impurities (relative to the crystal structure of the germanium) can be determined.

B. Results During FY 1968

Channeling of 3He ions in single-crystal germanium and its application to activation analysis was investigated.¹⁰ The crystal orientation was determined by directing an ion beam of low angular divergence and energy onto the crystal and observing the decrease in counting rate from Rutherford back-scattered particles as a function of incident beam angle. Some samples were activated with the beam aligned along the [111] axis of the crystal and others with the beam purposely misaligned from that axis. Samples of germanium from different sources were analyzed, and typical values of 10 ppm oxygen and 40 ppm carbon were obtained. Slight activation of the germanium was found at a beam energy of 6.5 MeV; activation at 8 and 12 MeV was substantial. Autoradiography was performed on some of the samples following activation to aid in the interpretation of the results. Results are given in Table III.

TABLE III

Results of 3He Activation Analysis on Germanium

Sample	Energy* (MeV)	Total Charge (coulomb)	Irradiation (min)	Concentration		Ratio C/O
				Carbon [†] (ppm)	Oxygen [†] (ppm)	
B-3	7.0	5.42×10^{-4}	50.0	85	21.0	4.0
D-4	6.5	2.26×10^{-3}	87.0	74	19.0	3.9
J-1	6.5	1.49×10^{-3}	90.0	70	12.0	5.8
T-7-B	6.5	1.42×10^{-3}	90.0	63	13.0	4.8
4-S	6.5	1.39×10^{-3}	90.0	53	12.0	4.4
NBS-53	6.5	1.51×10^{-3}	90.5	40	0.97	41.0
NBS-39-1	6.5	1.93×10^{-3}	122.0	55	0.5	100.0
D-8	8.0	1.01×10^{-4}	64.5	36	14.0	2.6
D-11 ^{††}	8.0	1.56×10^{-4}	60.8	80	13.0	6.3

*All samples were etched to depth of 0.55 mg/cm², reducing the actual energy at the final surface by 0.15 to 0.20 MeV, depending on initial energy.

[†]The estimated uncertainty in the absolute concentrations is $\pm 50\%$, but the relative uncertainty is about $\pm 10\%$.

^{††}Irradiated in channeling direction, but computations ignore this fact.

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