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SMALL-SCALE DEMONSTRATION OF THE MELT REFINING
OF HIGHLY IRRADIATED URANIUM-FISSIUM ALLOY

by

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SMALL-SCALE DEMONSTRATION OF THE MELT REFINING OF HIGHLY IRRADIATED URANIUM-FISSIUM ALLOY

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ABSTRACT

Five melt refining demonstration experiments have been conducted with highly irradiated EBR-II prototype fuel to verify earlier data on fission product removals obtained with unirradiated and low-activity alloys. In each experiment, approximately 0.4 kg of uranium-fissium fuel pins irradiated to burnups ranging from 0.22 to 1.75 total atom percent was melt refined for 1 or 3 hr at 1400 C in a lime-stabilized zirconia crucible.

The behavior of fission products was consistent with the earlier results. Fission product removals were over 99 percent for krypton, xenon, iodine, cesium, barium, and strontium, over 95 percent for yttrium, rare earths, and tellurium, and zero for the noble metals.

Because of the small scale of the experiments and necessary exposure of the irradiated fuel to air in the cave facility, it was not possible to obtain definitive data on product yields.

Swelling of the fuel pins and the associated release of fission product gases during the heating cycle caused no difficulty in the melt refining process on this scale.

I. INTRODUCTION

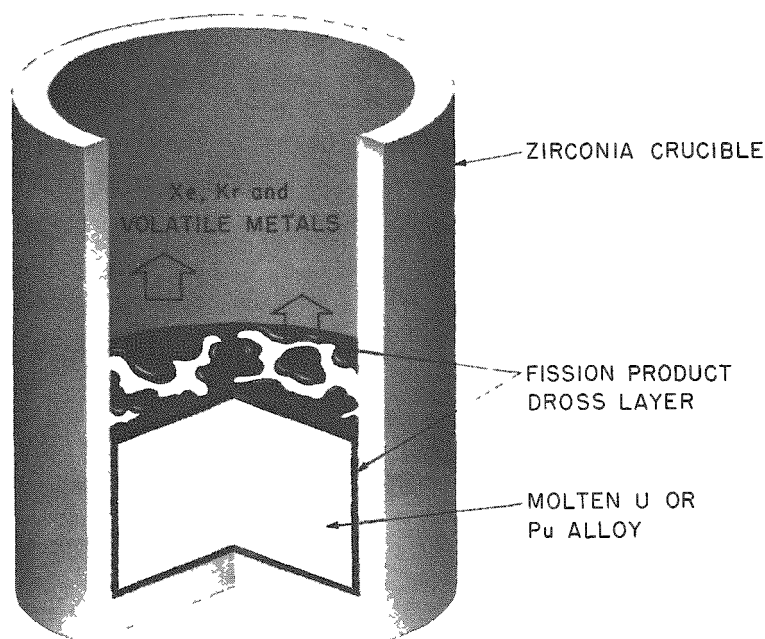
The Experimental Breeder Reactor No. 2 (EBR-II), located at the National Reactor Testing Station in Idaho, is a fast power breeder reactor designed to establish the feasibility of fast reactors for central-station power plants. It is an integrated nuclear power plant, incorporating the reactor and a fuel recycle processing facility. The spent fuel will be processed by pyrometallurgical methods, and new fuel elements will be fabricated remotely.

The fuel to be used in the first core loading of EBR-II contains approximately 50 percent enriched uranium alloyed with 5 w/o noble metal fission product elements and is commonly referred to as uranium-five percent fissium.* The fuel pins, about $\frac{1}{8}$ in. in diameter, are clad with stainless steel thermally bonded by a small amount of sodium.

The melt refining process has been developed for the recovery of uranium from the first core loading of EBR-II. The pins are declad mechanically, chopped, and charged to a lime-stabilized zirconia crucible in which they are melted and maintained at 1400 C in a liquid state under argon for a period of 3 to 4 hr. Approximately two-thirds of the fission products are removed during this treatment through volatilization, selective oxidation, and liquation, as illustrated in Figure 1. The purified metal product is top-poured to form an ingot from which new pins are prepared by injection casting. A mixture of oxides and unpoured metal remaining in the crucible as a skull is recovered by a separate process employing liquid metal solvents.

Figure 1

SIMPLIFIED SCHEMATIC ILLUSTRATION OF THE MELT REFINING PROCESS



*Fissium is a widely used name for a mixture of fission product metals that are not removed by the melt refining process. In the mixture, these metals (molybdenum, ruthenium, rhodium, palladium, zirconium, and niobium) are approximately apportioned according to their yield in the fission process.

The melt refining process offers promise of achieving a reduction in the reprocessing cost associated with nuclear power. The principal characteristics of the process which are likely to result in reduced costs are its simplicity, compactness, low volume of dry wastes, and capability for handling short-cooled fuels, with an attendant reduction in fuel inventories.

The first studies of the melt refining process were conducted with unirradiated and low-activity uranium and uranium alloys.⁽¹⁻³⁾ Nearly complete removal of the following fission product elements was achieved: rare earths, yttrium, barium, strontium, and cesium.⁽³⁾ The noble metal fission product elements (molybdenum, ruthenium, rhodium, and palladium) were not removed.⁽⁴⁾ In experiments with inactive alloys, yields obtained by top pouring at full plant scale (10-kg charge in a 5.125-in.-diameter crucible) averaged 92.5 percent.⁽⁵⁾

Five small-scale (~0.4 kg) demonstrations of the melt refining process were made with uranium-five percent fissium fuel pins irradiated to burnups of 0.22 to 1.75 total atom percent. (Fully irradiated EBR-II fuel is expected to reach a maximum burnup of about 2.0 total atom percent.) The primary objective of the demonstrations was to determine whether the same fission product behavior would be obtained in the melt refining of highly irradiated fuel as that observed in the previous studies with unirradiated and low-activity material. A secondary objective was to observe the behavior of highly irradiated fuel with respect to other aspects of the melt refining process, such as product yields, the handling of fission product gases, and any problems resulting from different physical properties of the irradiated alloy. During the course of the investigations, some incidental information was obtained on the removal of the highly radioactive skull from the crucible by air oxidation and the distribution of fission products between the oxidized skull and the crucible.

II. EXPERIMENTAL

A. Equipment

1. Cave Facilities

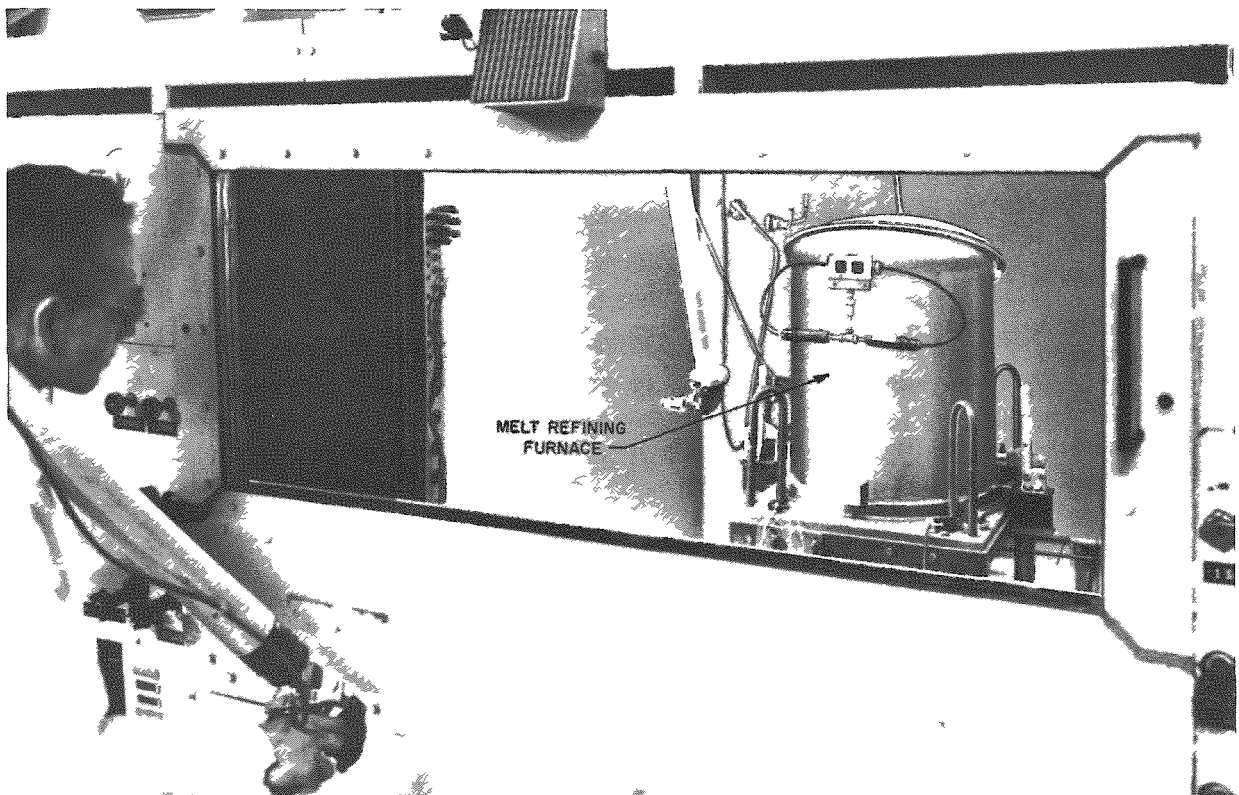
The high-activity-level melt refining experiments were conducted in the Chemical Engineering Senior Cave, which is an air-atmosphere facility with two high-level (kilocurie) cells and one low-level cell.⁽⁶⁾ The cave facilities were of a conventional design, with the exception of four Argonne Model 3 electric manipulators,⁽⁷⁾ which markedly simplified the problems of remote operation.

2. Melt Refining Furnace

All melt refining experiments were conducted in the stainless steel, 140-liter bell-jar-enclosed furnace shown in Figures 2 and 3. A vacuum seal between the baseplate and the bell jar was provided by a rubber "O" ring gasket with a steel frame for ease of remote handling. Services were supplied through the base plate.

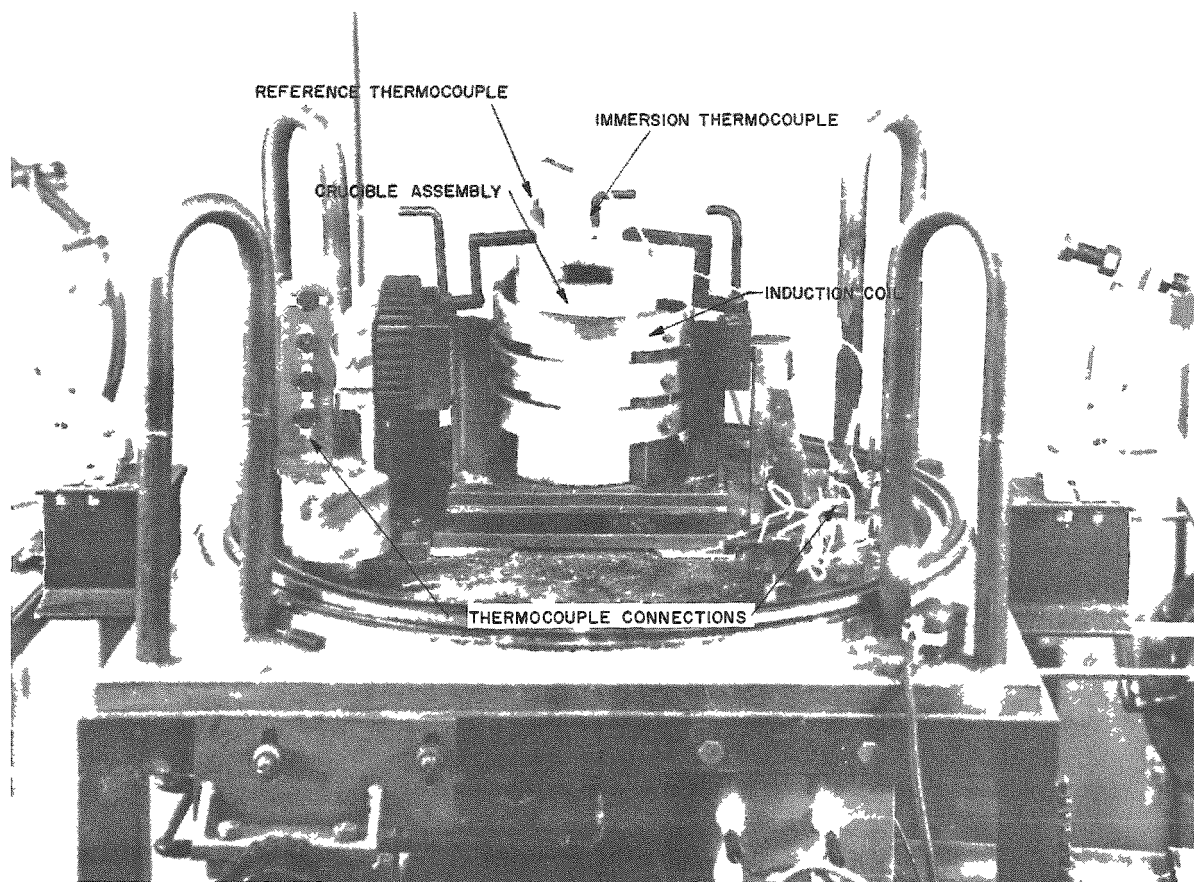
Figure 2

VIEW OF MELT REFINING FURNACE THROUGH CAVE WINDOW



(Photo Retouched)

Figure 3
VIEW OF MELT REFINING FURNACE WITH THE BELL JAR REMOVED

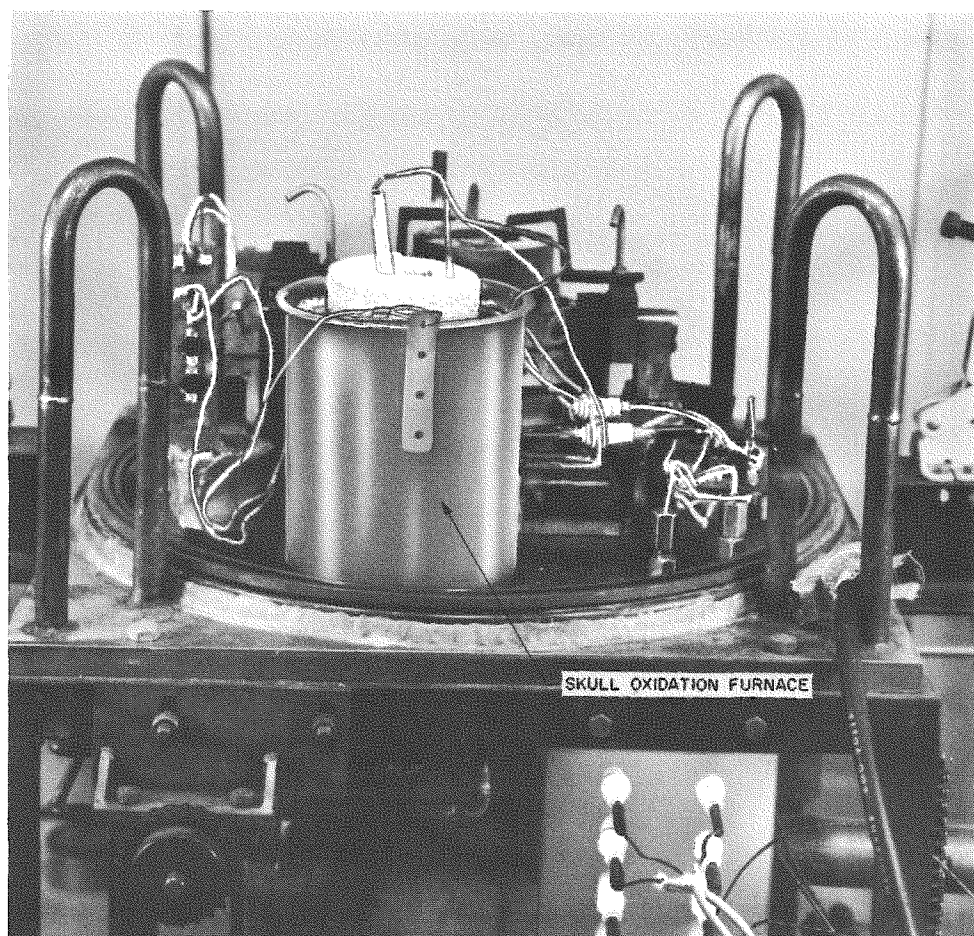


Induction heating was used for melt refining, with the power supplied by a 10,000-cycle motor-generator to a $2\frac{1}{2}$ -turn solid copper coil coupled to a 30-mil tantalum susceptor. For operation of a resistance heated furnace (Figure 4), used for skull oxidation and sample fusions, 110-v, 60-cycle power was also available inside the bell jar. The necessary connections were provided for platinum-platinum, 10 percent rhodium and chromel-alumel thermocouples.

Service lines through the baseplate provided for inlet gas, vacuum, and removal of radioactive gases. The inlet gas line terminated in a connection on the outside face of the cave. The vacuum line was connected to a mechanical pump (Kinney KC-15) located inside the cave a few feet from the furnace.

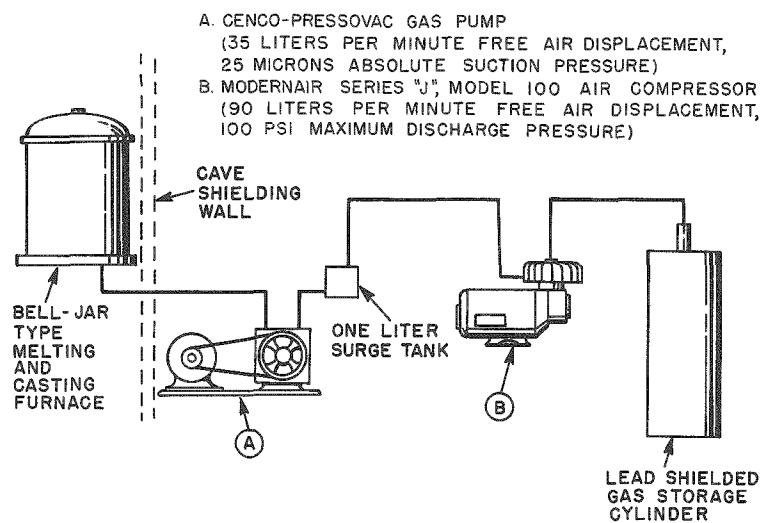
Exhaust gases from the furnace were passed through charcoal beds for control of radioactive iodine. The charcoal beds were located on the discharge side of the vacuum pump and in the exhaust stack of the cave. Over 99 percent of the atmosphere in the bell jar, which contained the bulk of the radioactive gases released during melt refining, was pumped to shielded gas-storage cylinders, by means of the equipment shown in Figure 5.

Figure 4
SKULL OXIDATION FURNACE INSTALLED ON BASE PLATE OF
THE MELT REFINING FURNACE



(Photo Retouched)

Figure 5
RADIOACTIVE GAS TRANSFER SYSTEM

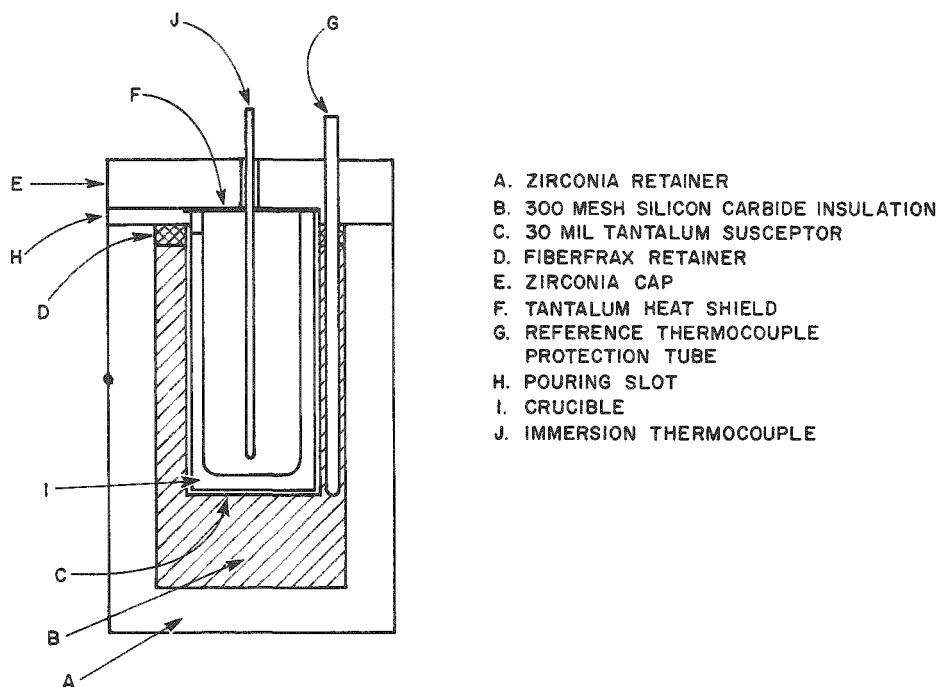


Both the gas pump and the storage cylinders were located outside the cave. The gas pump, a two-stage arrangement consisting of a vacuum pump (Cenco Pressovac) in series with a small compressor (Johnson Portable All Purpose Air Compressor Model MM60067-A), was capable of reducing the pressure in the furnace to 10 torr while delivering gas to the storage cylinder at 100 psig. Air-operated diaphragm valves (Crane Co. 150WOG) with neoprene seats were installed on gas service lines inside the cell close to the furnace.

3. Crucible Assembly

A schematic diagram (Figure 6) shows the principal components of the crucible assembly, i.e., crucible, tantalum susceptor, silicon carbide insulation, zirconia retainer, and zirconia cap. In Figure 3, the crucible assembly is shown installed in the furnace with immersion and reference thermocouples in place. The crucible assembly was mounted upon a cradle that could be rotated 120° for top pouring.

Figure 6
CRUCIBLE ASSEMBLY



Platinum-platinum, 10 percent rhodium was used for both reference and immersion thermocouples. A small-diameter beryllia tube, of 4-mm OD and 2-mm ID, served as a protection tube for the immersion thermocouple. Beryllia was chosen for this function, in preference to either alumina or zirconia, because of its superior chemical resistance to the molten uranium alloy and because it was not wetted by the alloy.

Dimensions and the chemical composition of the crucible (Norton Co. zirconia RZ5601) are presented in Table 1. The manufacturer's code, RZ5601, identifies the type of refractory mix used and the method employed in the fabrication of the crucible. In the EBR-II Fuel Cycle Facility, current plans call for the use of Norton Company Type 300SP zirconia crucibles for the melt refining process. According to Norton, the same refractory mix is used in the manufacture of the RZ5601 and the 300SP crucibles, and the difference between these crucibles is related only to the method of fabrication. The RZ5601 crucible is formed by pneumatic ramming, whereas the 300SP crucible is formed by a combination of pneumatic ramming and hydraulic pressing.

Table 1

DIMENSIONS AND COMPOSITION OF
ZIRCONIA CRUCIBLE

Manufacturer	Norton Company, Worcester, Massachusetts
Type	RZ5601
Dimensions (in.)	
Height	4
Outside diameter	2
Inside diameter	$1\frac{3}{8}$
Typical Composition (w/o) ^a	
Zirconium dioxide	92.0
Calcium oxide	4.5
Hafnium dioxide	1.5
Silicon dioxide	0.9
Aluminum oxide	0.6
Titanium dioxide	0.3
Ferric oxide	0.2

^aFurnished by the Norton Company

The RZ5601 crucible was selected for use in the high-activity-level experiments because of its superior performance in preliminary experiments in which the skull was transformed to a free-flowing powder by oxidation with air at 700 C for easy removal from the crucible. In preliminary trials of the skull oxidation procedure, it was noted that 300SP crucibles tended to disintegrate, thereby adding appreciable amounts of powdered crucible zirconia to the pulverized skull. The same oxidation treatment, however, had virtually no effect on the integrity of RZ5601 crucibles.

B. Uranium-Fissium Alloy

The uranium-five percent fissium pins used in the 0.4-kg-scale high-activity-level experiments were identical with those prepared for the first EBR-II core loading, except that a lower percentage enrichment was used, 10.73 percent vs 47.5 percent, to conserve uranium-235. The composition of the alloy is given in Table 2.

Table 2

COMPOSITION OF URANIUM-5 PERCENT FISSIUM ALLOY FUEL USED IN HIGH-ACTIVITY-LEVEL EXPERIMENTS (BEFORE IRRADIATION)

(Density at 25 C: 18.0 g/cu cm)

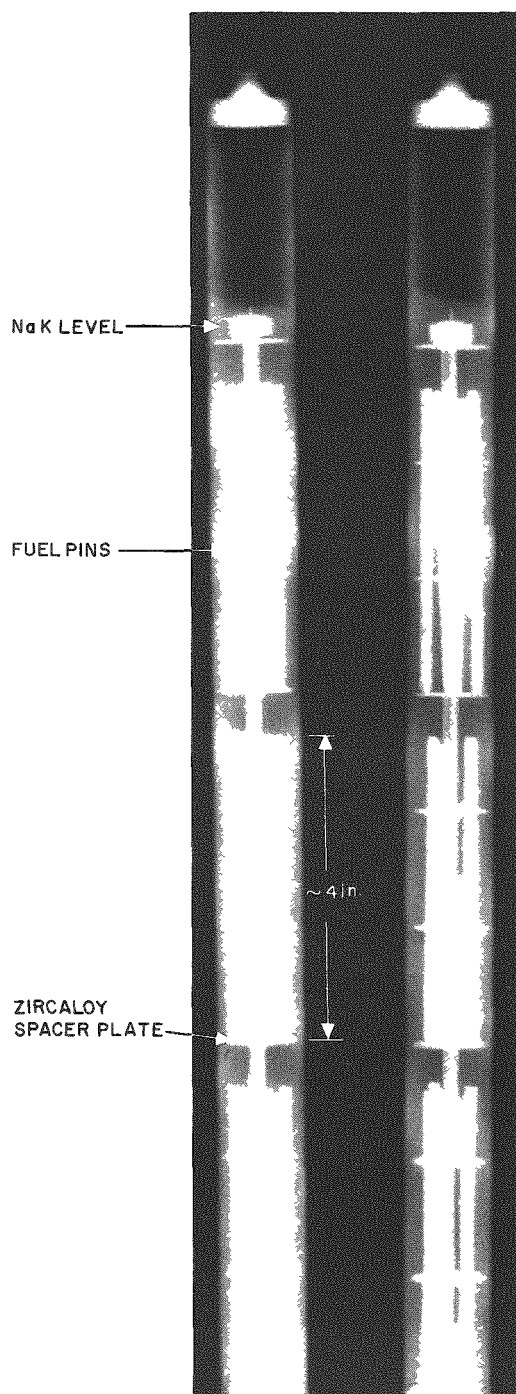
<u>Constituent</u>	<u>Concentration, w/o</u>	
	<u>Experiments 1, 2, and 3</u>	<u>Experiments 4 and 5</u>
Uranium-238	84.00	84.94
Uranium-235	10.73	9.44
Molybdenum	2.58	2.80
Ruthenium	2.11	2.25
Rhodium	0.26	0.27
Palladium	0.19	0.20
Zirconium	0.12	0.09
Niobium	0.01	0.01
Carbon	25 ppm	

To prepare the alloy pins, the constituent elements were first melted in a zirconia crucible and recovered as a massive ingot. The ingot was transferred to a special casting furnace, melted in a thoriated graphite crucible, and injection-cast into Vycor molds to form 0.144-in.-diameter pins.

The unclad, unrestrained fuel pins, held in an array by Zircaloy spacers, were irradiated in stainless steel capsules filled with sodium or NaK to provide for heat transfer. The pins used in Experiments 1 and 2 were irradiated in the CP-5 research reactor. The conditions of irradiation: unperturbed thermal flux* and central fuel temperature were 1.6×10^{13} nv and 240 C for the fuel pins used in Experiment 1, and 3.7×10^{13} nv and 400 C for the fuel pins used in Experiment 2. Frequent shutdowns of

*Estimated perturbation factors, relating the unperturbed flux to the effective flux in the fuel, were 0.361 for CP-5 and 0.392 for MTR.

Figure 7
X-RAY PHOTOGRAPH OF URANIUM-FISSIUM FUEL
PINS INSIDE MTR IRRADIATION CAPSULES
(BEFORE IRRADIATION)



the reactor, because of the research activities at the CP-5, resulted in thermal cycling of the fuel one or two times daily. The fuel pins used in Experiments 3, 4, and 5 were irradiated in the Materials Testing Reactor (MTR) at the Idaho testing station at an unperturbed thermal flux of about 5×10^{13} nv and a central fuel temperature of about 550 C. The MTR-irradiated fuel was thermally cycled once every 15 days.

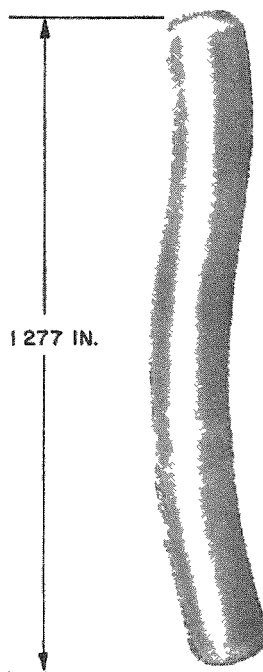
The loaded CP-5 irradiation capsules were 1.25-in. in OD by 21 in. long, and they contained about 400 g of alloy immersed in 200 g of sodium. The MTR capsules were smaller, of 1.125-in. OD by 16 in. long, with a fuel loading of about 200 g in 100 g of NaK. An X-ray photograph of loaded MTR irradiation capsules before irradiation is presented in Figure 7. Two capsules of MTR-irradiated alloy were required for each melt refining experiment.

Pins used in Experiments 1 through 4 were irradiated to less than one percent burnup. These pins showed little swelling but were slightly warped. A greater degree of warping was observed in pins irradiated to 1.75 percent burnup. (A short section of one of these pins is shown in Figure 8.) In the case of the 1.75 percent burnup pins, some swelling was evident at points where the pins passed through holes in the Zircaloy spacer plates used to position them in the irradiation capsule, probably as a result of local hot spots caused by greater resistance to heat transfer through the Zircaloy spacer than through the liquid NaK.

Figure 8

SHORT SECTION OF AN URANIUM-5 PERCENT
FISSIUM FUEL PIN IRRADIATED TO
1.75 ATOM PERCENT BURNUP

(This fuel pin was irradiated unclad in a NaK-filled capsule at a central fuel temperature of about 550 C and was not warped before irradiation. The photograph was taken through the periscope in the Chemical Engineering Senior Cave.)



(Photo
Retouched)

C. Experimental Procedure

1. Preparation of Fuel for Melt Refining

Sodium-filled capsules, in which the fuel used in Experiments 1 and 2 was irradiated, were opened in air. The tops of the capsules were cut off and the sodium was removed by submerging the opened capsule in a bath of molten paraffin at 150 C. As the sodium melted, it settled to the bottom of the bath and was shielded from contact with air by the protective paraffin cover. The fuel pins were washed with a kerosene-butanol mixture and rinsed with acetone to remove residual sodium and paraffin. At the completion of this treatment, a film of reaction products coated the fuel pins.

NaK-filled capsules used for the MTR irradiations were opened under nitrogen and the NaK was poured off. The fuel pins used in Experiment 3 were washed with butanol and acetone to remove residual NaK. Organic solvents were not used to wash the fuel pins for Experiments 4 and 5 because nitridation rate studies⁽⁸⁾ indicated that traces of organic material may remain on the pins after washing with organic solvents. Instead, the residual NaK was oxidized by means of a dilute oxygen (0.5 percent)-nitrogen mixture.

Oxide scale and loosely adhering reaction products remaining on the pins after removal of sodium were removed by abrasion with a mixture consisting of 200 g of 30-mesh and 100 g of 10-mesh silicon carbide. Fuel pins and abrasive were tumbled for 45 min in a jar mill under an air atmosphere. After abrading, the pins had a dull grey luster and were free of visible oxide scale.

To minimize exposure of the abraded fuel pins to air, they were sampled, weighed, loaded into a previously degassed crucible,* and placed in the melt refining furnace as quickly as possible. During these operations the fuel was exposed to air at atmospheric pressure for about 2 hr.

2. Melt Refining

In Experiments 1, 2, and 3, the furnace bell jar was lowered immediately after the loaded crucible was installed in the furnace. The bell jar was then evacuated and held under a pressure of about 5μ for several hours (11.5, 17, and 66 hr, in Experiments 1, 2, and 3, respectively). Argon was then added to the bell jar to provide an inert atmosphere which was maintained at a pressure somewhat higher than atmospheric during melt refining.

In preliminary experiments with unirradiated fuel, it had been shown that holding the fuel pins under vacuum for several hours prior to melt refining had a beneficial effect on the product yield. It is likely that the beneficial effect was the result of the degassing of the bell jar and the furnace components which had been exposed to the air atmosphere of the cave while the crucible was being installed in the crucible assembly. However, the yield data from the first three high-activity-level experiments indicated that holding irradiated fuel under vacuum for an extended length of time was the cause of a reduction in the yield (see Table 11). This difference in behavior between unirradiated and irradiated fuel was attributed mainly to a significantly greater degree of oxidation of the irradiated fuel by air while a vacuum (5μ) was being maintained in the bell jar. At 5μ pressure, the leak rate of the bell jar was about 10 cu cm/min. Because of fission product heating the temperature of the irradiated fuel was

*Crucibles were degassed under vacuum (25μ) for one hour at 1400 C.

about 300 C. Thus, during the length of time that a vacuum was maintained in the bell jar, the irradiated fuel at a temperature of about 300 C was exposed to a continuous flow of air at $5\text{-}\mu$ pressure. It appears that under these conditions the irradiated fuel was oxidized to an extent that the yield was adversely affected. Therefore, in Experiments 4 and 5, the procedure was modified so as to establish an argon atmosphere in the furnace in about 30 min. The furnace was twice evacuated to $5\text{ }\mu$ and refilled with fresh argon to a pressure of 600 torr. As the charge was heated, the pressure increased and remained at about 850 torr during the melt refining operation.

Charges were heated to the melt refining temperature of 1400 C at an average rate of 20 C/min and held at that temperature for 3 hr in Experiments 1 and 2 and for one hour in Experiments 3, 4, and 5. Purified metal was recovered by top pouring into a graphite-coated copper mold* in Experiments 1, 2, 3, and 4 and into a graphite mold in Experiment 5.

3. Removal of Skull Material from the Crucible

The skull remaining in the crucible, a mixture of scoria and unpoured metal, was isolated by breaking away the crucible in Experiment 3** and by oxidation with air in Experiments 1, 2, 4, and 5. The skulls were oxidized in a small, resistance-heated furnace which was specially constructed for use under the melt refining bell jar. The skull oxidation furnace is shown in position on the base plate on the melt refining furnace in Figure 4. Crucibles containing the skulls were heated under vacuum to 700 C. Air was then slowly admitted to the bell jar to an ultimate pressure of about 700 torr, taking care to avoid temperature excursions. The time required for complete oxidation of irradiated skulls was 6 to 8 hr, and the time for unirradiated skulls was 10 to 12 hr. In both cases, complete oxidation converted the skull to a free-flowing granulated product which could be poured from the crucible. Partial oxidation, sufficient to free irradiated skulls, required approximately 2 hr.

4. Sampling and Analytical Procedures

Three or four samples of each charge were obtained for analysis by breaking off small pieces from randomly selected irradiated pins. The product ingots were sampled by removing small cast protrusions from the bottom and sides. To obtain representative samples of the skull, it was

*The copper mold was coated by painting with a colloidal suspension of graphite in water and then heating the mold under vacuum for one hour at 200 C.

**In Experiment 3, the skull was separated by breaking away the crucible to permit visual examination of the residue.

completely oxidized and the resulting oxide mixture was ground and blended in an electric mortar (Spex Mixer/Mill). Crucibles were also prepared for sampling by grinding and blending in an electric mortar. Charge and ingot samples were dissolved in hot aqua regia. The ground and blended samples of crucibles and oxidized skulls were fused with sodium carbonate at 1050 C for 12 hr to permit aqueous dissolution.

The procedures used to analyze aqueous solutions of samples for various components of irradiated fuel are summarized in Table 3. Burnups were obtained by comparing mass spectrographically determined uranium-235, -236, and -238 concentrations before and after irradiation.

Table 3

SUMMARY OF ANALYTICAL PROCEDURES

<u>Component</u>	<u>Method of Separation</u>	<u>Method of Determination</u>
Uranium	Methyl isobutyl ketone extraction	Colorimetric
Plutonium	Methyl isobutyl ketone extraction	Radiochemical
Molybdenum	Extraction of thiocyanate with butyl acetate	Colorimetric
Rare Earths and Yttrium (Group IIIB elements)	Di(2-ethylhexyl) phosphoric acid extraction	Radiochemical
Tellurium	Precipitation as metal	Radiochemical
Zirconium	Precipitation as barium fluorozirconate	Radiochemical
Iodine	Carbon tetrachloride extraction	Radiochemical
Cesium	Tetraphenyl borate extraction	Radiochemical
Barium and Strontium (Group IIA elements)	Precipitation as carbonate	Radiochemical
Ruthenium	Distillation	Radiochemical

III. RESULTS

A. Behavior of Fission Products

The fates of selected fission products were studied to appraise the capability of the melt refining process to remove fission products from the fuel at irradiation levels approaching the two percent burnup anticipated in EBR-II fuel. The distributions of fission products among the purified product (ingot), the residue retained in the crucible (skull), and the crucible were determined.

1. Removals

Removal is expressed as the percentage decrease in the concentration of a constituent of the charge, i.e.,

$$\text{Removal} = \frac{C_c - C_i}{C_c} \times 100 \quad , \quad (1)$$

where C_c and C_i are the concentrations in charge and ingot, respectively.

During irradiation of the fuel, variations in neutron flux over the length of an irradiation capsule were as great as 20 percent, and the fission product content of random samples of the charge varied accordingly. The average concentration of a fission product element in the charge could be obtained by averaging the concentrations of the element in a large number of charge samples. However, by using the following alternative procedure, which required the analysis of only a single random sample of the charge, a considerable amount of analytical work was avoided.

The average concentration of a fission product in the charge can be expressed by the following equation:

$$\delta_c = \frac{\sum \delta_j w_j}{W_c} \quad , \quad (2)$$

where δ_c is the average concentration of a fission product δ in the charge; δ_j and W_j are the concentration of δ in segment j , and the weight of segment j , respectively; and W_c is the total weight of the charge. Since the entire charge was irradiated simultaneously, for any period of post-irradiation cooling, δ_j can be expressed by the equation*

$$\delta_j = A_j Z_\delta \quad , \quad (3)$$

* A derivation of Equation (3) is provided by LaPlante and Steunenberg.⁽⁸⁾

where A_j is the rate of fission of uranium-235 in segment j , and Z_δ is a function of the decay constant, fission yield, cooling time, and the cycles of reactor irradiation, and is virtually independent of neutron-flux variations of the magnitude encountered. Equation (3) is useful because it shows that the concentration of a fission product in a segment of the charge can be expressed as a function of two independent variables. The first independent variable, A_j , is a function only of the rate of irradiation and, therefore, has the same value for all fission products in segment j . On the other hand, the second independent variable, Z_δ , depends on the nature of the fission product and, therefore, has a different value for each fission product. The important characteristic of Z_δ is that it is not a function of the rate of irradiation; therefore, for a particular fission product, δ , the value of Z_δ is the same in every fuel segment in the irradiation capsule. Therefore, the average concentration of a fission product in the charge (δ_c) can be obtained provided the average rate of fission of uranium-235 (A_c) is known:

$$\delta_c = A_c Z_\delta \quad . \quad (4)$$

For those fission products not removed by melt refining (noble metals), melting of the charge and casting of a homogeneous ingot effects the summation ($\sum \delta_j W_j$) specified in Equation (2). Hence, in the case of ruthenium,* a typical noble metal, the concentration of fission product ruthenium in the ingot, Ru_i , is proportional to the concentration of fission product ruthenium in the charge:

$$Ru_i = (R)(Ru_c) \quad .** \quad (5)$$

Combining Equations (1) through (4), the average concentration of a fission product in the charge can be calculated as

$$\delta_c = \delta_j \frac{Ru_i}{(R)(Ru_j)} \quad . \quad (6)$$

Data obtained in Experiment 4 (see Table 4) are used in the following sample calculation to illustrate the application of Equation 6. The object is to estimate the average specific beta activity, β_c , in the charge.

*The concentration of Ru^{103} was chosen for use in the computations described in Equations (5) and (6) because of the simplicity of the analytical technique employed, and the precision and accuracy of the results obtained.

**The proportionality constant R is the noble metal enrichment factor. It was required because the noble metal concentration was slightly higher in the ingot than in the charge due to separations effected by melt refining. Usually R was taken as the ratio $(Mo_i)_W / (Mo_c)_W$ with molybdenum concentrations in weight percent. The error, attributable to irradiation level variation, in values of $(Mo_c)_W$ obtained from random samples of the charge was insignificant because, for a nominal one percent burnup, the amount of molybdenum produced by fission was less than five percent of the amount of molybdenum in the alloy.

In this case, the specific beta activity in four random samples varied from 1.085 to 1.35 (arbitrary units). The estimate of β_c based on Sample A is

$$\beta_c = \frac{(1.35)(2.43)(3.87)}{(2.54)(4.33)} = 1.16 \quad . \quad (7)$$

The other three random samples yielded estimates of 1.15, 1.18, and 1.12. Based on the mean of 1.15, the removal of beta activity in Experiment 4 was

$$\frac{1.15 - 0.195}{1.15} \times 100 = 83\% \quad . \quad (8)$$

Table 4

DATA USED TO CALCULATE REMOVALS OF BETA AND
GAMMA ACTIVITIES IN HIGH-ACTIVITY-LEVEL MELT
REFINING EXPERIMENT 4

	Sample				
	A	B	C	D	Mean
1. Activity per gram of alloy (arbitrary units) ^a					
a. Random charge samples					
1. Beta, β_j	1.35	1.415	1.212	1.085	-
2. Gamma, γ_j	4.50	4.945	4.22	3.915	-
3. Ruthenium, Ru_j	4.33	4.545	3.81	3.575	-
b. Ingot samples					
1. Beta, β_i	0.192	0.198	-	-	0.195
2. Gamma, γ_i	3.52	3.57	-	-	3.54
3. Ruthenium, Ru_i	3.87	3.86	-	-	3.86
2. Molybdenum concentration, w/o					
a. Charge $(Mo_c)_W$	2.43	2.46	2.44	2.41	2.44
b. Ingot $(Mo_i)_W$	2.54	2.55	-	-	2.54
3. Estimate of average activity per gram of charge (arbitrary units) ^a					
a. Beta, β_c	1.16	1.15	1.18	1.12	1.15
b. Gamma, γ_c	3.85	4.03	4.09	4.05	4.01

^a The arbitrary units are convertible to conventional activity units by application of appropriate factors of 10 and counter corrections.

Fission product removals observed in the five demonstration experiments appear in Table 5. No consistent effect of activity level or duration of melt refining is apparent. Removals of iodine, cesium, and barium and strontium were greater than 99 percent in all experiments in which the behavior of these elements was studied. The removal of total rare earths and yttrium was in excess of 99 percent in the first four runs and 97 percent in Experiment 5. Tellurium separation was 99 percent or greater in Experiments 3, 4, and 5, and more than 95 percent in Experiments 1 and 2. The overall removal of beta-active fission products ranged from 81 percent in Experiment 2 to 84 percent in Experiments 3 and 5.

Table 5

FISSION PRODUCT REMOVALS IN HIGH-ACTIVITY-LEVEL MELT
REFINING EXPERIMENTS AT 1400 C

	Experiment No.				
	1	2	3	4	5
Charge Wt (g)	387.6	392.3	362.5	364.2	382.2
Burnup (percent of total atoms)	0.56	0.22	0.74	0.87	1.75
Cooling (day)	42	28	14	35	25
Total Activity (c) ^a	1170	1970	3800	3600	5350
Specific Activity (c/g) ^a	3.0	5.0	10.5	9.9	14.0
Duration of Melt Refining (hr)	3	3	1	1	1
Fission Product Removals (percent) ^b					
Rare Earths and Yttrium	99	99	99	99	97
Tellurium	95	96	99	99	99
Zirconium	9	18	20	11	28
Iodine	99	c	99	99	99
Cesium	99	c	c	99	c
Barium and Strontium	99	c	c	99	99
Removal of Activity (percent of total)					
Total Gamma Activity	10	14	18	12	25
Total Beta Activity	82	81	84	83	84

^a Equation (4) was used to calculate these data.

^b Fission product removals were determined by radiochemical analysis of charge and ingot samples. Percent removal equals

$$(1 - \frac{\text{Conc ingot}}{\text{Conc charge}}) \times 100$$

^c Datum was not obtained.

Substantial variability was noted in the removal of zirconium activity, which varied from nine percent in Experiment 1 to 28 percent in Experiment 5. However, these data are not necessarily indicative of a reduction in the zirconium content of the alloy. Instead, they may reflect isotopic exchange between radioactive zirconium in the molten alloy and inactive zirconium in the zirconia crucible. The behavior of zirconium is discussed under a separate heading.

2. Distribution of Fission Products, Uranium, and Plutonium

In Experiments 4 and 5, the skull and crucible were separated and analyzed to determine the distribution of uranium, plutonium, and fission products within these fractions. Alternative methods of separation of the skull from the crucible were used. The skull produced in Experiment 4 was observed to be partially oxidized after several hours of exposure to air and to be separated from the crucible. During the period of air exposure, the skull temperature was about 250 C as a result of fission product heating. These comparatively mild conditions proved adequate to free the skull from the crucible but not to oxidize completely a button of unpoured metal. After transfer of the partially oxidized skull to a stainless steel crucible, the oxidation was completed by heating the skull at 700 C in air for 7 hr. Separation of the skull from the crucible in Experiment 5 was accomplished by complete oxidation of the skull at 700 C in air which resulted in the production of a free-flowing powder which was poured from the crucible.* In both experiments, the oxidized skulls were homogenized in an electric mortar before sampling.

Crucibles were prepared for sampling in the following manner. After first breaking the crucibles into small pieces, batches of fragments were ground to a powder in an electric mortar and the several batches were combined and blended in a jar mill.

Direct dissolution of the refractory skull and crucible samples in aqueous media was attempted but proved unsatisfactory; therefore, the samples were converted to a more soluble form by fusion with sodium carbonate at 1050 C for about 12 hr. The high-temperature treatments during oxidation and fusion may have affected the concentration of the more volatile fission products. Therefore, with the exception of cesium, data were not obtained for elements that were susceptible to volatilization during sample preparation.

Distribution data obtained in Experiments 4 and 5 appear in Table 6. These data are based on chemical (colorimetric) analyses for uranium and molybdenum, and on radiochemical analyses for all other components. In every case, the actual recovered weight of the fraction (ingot, oxidized skull, or crucible) was used in distribution calculations. Where analytical data were not obtained, no correction was made for missing data in making material balance summations.

* A similar technique for removing melt refining residues is planned for use in the EBR-II Fuel Cycle Facility. The oxidizing atmosphere will probably be a mixture of argon and oxygen.

Table 6

DISTRIBUTION DATA OBTAINED IN HIGH-ACTIVITY-LEVEL MELT
REFINING EXPERIMENTS 4 AND 5

Constituent	Distribution, percent of amount charged				
	Experiment No.	Ingot	Oxidized Skull	Crucible	Total Accounted for, percent of charge
Uranium	4	74	24	a	98
	5	73	26	1.5	100.5
Plutonium	4	70	25	a	95
	5	a	a	a	a
Molybdenum	4	77	24	a	101
	5	75	24	a	99
Zirconium ^b	4	66	33	a	99
	5	53	43	3	99
Ruthenium ^b	4	a	a	a	a
	5	74	25	1	100
Total Rare Earths and Yttrium ^b	4	1	67	16	84
	5	2	83	14	99
Tellurium ^b	4	1	66	6	73
	5	1	68	5	74
Barium and Strontium ^b	4	0	23	73	96
	5	0	15	78	93
Cesium ^b	4	0	a	36	36
	5	a	3	19	22
Gamma Activity	4	65	33	6	104
	5	54	38	3	95
Beta Activity	4	13	56	21	90
	5	12	70	16	98

^a Datum was not obtained.

^b Data were obtained by radiochemical analysis.

Numerical expressions of uncertainty were not included in Table 6 because, in most cases, they could not be estimated accurately. However, the error derived from analytical technique did not exceed three percent for those constituents determined colorimetrically and five percent for those determined radiochemically.* Weighing errors were negligible for the ingot and crucible but may have been significant for the oxidized skull because of the probable loss of some of the powdery material during handling operations. However, the material balances obtained for uranium and molybdenum suggest that oxidized skull losses were minor. Replicate sampling provided an overall test for error, including errors generated by sample inhomogeneities.** In general, the samples were

*All comments relative to uncertainties relate to the 95 percent confidence level.

**At least three random samples of charge, skull, and crucible were obtained. The precision of the data obtained from these samples was estimated by application of the methods of small-sample statistics.

representative for those elements present in macro amount (preirradiation components of the alloy, i.e., uranium, molybdenum, zirconium, and ruthenium), but were not representative for some fission products, the analyses of which showed considerable variability.

Excellent material balances were obtained for uranium, molybdenum, zirconium, and ruthenium. Molybdenum, a typical noble metal, showed a slight enrichment in the ingot, from 2.44 to 2.54 w/o in Experiment 5 (see Table 4), as a consequence of preferential oxidation of a small percentage of the uranium. Evidence of some metal loss by absorption in the crucible, 1.5 percent in the case of uranium and one percent in the case of ruthenium, is provided by distributions noted in Experiment 5.

Rare earths, yttrium, tellurium, barium, strontium, and cesium, present in the alloy as a result of fission of uranium-235, comprised about 50 percent of the total amount of fission products. Material balances for these elements were relatively poor, reflecting variations of as much as 20 percent in analyses of replicate samples. Accordingly, distribution data presented for these elements should be regarded as semiquantitative.

The group IIIB fission product elements, rare earths and yttrium, distributed largely to the skull. However, an appreciable portion, about 15 percent, of the group IIIB activity was found in the crucible. Uncertainties of about 20 percent in the analyses of these elements in the charge, skull, and crucible were sufficient to account for the incomplete material balances in Experiment 4.

Most of the tellurium activity was found in the skull with a small portion, about six percent, distributed to the crucible. Essentially identical distributions, with incomplete material balances, were observed in the two experiments. The variability in analytical data was not sufficiently great to account for the incomplete material balances.

Within the limits of analytical error, complete material balances were obtained for the group IIA fission products, barium and strontium. The bulk of these elements distributed to the crucible; however, about 20 percent remained in the skull.

The incomplete material balance for cesium is consistent with previous data which indicated that substantial removal of cesium occurred by volatilization⁽³⁾ during melt refining. A small amount (three percent) was found in the oxidized skull in Experiment 5, and a considerable amount was retained by the crucible. The difference in the cesium content of crucible samples in Experiments 4 and 5, 36 percent in Experiment 4 as compared with 19 percent in Experiment 5, may be attributable to the alternative procedures used to separate the skull from the crucible. In both cases the skull was

freed by air oxidation, but a higher temperature was used in Experiment 5 (700 C) than in Experiment 4 (~250 C). Thus, a greater amount of cesium may have been lost by volatilization during the preparation of samples in Experiment 5.

Plutonium was bred in the fuel by uranium-238 neutron capture. Its distribution to ingot and skull was noted in Experiment 4. The reproducibility of plutonium analyses was about ± 5 percent for charge and ingot samples, and ± 10 percent for oxidized skull samples. About 70 percent of the plutonium in the charge distributed to the ingot and about 25 percent to the skull. The data show no significant difference between the distribution of uranium and plutonium.

3. Distribution of Zirconium

In all experiments radioactive zirconium showed some depletion in the ingot, and material balances (see Tables 6 and 7) showed a corresponding enrichment in the skull. In Experiment 5, in which the distribution of fission products to the crucible was observed, the percentage of the fission product zirconium retained in the crucible was greater than the percentage retention of fission product ruthenium, a noble metal (see Table 6). Previous studies have shown that, in the absence of carbon, zirconium behaves as a typical noble metal with no preferential distribution.⁽⁹⁾

Table 7

COMPARISON OF DISTRIBUTIONS OF RADIOACTIVE ZIRCONIUM AND URANIUM IN HIGH-ACTIVITY-LEVEL MELT REFINING EXPERIMENTS

<u>Experiment No.</u>	<u>Fraction</u>	<u>Distribution, percent of charge</u>	
		<u>Radioactive Zirconium</u>	<u>Uranium</u>
2	Ingot	57	69
	Skull	37	29
	Crucible	a	a
3	Ingot	42	52
	Skull	57	46
	Crucible	a	a
4	Ingot	66	74
	Skull	33	24
	Crucible	a	a
5	Ingot	56	73
	Skull	43	26
	Crucible	3	1.5

^a Datum was not obtained.

Although the zirconium can be removed by liquation of the carbide,⁽⁹⁾ the preirradiation carbon content of the alloy, 25 ppm, in the present experiments was probably too low to have much effect on the solubility of zirconium, and in Experiment 5 there was not enough carbon to react with 28 percent of the approximately 3000 ppm zirconium in the irradiated fuel. However, in the first three experiments, organic solvents, which were used to remove sodium or NaK from the charge, were a possible source of carbon. Because of the intense radiation levels, the organic solvents probably were degraded to some extent, and a nonvolatile carbonaceous residue may have survived the charge preparation procedure. Therefore, in Experiments 4 and 5, the procedure was altered to eliminate the use of organic solvents, and it is evident from the movement of zirconium in these experiments that the use of organic solvents in prior experiments had little or no effect on zirconium distribution.

Charge and ingot samples from Experiment 5 were examined for evidence of the removal of radioactive zirconium by isotopic exchange with inactive zirconium from the crucible. The ratios of radioactive zirconium to total zirconium for two randomly selected charge samples and one ingot sample were 1.1, 1.1, and 1.0, respectively. These ratios are indicative of isotopic exchange, but, because of the degree of uncertainty, the difference between charge and ingot is of a low level of significance. Furthermore, a difference in these ratios of about 25 percent is required to account completely for radioactive zirconium removal by isotopic exchange in Experiment 5. Although these data are consistent with an isotopic exchange mechanism, it appears likely that carbide liquation contributed to the separation of zirconium.

B. Melt Refining Yields*

1. Experiments with Unirradiated Fuel Alloy

It was recognized from the outset that it would not be feasible to obtain yield data that are directly applicable to the EBR-II Fuel Cycle Facility because of the small scale of the experiments, the different conditions of irradiation, and the unavoidable exposure of the irradiated fuel pins to air in the cave facility. However, several experiments were conducted with unirradiated fuel alloy in an effort to examine some variables which were considered likely to affect the yield. These experiments afforded a comparison of yields obtained with unirradiated fuel pins which had been subjected to various treatments prior to melt refining, and they provided a basis for comparing the behavior of unirradiated and high burn-up fuel alloys.

In all the experiments with unirradiated uranium-fissium fuel, a piece of metallic cerium equivalent to 0.6 w/o of the alloy was added to the pins charged to the melt refining crucible in order to simulate the rare

* The melt refining yield is defined as the amount of purified metal recovered by top pouring, expressed as a percentage of the weight of alloy charged.

earth fission products that would be present in irradiated fuel. Previously reported results⁽⁵⁾ had shown that on a 2- to 10-kg scale this amount of cerium caused the melt refining yields to be lowered from about 97 percent to 93 percent. Unpublished results from 52 melt refining runs on a 10-kg scale showed that the average yield was the same in 48 runs in which the cerium was added separately to the charge as in four runs in which the cerium had been incorporated previously as a constituent of the uranium-fissium alloy.

The results of three experiments in which the fuel pins were subjected to no special treatment prior to melt refining are listed as Experiments A-1 through A-3 in Table 8. The average yield was 89.5 percent. The fact that this yield is about three percent lower than the yields reported for experiments on a 2- and 10-kg scale is attributed primarily to the larger ratio of wetted crucible area to charge weight⁽⁵⁾ (approximately 0.09 sq cm/g as compared with 0.031 to 0.056 sq cm/g for the larger-scale experiments).

Table 8

EFFECT OF PRIOR OXIDATION ON MELT REFINING YIELDS
FOR UNIRRADIATED URANIUM-FISSIUM FUEL PINS

Charge: ~ 400 g			
Melt Refining			
Temperature: 1400 C			
Duration of			
Melt Refining: 3 hr			
Crucible: Lime-stabilized zirconia, Norton Type RZ5601			
Conditions of Heating in Air			
Experiment	Temp (C)	Time (hr)	Yield (% of charge)
A-1	not heated		91.7
A-2	not heated		88.2
A-3	not heated		88.7
B-1	110	65	85.2 ^a
B-2	150	65	72.3 ^a
B-3	200	65	46.8 ^a

^a Loose oxide scale was removed with a nylon brush before melt refining

Since the presence of oxide coatings on the fuel pins is known to have an adverse effect on the melt refining yield,⁽⁴⁾ exposure of the irradiated pins to air in the cave facility was a matter of concern.* Estimates have been made of the temperatures that will result from fission product decay heat for irradiated EBR-II fuel pins in various configurations.⁽¹⁰⁾ These estimates, when applied to the conditions encountered in the present study, indicated that the irradiated fuel pins would reach temperatures of about 80 C in spread arrays during handling, about 150 C after they were loaded in the zirconia crucible, and about 300 C when the crucible was placed in the insulated crucible assembly.

Three melt refining experiments were performed with unirradiated pins which had been heated in air. In these experiments (see Experiments B-1 through B-3, Table 8), no effort was made to remove the oxide film, other than brushing off the loose scale. It is apparent that the melt refining yield decreased markedly as the conditions of prior oxidation were increased in severity.

Since the irradiated fuel pins were coated with sodium or NaK after removal from the irradiation capsule, they were either treated with organic solvents or exposed to oxygen under controlled conditions before they were handled in the air atmosphere of the cave. Both treatments resulted in the formation of a layer of reaction products on the fuel pins.

In EBR-II, sodium is used to effect a thermal bond between the fuel pin and its stainless steel container. The fuel pins which will be melt refined in the EBR-II Fuel Processing Facility are expected to be coated with sodium. The effect on the melt refining yield of a sodium coating in the fuel pins has been studied. The presence of a sodium coating had no effect on yield provided the sodium-coated fuel pins were not exposed to an oxygen-contaminated atmosphere prior to melt refining. However, when sodium-coated fuel pins that had been exposed to an oxygen-contaminated atmosphere were melt refined, the average yield in a series of 2-kg-scale experiments was reduced about ten percent.^(16,17) No reduction in yield as a consequence of a sodium coating on the fuel pins is expected in the EBR-II Fuel Cycle Facility because the sodium-coated fuel pins will be handled in an argon atmosphere. However, in the present work it was not possible to avoid the exposure of the sodium- or NaK-coated fuel pins to air. Therefore, it was necessary to develop a procedure for cleaning the fuel pins before they were melt refined.

Three melt refining experiments (Experiments C-1, C-2, and D) were conducted with unirradiated fuel pins which, prior to melt refining, had been coated with reaction products by first soaking them in NaK and then washing them with organic solvents. After being coated with reaction products, the fuel pins were tumbled in a jar mill containing silicon carbide grit to clean them. With the exception of the NaK soak, these operations

* This problem will not exist in the EBR-II Fuel Cycle Facility because of the argon atmosphere.

were conducted in air. The experimental conditions employed and the yields obtained in the three experiments are presented in Table 9. Also appearing in Table 9 are the conditions used and the results observed in an experiment (Experiment C-3) that employed fuel pins that had been carefully polished with emery cloth. The surfaces of the pins used in Experiment C-3 had a bright shiny metallic luster and the melt refining yield was 86.7 percent. The yields were about three percent lower in Experiments C-1 and C-2 for which the pins had been coated with reaction products and abraded with silicon carbide grit. The yield in Experiment D, in which the fuel pins had undergone an identical pretreatment, was slightly higher than that obtained in Experiment C-3. The fuel pins used in Experiments C-1, C-2, and D were free of visible reaction products after they had been abraded with silicon carbide grit, but the surfaces of the pins had a dull metallic luster rather than the bright shiny finish which was obtained in Experiment C-3 by polishing the pins with emery cloth. Before treatment with NaK and organic solvents, the unirradiated fuel pins melt refined in Experiment C-2 were exposed to air at 150 C for 16 hr. Visual inspection of the fuel pins after they had been exposed to heated air indicated that the surface of the pins had been oxidized. The yield in Experiment C-2 of 84.2 percent was practically the same as the yield of 84.0 percent in Experiment C-1

Table 9

EFFECT OF VARIOUS PRETREATMENTS ON MELT REFINING
YIELDS FOR UNIRRADIATED URANIUM-FISSIUM FUEL PINS

Melt Refining Temperature: 1400 C Crucible: Lime-stabilized zirconia, Norton Type RZ5601				
Experiment	Charge Wt (g)	Duration of Melt Refining (hr)	Pretreatment of Pins	Yield (% of charge)
C-1	419.4	3	Soaked in NaK, washed with organic solvents, abraded with SiC grit.	84.0
C-2	397.5	1	Heated in air at 150 C for 16 hr, soaked in NaK, washed with organic solvents, abraded with SiC grit.	84.2
C-3	359.6	3 ^a	Polished with emery cloth to a bright shiny finish.	86.7
D	398.1	3 ^b	Soaked in NaK, washed with organic solvents, abraded with SiC grit.	87.2

^a Melt refining crucible reclaimed from an earlier experiment with tracer-level fuel alloy.

^b Melt refining crucible reclaimed from high-activity-level Experiment 2; activity level estimated to be about one-tenth of that present in Experiment 2.

in which fuel pins had been given the same pretreatment except that they had not been exposed to heated air. The results of this series of experiments (Experiments C-1, C-2, C-3, and D) indicated that by tumbling the unirradiated pins with silicon carbide grit in a jar mill oxide scale and NaK-organic solvent reaction products could be removed to the extent that the residual amounts remaining on the pins would not significantly affect the melt refining yield.

In Experiment D, the effect of an intense radiation field at the molten metal-zirconia interface was investigated by melt refining unirradiated fuel pins in a highly radioactive crucible which had been reclaimed from the high-activity-level Experiment 2 by heating the crucible in air.* The fuel pins had been soaked in NaK, washed with organic solvents, and abraded with silicon carbide. The resulting yield of 87.2 percent on melt refining was not significantly different from those obtained in the other experiments with unirradiated alloy. These results indicate that an activity level corresponding to about one-tenth of that present in the high-activity-level Experiment 2 had no significant effect on the yield. It was therefore believed likely that any reduction in yield obtained in the high-activity-level experiments was probably a result of changes occurring in the fuel during irradiation and handling, and was not a consequence of the presence of activity during melt refining.

2. High-activity-level Experiments with Irradiated Fuel

Compared with the average yield of approximately 85 percent obtained in the experiments in which unirradiated fuel pins (see Table 9) were pretreated in a manner similar to that used for the irradiated pins, the yields with the highly irradiated fuels were lower by about 10 to 15 percent in Experiments 1, 2, 4, and 5, and by 33 percent in Experiment 3.

Evidence suggesting some correspondence between the amount of air exposure of irradiated alloy and subsequent pouring difficulties upon melt refining is summarized in Table 10. In the first four experiments, the crucibles, with skull intact, were examined after melt refining. Smooth, continuous crusts, completely covering the volume previously occupied by the melt, were observed in the skulls from the first three experiments. It appeared that the recovered metal had poured through small cracks in the crust. Pouring difficulties were encountered in these experiments to the extent that the amount of metal recovered in the first attempt to pour was comparatively low in Experiments 2 and 3, and nil in Experiment 1. The procedures used to recover the melt refined metal are listed in Table 10.

* Studies of the reaction of molten uranium with zirconia under conditions representative of melt refining suggest that the reaction products are uranium dioxide and oxygen-deficient zirconia. Visual observations indicate that restoration to stoichiometric zirconia is accomplished by heating in air.⁽¹¹⁾

Table 10

CORRESPONDENCE BETWEEN AIR EXPOSURE OF IRRADIATED FUEL AND POURING DIFFICULTIES UPON MELT REFINING^a

High-activity-level Experiment No	Comments on Air Exposure ^b	Description of Pouring Difficulties and Other Pertinent Observations	Yield (% of charge)
1	3-1/2 hr exposure to air at 760 torr and 11-1/2 hr exposure to air at 5×10^{-3} torr	A layer of slag on the surface of the melt prevented pouring on the first attempt. The crucible and contents were cooled to about 200 C, then reheated to above 1400 C, and a pour was obtained apparently through fissures in the surface crust.	72.4
2	2-hr exposure to air at 760 torr and 17-hr exposure to air at 5×10^{-3} torr	A layer of slag on the surface of the melt hindered pouring. On the first attempt to pour, a yield of 54 percent was obtained. The crucible and contents were cooled to about 200 C, then reheated to above 1400 C, and a second pour provided an additional yield of 15 percent. The layer of surface slag was still present after the second pour.	69.3
3	2-hr exposure to air at 760 torr and 66-hr exposure to air at 5×10^{-3} torr	A layer of slag on the surface of the melt hindered pouring. No additional metal was recovered in an attempted second pour.	52.2
4	Air exposure kept to a practical minimum by the use of argon blanketing whenever feasible.	A layer of slag on the surface of the melt apparently hindered pouring. This layer ruptured upon pouring and about half the layer was still present after pouring.	73.6
5	2-hr exposure to air at 760 torr	No pouring difficulties. ^c	72.7

^aThe fuel pins were melt refined under an argon atmosphere in a zirconia crucible for 3 hr in Experiments 1, 2, and 3, and for one hour in Experiments 4 and 5.

^bThese comments apply to air exposure after the polishing of the fuel pins with silicon carbide grit.

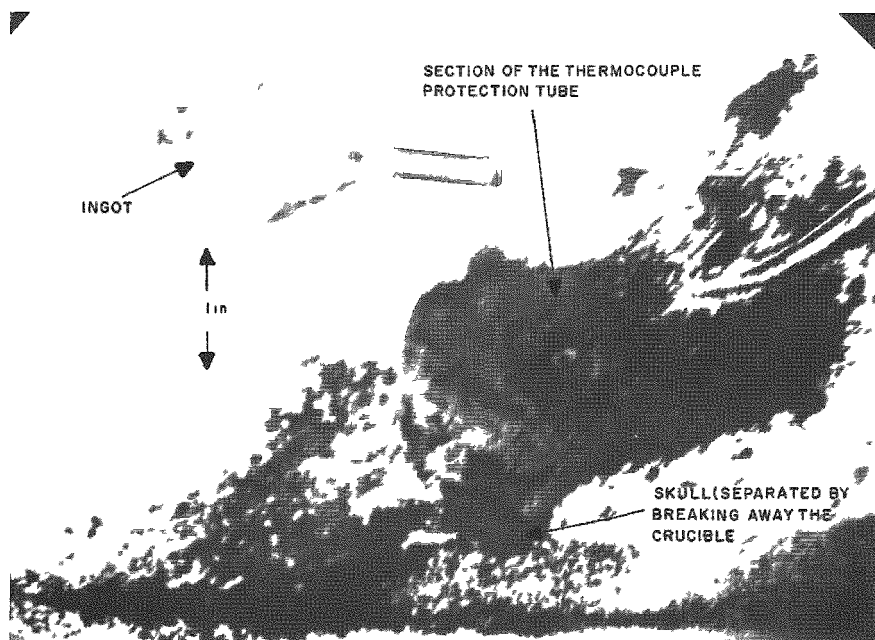
^cThe melt refining residue was not examined; therefore, no comments based on visual observations can be made relative to the presence or absence of a surface slag layer.

The skull produced in Experiment 3 was removed by breaking away the crucible.* As may be seen in Figure 9, the volume previously occupied by the melt appeared to contain a matrix of oxidized and unpoured metal.

Figure 9

SKULL PRODUCED IN HIGH-ACTIVITY-LEVEL EXPERIMENT 3

(Photograph taken through periscope in the
Chemical Engineering Senior Cave)



(Photo Retouched)

*The residues were exposed to air for several hours before the furnace was opened.

In high-activity-level Experiment 4 argon blanketing was employed whenever possible in an effort to reduce exposure to air while the pins were being weighed, sampled, and loaded into the crucible. The yield shown in Table 11 was obtained on the first attempt at pouring. However, a residual surface crust covering about half of the melt cavity was observed when the furnace was opened.* In Experiment 5, the operating procedure was revised to reduce exposure of the alloy to air and the yield was again obtained on the first attempt to pour.

Table 11

YIELDS OBTAINED IN HIGH-ACTIVITY-LEVEL
MELT REFINING EXPERIMENTS AT 1400 C

Experiment No.	Charge Wt (g)	Burnup a/o	Activity Level of Charge (c/g)	Duration of Melt Refining (hr)	Yield (% of Charge)
1	387.6	0.56	3.0	3	72.4
2	392.3	0.22	5.0	3	69.3
3	362.5	0.74	10.5	1	52.2
4	364.2	0.87	9.9	1	73.6
5	382.2	1.75	14.0	1	72.7

* The residues were exposed to air for several hours before the furnace was opened.

IV. DISCUSSION AND CONCLUSIONS

A. Physical Character of Irradiated Alloy

Fuel-handling procedures in the EBR-II Fuel Cycle Facility include mechanical decladding, chopping the irradiated uranium-five percent fission pins into $1\frac{1}{2}$ -in. sections, dumping of the chopped pins into a $5\frac{1}{8}$ -in. (inside diameter) zirconia crucible, and melt refining under argon at 1400 C.⁽¹⁰⁾ Changes in the physical properties of the fuel as a result of irradiation may affect these operations. Hardness, brittleness, and the tendency of irradiated fuel to shatter on impact are factors which could prove troublesome in chopping operations. Other properties, such as the coefficient of thermal expansion and especially the swelling phenomenon characteristic of irradiated alloy,⁽¹²⁾ were of concern because of the possibility that the expanding pins may exert sufficient force to break the crucible. These possible sources of operational difficulties were examined qualitatively during the high-activity-level experiments.

Few data are available on the physical properties of unirradiated uranium-five percent fission alloy, and even fewer on the physical properties of highly irradiated alloy. At room temperature the unirradiated alloy is roughly similar to cast iron in hardness and ductility. As cast and rapidly cooled, the hardness of the alloy at room temperature is about 200 VHN (Vickers Hardness Number) according to Ziegler and Nevitt⁽¹³⁾ and about 125 VHN according to Saller *et al.*⁽¹⁴⁾ The difference in the two numbers may be a function of the percentage retention of the relatively soft gamma phase in the samples tested. The ductility, as measured by the elongation test, was negligible, although considerable stress was required to fracture the alloy.⁽¹⁴⁾ At 690 C the alloy was no longer brittle but flowed readily under light stress⁽¹⁴⁾ and had tensile properties quite similar to those of soft (annealed) copper.

As a result of irradiation, the Rockwell A hardness of retained gamma uranium-five percent fission (as cast and rapidly cooled) increased from a value of 45 for the unirradiated fuel to a value of 70 for the irradiated fuel.⁽¹⁵⁾ This increase in hardness is similar to that resulting from a phase transformation from retained gamma to alpha uranium.⁽¹⁴⁾ No data are available on the tensile properties of the irradiated alloy, but experience in the high-activity-level experiments showed the irradiated pins to be very brittle, easily broken into smaller pieces (similar to a ceramic material), and prone to fragmentation under compressive stress in a vise or on sharp impact.

Upon heating through the temperature interval from about 650 to 900 C, irradiated uranium-five percent fission pins undergo an irreversible diametrical expansion of about 47 percent and rare gas fission products are completely released.⁽¹²⁾ To determine the dimensional changes in the lower part of the temperature range over which swelling occurs, a

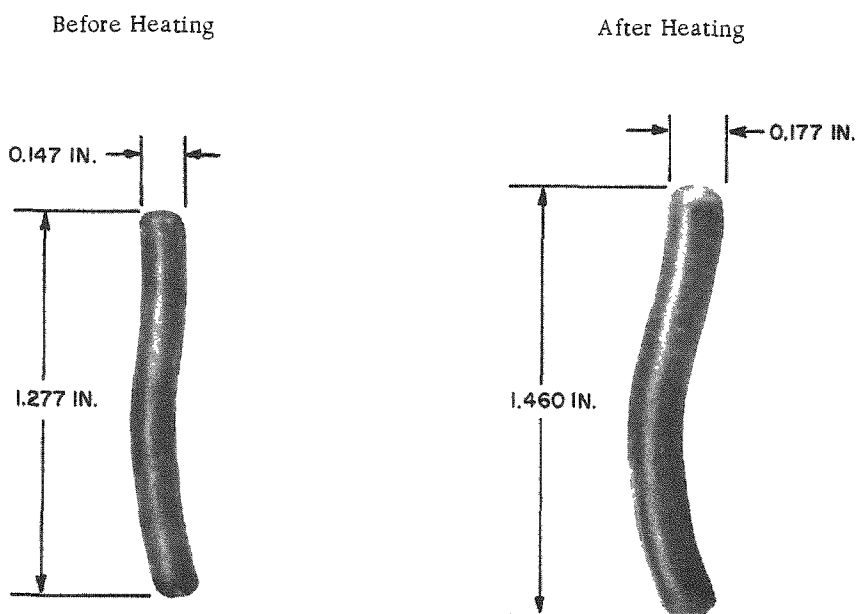
1 $\frac{1}{4}$ -in. section of alloy irradiated to 1.75 a/o burnup* was heated under argon to 700 C and held at that temperature for one hour. Photographs of the pin before and after heating (see Figure 10) show an irreversible diametrical swelling which amounted to 20.6 percent and an increase in length which amounted to 14.4 percent.

Figure 10

SWELLING OF IRRADIATED URANIUM-5 PERCENT
FISSIUM ALLOY UPON HEATING TO 700 C

Alloy: Uranium-5 percent fission irradiated
to 1.75 a/o burnup.

Treatment: Alloy heated in argon to 700 C, main-
tained at this temperature for one hour,
and then cooled to room temperature



(Photo Retouched)

It appears unlikely that the melt refining crucible in the EBR-II Fuel Cycle Facility will crack as the charge is brought to temperature because of swelling of the pins. As loaded (chopped pins will simply be dumped into the crucible), the pins are randomly oriented and the void space of more than 75 percent in the crucible is ample to accommodate swelling. If the increase in hardness upon irradiation is merely indicative of a transformation to alpha-phase uranium and the hot-hardness values of

*The pin selected for this demonstration was from the batch of irradiated alloy used in Experiment 5.

unirradiated alloy are applicable, at 700 C the alloy would be soft (Vickers Hardness Number of 125 at room temperature and 7 at 700 C), ductile, and its ultimate strength would be low.⁽¹⁴⁾ Under these conditions the alloy upon expansion should flow into the available void space. This conclusion was supported by the fact that there was no case of crucible cracking in any of the five high-activity-level experiments.

Another indication of the softness and ductility of irradiated alloy in the temperature range of gross swelling was obtained from observations of the immersion thermocouple protection tube used in the melt refining experiments. This fragile beryllia tube, 4 mm in outside diameter and 2 mm in inside diameter, was deeply imbedded in the mass of pins and was subject to stresses which might have developed during the heating cycle. In the five experiments, there was only one malfunction of the immersion thermocouple, and in this case its behavior was more indicative of electronic difficulties than of mechanical failure of the protection tube.

B. Behavior of Fission Products

1. Removals

The results of the high-activity-level experiments generally confirmed the data from previous studies of the melt refining process. Nearly complete removals were noted for the rare earths and yttrium, barium and strontium, tellurium, iodine, and cesium. The noble elements molybdenum and ruthenium were not removed. As anticipated, krypton and xenon appeared in the argon atmosphere used for melt refining and were pumped to shielded storage tanks. The following variables, over the ranges indicated, had no significant effect on the extent of fission product removal: (1) the duration of melt refining from 1 to 3 hr, (2) total fuel burnup between 0.22 and 1.75 a/o, (3) activity level from 3.0 to 14.0 c/g, and (4) charge preparation procedures for the removal of NaK or sodium from the pins. These procedures entailed the use of organic solvents in Experiments 1, 2, and 3, and controlled air oxidation in Experiments 4 and 5.

The rates of fission product removal are believed to be affected by the geometric differences between small-scale and large-scale melt refining equipment. Although identical results were obtained in small-scale experiments of 1- and 3-hr duration, the longer 3-hr period specified for the plant operation is believed to be necessary because of the longer diffusion paths that the fission products must traverse to reach the crucible wall where oxidation occurs. The percentage of cerium retained during the melt refining of unirradiated fuel has been correlated with the duration of melt refining and the ratio of the wetted crucible area to the charge weight.⁽³⁾ On the basis of this correlation, one hour of melt refining on the 0.4-kg scale used in these experiments is approximately equivalent to 3 hr of melt refining in the plant-scale crucible.

2. Distribution to Skull and Crucible

An auxiliary liquid metal process is currently being developed for the recovery of uranium from melt refining skulls. The feed material to this process is the granular product produced during removal of the skull material from the crucible by oxidation.* The used crucibles are discarded as waste. It was therefore of interest to determine the distribution of fission products between the oxidized skull material and the crucible.

Since the skull consists of oxide and a variable amount of unpoured metal, the relative amounts of noble metal and other fission products in the skull depend upon the pouring efficiency during melt refining. Therefore, the fission product distribution data shown in Table 6 for high-activity-level Experiments 4 and 5 probably show a higher percentage of noble metals (represented by ruthenium) in the skull than would be expected on the plant scale, for which the pouring efficiency should be higher. Those fission products that are removed by melt refining would be expected to distribute among the ingot, skull, and crucible in approximately the same proportions in the small-scale experiments and in the plant-scale process.

A significant amount of the fission product activity, about 20 percent of the beta and 5 percent of the gamma, was found in the crucible. Feder *et al.*,⁽⁴⁾ in an early review of the melt refining process, expressed the opinion that a portion of the more volatile fission products probably would diffuse into the crucible, and confirmation of this point was provided by later work.⁽³⁾ Thus the results of the high-activity-level experiments, showing roughly 75 percent of the barium and 30 percent of the cesium in the crucible, can be explained on the basis suggested by Feder. The retention in the crucible of 15 percent of the rare earths, one percent of the ruthenium, and 1.5 percent of the uranium,** is attributed to trapping of oxide and possibly some metal in the wall of the relatively porous crucible.

C. Melt Refining Yield

In the high-activity-level experiments the yields were consistently lower than those obtained with unirradiated fuel pins under equivalent melt refining conditions. The pouring difficulties that were encountered and the appearance of the skulls from the high-activity-level experiments suggested that a layer of oxidized material on the surface of the molten metal had

*A gaseous mixture composed of 80 v/o argon and 20 v/o oxygen is presently being used as the oxidant.

**The small-scale results cannot be extrapolated directly to the plant-scale operation because of the difference in geometric factors. Unpublished results of studies of the removal of skulls from plant-scale crucibles by oxidation of the residue with a mixture of argon and oxygen show the uranium retained in the crucible to be 0.05 to 0.2 percent of the uranium in the melt refining charge.

interfered with the pouring operation. Since the yield was not affected consistently either by the irradiation level, between 0.22 and 1.75 a/o burnup, or by the activity level, between 3.0 and 14.0 c/g, it does not appear that insoluble fission product oxides were a significant source of the oxide layer. On the other hand, the results in Table 10 showing the correspondence between the extent of oxidation of the irradiated alloy and the pouring difficulties upon melt refining does indicate that the presence of oxidized uranium contributed to a decrease in the yield.

Although the oxide formed on the irradiated fuel pins prior to melt refining undoubtedly resulted in lower yields, a phenomenon peculiar to the irradiated pins is believed to have had an even greater effect. The irradiated pins, when heated through the temperature interval from 650 to 900 C, undergo a diametrical expansion of about 47 percent,⁽¹²⁾ while unirradiated pins expand less than 2 percent under similar conditons.⁽¹³⁾ The gross expansion of the irradiated pins appears to cause the oxide coating to slough off the pins in the form of fragments which tend to float to the surface of the molten metal. In contrast, oxide coatings on the unirradiated pins tend to remain intact as the pins melt, forming cylindrical "pin shells."

Evidence in support of this hypothesis is provided by comparing the melt refining skull produced in Experiment E with unirradiated fuel pins with one obtained from high-activity-level Experiment 3. The 355-g charge of the unirradiated fuel pins was heated in air to red heat, cooled, lightly abraded to remove loose oxide, combined with 0.6 g of irradiated alloy (0.56 a/o burnup),* and melt refined for 3 hr at 1400 C. A yield of 55 percent was obtained. The skull, shown in Figure 11, contained a mass of cylindrical pin shells but no surface crust, indicating that as the fuel melted it collected in the bottom of the crucible and left behind oxide shells in the shape of the original pins. However, in high-activity-level Experiment 3, in which a similar yield was obtained (52.2 percent), the skull had a surface crust, and as shown in Figure 9, appeared to consist of a mass of pin shell fragments and unpoured metal; no complete pin shells were visible.

D. Significance of Results to Melt Refining in the EBR-II Fuel Cycle Facility

Because of experimental limitations, it was necessary to conduct the high-activity-level experiments on a reduced scale (about 0.4 kg compared with approximately 10 kg in the EBR-II Fuel Cycle Facility). Since geometric factors will differ greatly,** the small-scale results cannot be

*Tracer level activity was included because it was originally thought that comparison of fission product distribution data from the two experiments might be useful in interpreting the results.

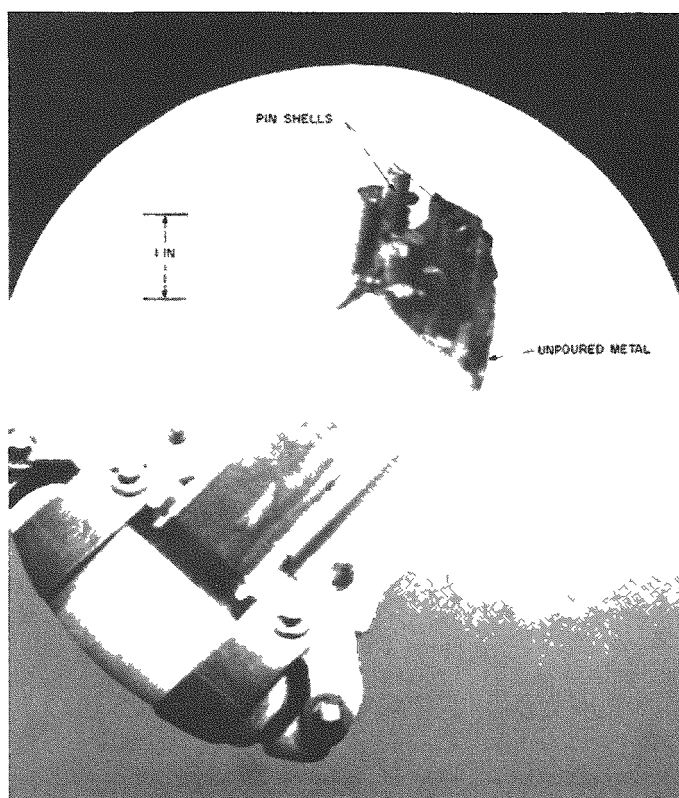
**For example, the crucible surface area in contact with molten metal per gram of fuel (sq cm/g) is about 0.03 for the full-scale crucible compared with about 0.09 for the small-scale crucible.

extrapolated directly to the plant-scale operation. However, the results of the small-scale experiments should provide a guide to preventive or corrective measures if difficulties are encountered in the plant-scale melt refining of irradiated fuel.

Figure 11

SKULL PRODUCED IN EXPERIMENT E

(Photograph taken through periscope in the Chemical Engineering Senior Cave)



(Photo Retouched)

In the EBR-II plant-scale operation, it is reasonable to expect that the yields will be higher than those found in the small-scale experiments with irradiated fuel. Full-scale melt refining runs with unirradiated alloy have generally resulted in yields exceeding 95 percent,⁽⁵⁾ as compared with yields of about 85 percent for small-scale control experiments with unirradiated alloy.

The reduction in yield associated with irradiation of the fuel in small-scale experiments was the result of inefficient pouring which, in turn, appeared to be related to the presence of a layer of oxidized uranium on the surface of the molten metal. Apparently, this surface layer was mainly composed of fragments of uranium oxide from the irradiated pins

which had been handled in an air atmosphere prior to melt refining. Since the atmosphere of the EBR-II Fuel Cycle Facility is argon,* no reduction in yield as a result of exposure to air is expected.

SUMMARY

Five 0.4-kg-scale high-activity-level experiments were conducted to demonstrate the EBR-II melt refining process and to reveal any difficulties that might result from the use of highly irradiated fuel. The alloy, 10 percent enriched uranium containing 5 percent fission, was irradiated to total burnups of 0.22 to 1.75 a/o and was then melt refined in a lime-stabilized zirconia crucible at 1400 C for 3 hr in Experiments 1 and 2, and for one hour in Experiments 3, 4, and 5. For purposes of comparison, several additional experiments were conducted in the same equipment with unirradiated alloy.

The fission product removals obtained in the melt refining experiments with highly irradiated fuels confirmed those from earlier studies with inactive and low-activity fuel. The results showed no significant dependence on burnup, radiation level, or the duration of melt refining. Rare earths and yttrium, tellurium, iodine, cesium, and barium and strontium were removed, whereas the noble metals ruthenium and molybdenum were not removed. The fission product zirconium showed isotopic exchange with the inactive zirconium in the crucible. Small amounts of carbon contamination probably resulted in the removal of some zirconium as the carbide.

Compared with the experiments with unirradiated fuel, the melt refining yields for the highly irradiated alloys were lower by 15 to 30 percent. These lower yields were the result of less efficient separation of purified metal because of the presence of a surface crust which hindered top pouring. The formation of this crust appeared to be characteristic of highly irradiated but not of unirradiated fuel, and was attributed to exposure of the irradiated fuel to air before melt refining and to an accumulation of oxide fragments on the surface of the melt. Gross expansion of the irradiated pins during heating is believed to have caused the oxide fragments to slough off the surface of the pins. It is expected that the effect of these crusts on the yield will diminish as the scale of melt refining is increased and that pouring difficulties from crust formation will be less likely to occur in the EBR-II Fuel Cycle Facility because of its argon atmosphere.

Certain physical properties of highly irradiated uranium-5 percent fission alloy which may have an effect on operations in the EBR-II Fuel

*The design of the atmosphere-purification system is based on maintaining impurity levels at or below 5 ppm water vapor, 20 ppm oxygen, and five percent nitrogen in the atmosphere.(10)

Cycle Facility were observed qualitatively. The irradiated pins, subject only to self-heating by the decay of radioactive fission products, were very brittle, were easily broken into smaller pieces (similar to a ceramic material), and tended to shatter under compressive stress in a vise or on sharp impact. The gross swelling phenomenon that is characteristic of irradiated uranium-5 percent fission upon heating through the temperature interval from about 650 to 900 C was of concern because of possible crucible damage. In the five experiments with highly irradiated fuel, there was no case of crucible cracking, probably because of the lack of strength of the alloy at these temperatures.

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