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THE EBR-II SKULL RECLAMATION PROCESS

PART II. OXIDATION OF MELT-REFINING SKULLS

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Part II. Oxidation of Melt-refining Skulls

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ABSTRACT

Discharged fuel from the first core of the Second Experimental Breeder Reactor (EBR-II) will be an enriched uranium-fissium alloy and will be processed by melt refining. In the melt-refining process, the metallic fuel is melted in a zirconia crucible and liquated for about three hours at 1400°C, a procedure that removes most of the fission products through volatilization and oxidative slagging. When the purified metal product is poured into a mold to form an ingot, about 5 to 10% of the charge remains in the crucible as a skull (a mixture of oxides and unpoured metal). Among various methods investigated for removing skull material from crucibles for further processing, the most satisfactory technique consisted of oxidizing the skull in a 20 v/o oxygen-argon mixture at temperatures of 700 to 800°C. This procedure results in the formation of a free-flowing oxide powder that can be poured from the crucible with recoveries of about 98%. Iodine appears to be the only major fission product to undergo significant volatilization under these conditions. The product of the oxidation procedure has been found to have satisfactory properties for further processing by the liquid-metal methods used in subsequent steps of the skull-reclamation process. Plant-scale equipment for the oxidation of skulls has been built and tested, and is being installed in the EBR-II Fuel Cycle Facility in Idaho.

I. INTRODUCTION

In the EBR-II melt-refining process, the enriched uranium-fissium fuel alloy is melted and liquated for about three hours at 1400°C in a lime-stabilized zirconia crucible. The molten fuel is then top-poured into a mold to form a product ingot. In the pouring operation, about 5 to 10% of the uranium alloy remains in the crucible in the form of a skull (a mixture of oxidic dross and unpoured metal).

The objective of the skull-oxidation procedure is to convert this skull into a material that can easily be removed from the crucible for recovery by the skull-reclamation process.⁽¹⁾ It is desirable to minimize the amount of crucible zirconia in the oxidized skull material because of the limited capability of the skull-reclamation process for zirconium removal. The skull removal procedure must be simple, adaptable to remote operation, and capable of integration with the subsequent steps of the process.

This report deals with the development work leading to the adoption of oxidation as a means of skull removal. Oxidation converts the skull to a free-flowing powder which is easily poured from the crucible and is a suitable feed for the subsequent steps of the skull-reclamation process.

II. CHARACTERISTICS OF MELT-REFINING SKULLS

A. Composition

The skull remaining in the zirconia crucible on completion of the melt-refining process normally contains 5 to 10% of the original melt-refining charge, the other 90 to 95% being in the product ingot. The skull usually consists of 70 to 90% unpoured metal, and a mixture of UO_2 and fission-product oxides. An estimated composition for 10 kg of typical skull material is presented in Table 1. Uranium is the major component of skulls, constituting about 86 w/o of the metal content. Yttrium and rare earths, noble metals, and alkaline earth metals constitute about 6.4, 5.3, and 1.5 w/o, respectively. The approximate distribution of Curies of activity is: yttrium and rare earths, 68%; barium and strontium, 25%; noble metals, 5%.

The exact constitution of oxidic phases in crucible reaction layers and drosses derived from melt refining of high-burnup uranium-fission alloys is not known. However, kinetic,^(2,3) X-ray, and phase-diagram⁽⁴⁾ studies of related, but simpler, systems indicate that the material will probably contain such phases as solid solutions of UO_2 - ZrO_2 , UO_2 -rare earth oxide, UO_2 - SrO , $\text{U}(\text{O}, \text{C}, \text{N})_2$, oxygen-deficient zirconia, and unpoured metal.

In practice, the skull composition will depend upon (1) the composition of the melt-refining charge, which is influenced by various separations throughout the fuel cycle; (2) the melt-refining conditions, which affect the distribution of fuel constituents; (3) pouring yields, which determine the uranium, plutonium, and noble-metal content of the skulls; and (4) the processing schedules and cooling times. (If several weeks' production of skulls are combined for processing, short-lived fission products such as 12.8-day Ba^{140} and its 40-hr La^{140} daughter, 13.7-day Pr^{143} , and 11.3-day Nd^{147} will have undergone considerable decay.*) The quantity of 8.05-day I^{131} that will be

*Since rare earths decay to other rare earths, cooling of skulls has a more important influence on activity and heat generation than on the net chemical composition.

present in skull material has not been determined reliably, but cooling time may be of particular importance in this connection. Composition of the feed to the skull-reclamation process may also vary through use of the process for the recovery of certain types of scrap material. It is therefore essential that the process be capable of handling materials of varying composition.

Table 1

FEED TO THE OXIDATION STEP OF THE
EBR-II SKULL-RECLAMATION PROCESS

Basis: Ten melt-refining skulls and crucibles

Constituent	Weight (g)	Constituent	Weight (g)
U	7,646	Ru	165.6
UO ₂	965	Rh	27.1
Pu	93.7	Pd	17.4
PuO ₂	11.8	Ag	0.1
Kr	~0.0	In	0.1
Rb ₂ O	1.1	Sn	0.3
SrO	79.5	Sb	0.2
Y ₂ O ₃	44.8	Te	21.3
Zr	137.1	Cs ₂ O	8.6
ZrO ₂	20.4	BaO	93.9
Nb	8.7	(RE) ₂ O ^a	682.1
Mo	212.9	I (~5000 Curies) ^b	2.0
Tc	32.9	ZrO ₂ crucibles (inactive)	94,000.0
Total weight of skull material (excluding ZrO ₂ crucibles):		~10 kg	
Total volume, including ZrO ₂ crucibles:		~50 liters	
Activity (beta and gamma):		1.8 x 10 ⁶ Curies	
Fission product heat:		1.6 x 10 ⁴ BTU/hr ^c	

^a The symbol "RE" is used to designate the rare-earth fission products as a group.

^b Based on 1/16th of the iodine in the melt-refining charge, with decay corrections.

^c Assuming all beta and 10% of the gamma activity are absorbed.

B. Physical Character

The alkaline earth and rare earth elements, which constitute about 40% of the expected fission products, form oxides that are more stable than the ZrO₂ in the melt-refining crucible. Uranium metal is also oxidized to a limited extent by zirconia to form UO₂. During melt refining, these oxides,

which are produced by reaction of the metals with the zirconia crucible, form a cross that adheres to the crucible surfaces when the molten metal is poured. The oxygen consumed in these reactions is supplied from the crucible wall, where a blackened, oxygen-deficient zone is formed.⁽⁵⁾ In addition to the oxides, or dross, the skull contains a thin layer of unpoured metal on the crucible walls.* The components of a typical skull in a melt-refining crucible are illustrated in Figure 1.

Figure 1

COMPONENTS OF THE MELT-REFINING CRUCIBLE SKULL

For a plant-scale, melt-refining run, with a pouring yield of 90%, the total weight of the skull would be about 600 to 700 g. Since the skull adheres tightly to the comparatively fragile zirconia crucible, complete recovery of the skull without the introduction of crucible fragments poses a difficult problem.

C. Condition of Crucible

During melt refining, deterioration of the zirconia crucible is such that present plans do not call for reuse. The crucibles are made of pressed and sintered ZrO_2 , stabilized by the addition of 5 w/o CaO (Norton Mix RZ 300).**

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Numerous observations of plant-scale crucibles used for melting unirradiated uranium-fissium alloys have shown two principal types of damage. (1) A horizontal hairline crack at the junction of the wall and the base is nearly always present, and vertical hairline cracks are found occasionally near the top. (2) The blackened, oxygen-deficient zirconia is observed in the region of the skull. Although neither of these effects has resulted in a loss of crucible integrity during melt refining, they can lead to destruction of the crucible under the severe conditions imposed by various skull-removal treatments. Accordingly, the crucibles were often placed in closely fitting steel cans which restrained them so as to prevent crumbling.

*A portion of the unpoured metal often appears in the crucible as a metallic "button" after completion of the pouring operation. The relative size of this button decreases as the scale of the melt-refining operation increases. Thus, a button is almost always obtained on a scale of less than 1 kg, whereas it is seldom seen on the 10-kg scale.

**This mix also contains minor amounts of other oxides. A typical analysis is as follows (w/o): CaO (5), SiO_2 (0.7), TiO_2 (0.3), Fe_2O_3 (0.2), HfO_2 (< 2.0), Al_2O_3 (0.5), balance ZrO_2 .

D. Fission-product Decay Heat

Concentration of the fission products into the skull fraction during melt refining produces an intensely radioactive material. Depending on the materials and geometry involved, sufficient activity is absorbed to generate a large amount of heat. Fission-product heating in skulls results largely from the decay of rare earths, yttrium, strontium, and barium, with much smaller contributions from the noble metals. To date, it has been necessary to rely on calculations of skull temperatures brought about by self-heating, since no full-scale, high-burnup material has been available for experimental measurements. Computed data for skull composition, activity, and heat generation are summarized in Table 1. Using these data and certain assumptions regarding heat-transfer coefficients, emissivities, ambient temperatures, and crucible-skull geometries, skull temperatures have been estimated. The assumptions used were intentionally conservative so as to yield high, rather than low, estimates.

For 10 kg of fuel irradiated to two total a/o burnup and cooled 15 days, the melt-refining skull may attain a steady-state temperature as high as 600 to 800°C during storage in the zirconia crucible. This effect is illustrated in Figure 2. The higher temperatures shown in Curve A can be expected if the crucibles are stored close together, and the lower temperatures of Curve B if they are well separated. If the fragility of the crucibles after melt refining requires secondary metal containers for safe handling and storage, the steady-state temperature will be higher. If, on the other hand, the melt-refining charge contains some inactive uranium, or if longer cooling times are involved,* the temperature will be lower.

Figure 2
FISSION-PRODUCT DECAY HEATING OF
EBR-II MELT-REFINING SKULLS

BASIS:

CURVE A - ALL HEAT REMOVED BY RADIATION
OUT TOP OF CRUCIBLE
CURVE B - HEAT REMOVED BY RADIATION OUT
TOP AND OFF SIDES AND BY NATU-
RAL CONVECTION FROM OUTSIDE WALLS.

EMISSION: SKULL = 0.5
CRUCIBLE = 0.75

CONDUCTIVITY:
CRUCIBLE = 0.5 Btu/hr ft² (°F/ft)

NATURAL CONVECTION FROM
OUTSIDE CRUCIBLE WALL:
 $h_c = 2 \text{ Btu}/(\text{hr})(\text{sq ft})(°\text{F})$

For skulls produced in melt refining two-percent-burnup, 15-day-cooled fuel, little external heat would be required to reach the temperature of 800°C used in the proposed oxidation procedure.⁽⁶⁾ Full heating provisions are necessary, however, to process longer-cooled and lower-burnup skulls.

*It is expected that several skulls will be accumulated for processing, so several cooling times may be involved in one batch. According to current plans, each skull will be oxidized immediately after the melt-refining operation, and will be stored as the oxide while awaiting processing.

III. METHODS OF REMOVING SKULL FROM CRUCIBLE

A. Mechanical Separation

Various attempts have been made to separate skulls from melt-refining crucibles by mechanical means alone. In general, this procedure consisted of breaking the crucible into fragments and separating the skull material by hand.

Ten experiments were performed in which mechanical removal of skulls from full-scale crucibles was investigated (Table 2). The skulls ranged in weight from 350 to 1000 g. Nearly complete recovery of three skulls was achieved, but in two of the three runs (DL-19 and DL-24), the presence of very fine material suggested that some prior oxidation had occurred. In each of the other seven experiments, about 100 g of the skull adhered tenaciously to the crucible fragments. In all the experiments, it was necessary to effect the separation by laboriously picking out pieces of the skull with tweezers.

Table 2

MECHANICAL SEPARATION OF SKULLS FROM MELT-REFINING CRUCIBLES

Melt-refining runs performed in a full-scale "mock-up" facility, using unirradiated uranium-fissium alloy. Melt-refining conditions: 3 to 4 hr at 1400°C. Crucible broken away from skull, and remaining crucible fragments separated by hand.

Melt-refining Run	Condition of Crucible	Skull Weight ^a (g)	Weight of Size Fractions of Skull Recovered (g) ^b			Weight of Balance Tightly Adherent (g)	Total Weight (g)
			1 cm ²	>1 cm ² <45 mesh	>45 mesh		
DL-4	Bottom off; severe cracks	341	71	20	~5	319	415
DL-6	Severe cracks	295	152	63	18	191	424
DL-7	Cracked	340	192	15	~5	152	364
DL-8	Minor cracks ^c	543	288	131	7	97	623
DL-19 ^d	Cracked	942	806	110	79	nil	995
DL-22A	Bottom off, badly cracked	513	403	105	~5	89	602
DL-22C	Severe horizontal crack	562	409	147	~5	3	564
DL-23	Bottom off; cracked	377	272	53	~5	80	410
DL-24	Bottom off; cracked	453	110	178	173	2	463
DL-27	Severe cracks	342	186	75	~5	81	347

^a Difference between metal charged and product ingot in melt refining.

^b A certain amount of crucible zirconia is included in this weight.

^c This was the only crucible that did not have a complete circumferential crack at the junction of the wall and the base.

^d The only run in which cerium was added.

This procedure was discarded as a practical possibility for three major reasons: (1) recoveries of skull material were inadequate in most cases, (2) the recovered skull material contained excessive amounts of crucible zirconia, and (3) the technique is not adaptable to remote operation.

B. Dissolution in Liquid Metals

Since the subsequent steps of the skull-reclamation process entail the use of liquid-metal solutions as process media, some consideration was given to the possibility of dissolving melt-refining skulls directly in liquid zinc or zinc-magnesium alloys. Upon further examination, this approach showed little promise because of the porosity and poor integrity of the zirconia crucibles after melt refining. A further difficulty is that the liquid metal must be capable of reducing the uranium oxides, as well as dissolving the metallic portion of the skull, but must not reduce significant amounts of zirconia from the crucible. Attempts to reduce uranium oxides without reducing ZrO_2 have not been successful. Therefore no further consideration was given to this method.

C. Partial Oxidation

Oxidation of UO_2 and metallic uranium is effected by the following reactions:

If carried to completion, these reactions convert the skull to a free-flowing powder which is easily poured from the zirconia crucible. If the crucible is held in an inverted position during oxidation, however, the skull is released and falls free before extensive oxidation has taken place. In earlier versions of the skull-reclamation process, this procedure had the advantage that the bulk of the uranium metal was not oxidized and did not need to be reduced again later in the process.

In two preliminary experiments, partial oxidations were performed on skulls that had been produced by melt refining on a 2-kg scale. The unrestrained crucibles were inverted to permit the skull to fall as soon as it was freed. One skull fell completely free after 20 min of exposure to 25% oxygen in argon at a total pressure of 800 torr and a temperature of 700°C . The second skull fell free in four minutes at 750°C in the same atmosphere. Complete oxidation under these conditions would have required about four hours. The crucibles broke in several places, indicating the need for restrainers.

Four additional runs were made to liberate full-scale skulls by partial oxidation. Two of these oxidations were performed with upright crucibles, and two with inverted crucibles. In both oxidations with the crucibles in an upright position, the crucibles were placed in stainless steel restrainers, and the skulls were oxidized to about 50% of completion.

In each case, when an attempt was made to dump the oxidized skull, about half the product was poured out, but a metallic cup-like portion that was loose from the walls became wedged in the crucible. It was concluded that partial oxidation could only be attractive if the crucible were inverted during the oxidation.

The oxidations in inverted crucibles were performed at about 600°C in an atmosphere of approximately 20% oxygen in argon. In the first experiment, the zirconia crucible was not jacketed with a steel secondary in the furnace, thus permitting some oxygen penetration through the crucible walls, and oxidation at the skull-crucible interface. The skull material fell into the receiver when the reaction was about 25% complete. In the second experiment, the crucible was contained in a close-fitting, stainless steel can. The oxidation was stopped when about 22% of the skull had been oxidized. Later examination showed that much of the skull material had fallen into the receiver, but a cup-like portion which had fallen only part way was found wedged in the crucible. This "cup" appeared to be nearly broken and probably would have fallen free with little additional oxidation. Although the crucible was held together by the steel can in the latter run, there was no apparent difference in the oxidation behavior of the skulls in the two runs. The crucibles cracked during both oxidations; the bottoms came loose and had broken along a diameter. In the second run, the side wall in the region of the original melt broke into several pieces which fell apart when the stainless steel can was removed.

These two experiments indicate that about 25% of the skull material must be oxidized before a skull will be completely freed from the crucible. The resultant mixture of metal and oxide might have some advantage over an all-oxide charge in the subsequent process, but because of the large fraction of oxide, the advantage seems small. Therefore, the partial oxidation procedure was not developed further.

D. Oxidation-reduction Cycles

Oxidation-reduction cycling with oxygen and hydrogen has been adapted by Atomics International^(7,8) to the reconstitution of UO₂ reactor fuels. The following reactions are involved in this procedure:

As the cycling is continued, the particle size of the material decreases progressively.

This technique was investigated as a possible method of converting skull material to a powder which could be recovered by pouring the product from the zirconia crucible. In preliminary experiments, the highly exothermic oxidation reaction was initiated at temperatures as low as 200°C, but a temperature of 800°C provided better control of the reaction. The low-temperature oxidation produced a large temperature excursion which fractured the crucible. The oxidation was conducted with 100 to 500 torr of pure oxygen, and the reduction with approximately 300 torr of hydrogen.

Exploratory oxidation-reduction experiments are summarized in Table 3. In several of the runs, graphite had been added as a means of removing zirconium during the preceding melt-refining operations.⁽⁹⁾ The results were encouraging in that a pourable powder was produced consistently.

Table 3

SUMMARY OF OXIDATION-REDUCTION STUDIES WITH MELT-REFINING SKULLS

Material	Conditions	Results
1. Uranium-fissium (without cerium) skull in zirconia crucible.	O ₂ oxidation for 1 hr at 800°C H ₂ reduction for 1 hr at 800°C	Skull powdered. Product could be poured from crucible. Crucible integrity maintained.
2. Uranium-fissium A ^a (with cerium) skull in graphite-coated zirconia crucible	O ₂ oxidation for 1 hr at 800°C H ₂ reduction for 1 hr at 800°C	Skull powdered. Product could be poured from crucible. Crucible integrity maintained.
3. Uranium-fissium A (with cerium) skull in zirconia crucible. Crucible also contained 3 x 0.5-in. graphite disc. Disc mechanically removed before run.	O ₂ oxidation initiated at 200°C H ₂ reduction for 1 hr at 600°C	Ignition at 200°C, followed by extreme temperature excursion. Maximum attained temperature not known, but certainly exceeded 1000°C. Crucible cracked. Product was a pourable powder.
4. Uranium-fissium A (with cerium) skull in graphite-coated zirconia crucible.	O ₂ oxidation initiated at 300°C H ₂ reduction for 1 hr at 600°C	Ignition at 300°C, followed by extreme temperature excursion. Crucible cracked. Product was a pourable powder.
5. Uranium-fissium (without cerium) skull in zirconia crucible.	O ₂ oxidation initiated at 200°C H ₂ reduction for 1 hr at 600°C	Ignition at 200°C, followed by extreme temperature excursion. Crucible cracked. Product was a pourable powder
6. Uranium-fissium A (with cerium) skull. Crucible contained 3 x 0.5-in. graphite disc. Crucible was cracked before run.	O ₂ oxidation for 1 hr at 800°C H ₂ reduction for 1 hr at 800°C	Skull powdered. Product was pourable. Large mass of material adhering to graphite disc was not powdered. Disc was not consumed
6A. Graphite disc and adhering reaction mass from Run 6.	O ₂ oxidation for 1 hr at 800°C H ₂ reduction for 1 hr at 800°C	Approximately $\frac{1}{3}$ of reaction mass was powdered. Unburnt portion probably UC plus some ZrC. Graphite disc was not consumed.

^aUranium-fissium A is a uranium alloy containing 7.5 w/o Mo, 0.5 w/o Zr, and 0.6 w/o Ce

Further oxidation-reduction studies were made, using thin biscuits of uranium-fissium alloy containing 3.9 w/o molybdenum and 2.6 w/o ruthenium. (The principal purpose of the experiments was to determine the amounts of molybdenum and ruthenium removed as volatile oxides.) With pure oxygen at 800°C, the oxidation rate was sufficiently rapid to require control by metering the oxygen supply. Satisfactory results were obtained with less than 100 torr of oxygen pressure. Exposure to air at 800°C for two hours, and subsequent exposure to oxygen at 800°C, oxidized only about 25% of the material, suggesting that air is not suitable for this purpose.

In two later experiments, oxidized skull material was reduced with hydrogen. Some further particle-size reduction was achieved. Since material of a satisfactory particle size for further processing can be produced by oxidation alone, the problems of handling hydrogen and disposing of the by-product water in the fuel-processing facility seem to outweigh any advantage. Further research and development work was therefore confined to oxidation alone.

E. Complete Oxidation

Since preliminary investigations of the oxidation-reduction procedure had indicated that oxidation alone may be a satisfactory method of recovering skulls from crucibles, some exploratory oxidation experiments were performed. Several full-scale skulls were oxidized in an oxygen-argon atmosphere. Dilution of the oxygen with argon helped to achieve more uniform temperature control. The skulls, which weighed between 300 and 100 g, were oxidized in a 40-liter, stainless steel bomb. The total pressure was maintained at 800 torr, and the oxygen concentration was increased from 20 to 50%. The reactions progressed smoothly, and the temperature was easily held within the desired limits ($\pm 10^\circ\text{C}$ at 800°C, and $\pm 20^\circ\text{C}$ at 600°C). Typical results are presented in Table 4. These data indicate that a finer product was produced at the lower temperatures. In all the runs, over 98% of the oxidized skull could be poured from the crucibles.

Table 4

OXIDATION OF URANIUM-FISSIUM SKULLS

Equipment 40-liter Type 304 stainless steel vessel
Total pressure: 800 torr
Oxygen concentration: 20 to 50% in argon (increased during run)

Run	Temp (°C)	Skull Weight (g)	Time (hr)	Product Screen Analysis (%)		
				+20 mesh	-20, +100 mesh	-100 mesh
1	590	515	6.5	5	34	61
2	770	370	6.0	15	42	43
3	820	945	4.5	23	49	28
4	970	900	5.0	33	37	30
5	720	a	2.5	33	41	26

^a Plus 20-mesh material from Runs 3 and 4.

Since this procedure proved satisfactory and was finally adopted for use in the process, additional investigations were conducted as a process development effort. These investigations are described in detail in Section IV.

F. Nitridation

Nitrogen reacts with skull material in much the same way as oxygen and forms a nitride powder. Although nitridation was considered briefly as a method of removing skulls from crucibles, because the reaction is less exothermic than the oxidation reaction, it proved to have no significant advantage. Nitridation has a serious disadvantage, however, in that oxidation of the nitride product is necessary to render it suitable for the following steps of the liquid-metal process.

The nitridation characteristics of skulls are nevertheless pertinent for another reason. Since the argon atmosphere of the processing cell is expected to contain as much as 5% nitrogen, and the skulls awaiting processing may attain temperatures as high as 600 to 800°C as a result of fission-product decay heat, some nitridation of the skulls may occur. It was considered desirable to determine whether this possibility should be eliminated by oxidizing the skulls immediately after melt refining, or by storing them in containers that are either sealed or purged with high-purity argon.

Laboratory Experiments

Laboratory studies of skull nitridation rates have been reported in detail in a separate report.⁽¹⁰⁾ Between 300- and 500-g charges of uranium-fissium alloy, with 0.6 w/o cerium added to represent fission-product yttrium and rare earths, were melt-refined for two hours at 1350°C in two-inch-diameter zirconia crucibles. The resulting skulls were then nitrided at temperatures from 400 to 800°C and at nitrogen pressures of 8, 38, and 76 torr. In most of the runs, the small crucibles remained intact throughout the melt-refining and nitridation steps. In general, the thin portions of the skull were nitrided, forming a pyrophoric powder. A relatively massive button of unpoured metal was not attacked significantly. After nitridation, it was possible to pour the skull material, including the button, cleanly from the crucible.

Several compounds in the uranium-nitrogen system have been reported,⁽¹¹⁾ but only UN, U_2N_3 , and UN_2 can be considered stoichiometric. Single-phase regions in the phase diagram occur between U_2N_3 and UN_2 , and at nitrogen contents less than that corresponding to UN. The principal phase found in the skull nitridation studies was U_2N_3 .

The rate of the nitridation reaction increased with temperature and nitrogen pressure, except at low pressures. (At the lowest pressure used, 8 torr, the rate was greater at 700°C than at 600°C or 800°C.) The rate was appreciable at 500°C and 38 torr pressure, and at 600°C and 8 torr pressure. At 400°C and 76 torr, however, the rate was too slow to be measured with the apparatus used. At the higher temperatures and nitrogen pressures, the skull was completely nitrided in two to three hours.

The nitrided skull material was easily burned in air to form an oxide mixture suitable for subsequent liquid-metal processing. Typical screen analyses of the nitrided skull material after oxidation are listed in Table 5.

Table 5

SCREEN ANALYSES OF NITRIDED SKULLS AFTER SUBSEQUENT AIR OXIDATION

Skull weight: 20-40 g

Run No.	Nitridation Conditions		Screen Analyses of Product (w/o)				
	Temp (°C)	N ₂ Pressure (torr)	+60 mesh	-60, +100 mesh	-100, +200 mesh	-200, +325 mesh	-325 mesh
804 ^a	700	76	58.9	17.8	12.5	4.9	5.1
820	500	76	56.2	7.9	9.5	10.6	15.4
821	600	76	61.0	17.8	13.3	4.5	2.7
824	700	76	76.9	10.1	6.7	3.0	2.2
825	800	76	50.1	17.4	13.5	8.4	9.7
827	600	38	52.0	12.7	20.5	8.3	5.6
831	700	38	59.8	23.1	8.1	4.1	3.4

^a The uranium-fissium alloy used in this experiment had a zirconium content of 2.8 w/o; in all others, the zirconium content was 0.5 w/o.

Full-scale Experiments

Several full-scale nitridation experiments were performed, using skulls prepared in the melt-refining, mock-up facilities. In an exploratory run, a skull was maintained at 830°C for six hours in an argon atmosphere containing 25% nitrogen. About half the skull was converted to a black powder.

To provide material for further studies, a 1.65-kg charge of skull and uranium-fissium alloy was nitrided. The reaction was conducted for 13 hr at 850°C in an atmosphere of 50% nitrogen and 50% argon. The reaction was smooth, but somewhat slow in the later stages. Selected portions of the nitride product were then combined and oxidized for seven hours at 850°C. The consumption of oxygen was difficult to follow by pressure measurement, since approximately equivalent amounts of nitrogen were released in the reaction. However, it was possible to follow the reaction by observing the temperature rise and to evacuate the vessel and add fresh oxygen and argon as required. X-ray analyses of the product showed no uranium

nitrides, and the oxidized particles were markedly smaller than the original nitride, as shown by the screen analyses in Table 6.

Table 6

SCREEN ANALYSES OF NITRIDED SKULL AND OXIDIZED NITRIDE

Full-scale, melt-refining skulls

Mesh Size	Nitrided Skull (%)	Nitrided Material Charged to Oxidation (%)	Oxidized Material (%)
+14	9.7	~0	0
-14, +25	20.7	~0	0
-25, +45	21.1	~0	0.6
-45, +80	15.8	32.7	11.9
-80, +170	15.2	31.4	24.0
-170, +325	9.5	19.6	26.0
-325	7.8	16.2	37.7

G. Other Methods

A few other possible methods of skull removal, such as dissolution by molten salts and volatilization of uranium chlorides, were considered briefly. None seemed likely to fulfill the requirements of simplicity and feasibility, however, and no experimental work was done.

IV. EXPERIMENTAL INVESTIGATIONS OF THE TOTAL OXIDATION PROCEDURE

A. Small-scale Experiments

Preparation of Melt-refining Skulls

Although oxidation rates and ignition temperatures of uranium alloys in oxygen had been measured earlier by Schnizlein *et al.*,⁽¹²⁾ in connection with reactor safety investigations, it was considered desirable to augment these data with results obtained under conditions more nearly typical of the skull-oxidation process. These studies were carried out in several different types of apparatus. For small-scale laboratory experiments, melt-refining skulls weighing about 20 to 30 g were prepared in a manner as similar to the full-scale operation as possible. To simplify the experiments, minor fission products were omitted from the alloy, and cerium was substituted for the rare earths and yttrium. The quantity of cerium added (0.6 w/o) was equivalent to the total amount of rare earths and yttrium present in fuel irradiated to two total a/o burnup. The melt-refining crucibles were dry-pressed ZrO_2 , stabilized with 5 w/o CaO (Norton mixture Z300 SP). The crucible dimensions were: 2 in. OD, $1\frac{3}{8}$ in. ID, 4 in. outside height, and $3\frac{1}{2}$ in. deep.

To prepare the skulls, a uranium-fissium alloy ingot* (300 to 600 g), together with a freshly cut piece of the cerium metal corresponding to 0.6 w/o of the alloy, was placed in the crucible in an induction-heated furnace. The system was evacuated to less than 3×10^{-4} torr, and the charge was heated to 700°C for a degassing period of about 30 min. About 650 torr of purified helium was added to the furnace, and the temperature was raised to $1350 \pm 25^\circ\text{C}$ at an average heating rate of $30^\circ\text{C}/\text{min}$. Optical pyrometer measurements were corrected $+30^\circ\text{C}$ for emissivity of the molten metal and transmittance of the furnace window. The melt was held at 1350°C for two hours, then poured into a copper mold with the furnace power on. The ingot that had been cast from each run was used as a charge for the next run. The furnace was allowed to cool to room temperature before air was admitted.

Oxidation Apparatus

The apparatus used for the oxidations consisted of a gas-metering manifold and various resistance-heated furnace tubes (see Figure 3). The temperature of the crucible was measured by a central chromel-alumel thermocouple in a well extending within one in. of the bottom of the crucible.

*Alloy composition (w/o): Zr, 0.5; Mo, 2.5; Ru, 2.2; Pd, 0.6; balance, uranium.

Figure 3
APPARATUS FOR OXIDATION OF MELT-REFINING SKULLS

Before an experiment was started, the gas-metering tanks were evacuated and then filled with the required gases. The crucible containing the skull was placed in the furnace tube; then the tube was closed, evacuated (~ 0.1 torr), and heated to the desired temperature. Both static and flow experiments were conducted. For the static-atmosphere runs, a measured amount of the diluent gas (argon) was added to the furnace tube; then the oxygen was admitted. The partial pressure of oxygen was controlled manually, and the amount consumed was measured by manometers on the gas-metering tanks. For the flowing-atmosphere runs, the gases were premixed in the metering tanks, the furnace tube was evacuated, heated, and filled with argon, and the flow of oxidizing gas was started. The flow rate was measured with rotameters. The inlet and outlet gas compositions were determined with a standard Orsat gas analyzer. In some of the experiments, the inlet gas stream was directed within one in. of the bottom of the crucible to achieve a high reaction rate and a high gas velocity out of the crucible.

Most of the small crucibles were severely cracked by the oxidation procedure. The skull oxide was separated from the larger crucible fragments by hand. Crucible fragments were estimated to amount to 5 to 10% of the skull-oxide product.

Results of Skull-oxidation Experiments

The initial oxidation studies were made with undiluted oxygen. In one experiment, unalloyed uranium, which was burned in oxygen in a resistance-heated tube furnace, yielded U_3O_8 with the following particle size distribution:

<u>Mesh</u>	<u>w/o on Screen</u>
+60	14.0
-60, +100	15.7
-100, +200	29.5
-200, +325	17.0
-325	23.9

The following four experiments were conducted, in which uranium-fissium alloy skulls were oxidized in undiluted oxygen:

Run 1. The pressure was maintained at 75 torr for 135 min with the skull at 800°C. The pressure was then raised to 135 torr, and the oxidation was stopped after a total time of 165 min, although the reaction was still proceeding. The button of unpoured metal was incompletely oxidized, and the crucible was shattered.

Run 2. A uranium-fissium skull that contained cerium was oxidized at 700°C in 75 torr of oxygen. After 68 min, increasing the oxygen pressure to 490 torr caused a slight increase in the oxidation rate. The skull was completely oxidized, and the crucible was broken into several large pieces.

Run 3. Addition of oxygen to a skull initially at 800°C caused an excessive temperature rise, although the oxygen pressure was less than 5 torr. When the pressure was raised to 75 torr after 37 min, no large temperature increase was noted. The crucible was shattered, and the skull was fully oxidized. The product contained several large pieces of oxide.

Run 4. An attempt was made to use a 500°C temperature and 75-torr oxygen pressure. The skull ignited and melted the stainless steel thermocouple well, thereby admitting air to the system. The crucible was broken, and the skull had been attacked. The partially oxidized skull was not pulverized, but consisted of several large pieces.

Figure 4 shows the number of moles of oxygen consumed per equivalent of metal in the skull for Runs 1, 2, and 3, as a function of time. It was assumed that uranium formed U_3O_8 , and that the fissium metals formed their corresponding higher oxides (ZrO_2 , MoO_3 , RuO_2 , PdO , and CeO_2). It was further assumed that during the preparation of the skulls all of the oxide formed during melt refining resulted from reduction of the zirconia

crucible, and that the oxidation treatment reoxidized the depleted zirconia. This is equivalent to assuming that the skull consisted only of the metals that were not poured during melt refining.

Figure 4

SMALL-SCALE OXIDATION OF MELT-REFINING SKULLS

Oxidant: Undiluted Oxygen (pressure as indicated)

On the basis of these preliminary experiments, the use of undiluted oxygen was abandoned. The reaction was erratic and difficult to control. The skull tended to ignite, causing damage to the equipment, and the thermal shock produced extensive crucible degradation, which introduced excessive quantities of zirconia into the skull oxide.

The subsequent laboratory experiments used oxygen diluted with argon on the assumption that the reaction rate would be limited somewhat by diffusion, and that the presence of argon would aid in heat removal. Ten additional experiments were performed, using static or flowing atmospheres of diluted oxygen. The results are shown in Table 7. The argon effectively slowed the initial reaction, and the consequent decrease in thermal shock resulted in fewer crucible fragments in the skull-oxide

product. The weight of crucible fragments in Table 7 was calculated as the weight of the final product, less the weights of the original skull and the oxygen added.

Table 7

OXIDATION OF SKULLS WITH OXYGEN-ARGON MIXTURES

Skull Weight (g)	O ₂ Concentration in Ar (v/o)	Type of Atmosphere	Furnace Temp (°C)	Oxidation Time (min)	Weight of Crucible Fragments in Recovered Oxide (g)
25.4	33 ^a	static	500	180	1.2
17.6	33	static	700	45	0.0
32.8	33 ^a	static	700	270	1.3
19.3	26	flow	700	280	-
49.6	26	flow	700	325	8.1
24.1	29	flow	800	340	5.8
34.8	20 ^a	static	850	120	0.0
26.5	25 ^a	static	850	120	3.1
30.8	27 ^a	static	850	170	2.1
17.8	33	static	850	300	0.0

^aOxygen concentration lower at beginning of experiment.

The rates of oxygen consumption are compared in Figure 5. The ordinate in Figure 5 was based on the estimated number of equivalents of metal in the skull and the amount of oxygen consumed. The reaction layer between the crucible and the skull oxidized rapidly, forming the finely divided portions of the product. The button of unpoured metal oxidized more slowly and formed larger particles.

Figure 5

OXIDATION OF MELT-REFINING SKULLS WITH DILUTED OXYGEN

B. Full-scale Experiments

Numerous full-scale skulls weighing 300 to 1000 g were available as a result of melt-refining demonstrations with unirradiated uranium-fissium alloy in the EBR-II melt-refining mockup facility. Approximately 30 of these skulls were oxidized in a routine manner to provide skull oxides for studies of the steps in the subsequent skull-recovery process.

The apparatus used for the oxidations is shown in Figure 6. It consisted of a 40-liter, inductively-heated, vessel in which the skulls were oxidized at temperatures of about 700 to 900°C. The usual atmosphere was 25% oxygen and 75% argon, at a total pressure of 800 torr. The pressure was maintained by adding oxygen as the reaction proceeded. The oxidations proceeded smoothly, and the overall temperatures were controlled within the desired limits under these conditions.

Figure 6
FULL-SCALE SKULL-
OXIDATION FURNACE

Direct observations of the oxidation that were made through a viewing port indicated that the oxidation was not a uniform process. Local hot spots appeared and then faded after several minutes. Temperatures in these locations were estimated to have risen as high as 200°C above the furnace temperature. The dross on the side walls of the crucible reacted very rapidly. Within about 20 min, this dross collapsed and covered the more slowly oxidizing button and heavy dross on the bottom of the crucible. After 40 min, the visible surface material had darkened, with oxidation occurring beneath the oxide blanket.

To prevent excessive contamination of the oxide product by crucible fragments and losses of the product in crucible cracks, a stainless steel

jacket was used to restrain the zirconia crucible during the oxidation. After oxidation, the crucibles were generally broken into several pieces, particularly in the region where they had contacted the molten metal during melt refining. One experiment was conducted to determine if vertical, as well as horizontal, restraint was necessary. An oxidation with the crucible restrained only around the wall resulted in horizontal cracks in the crucible as large as $\frac{1}{4}$ in. which trapped oxide, increasing the loss of oxide by a factor of about three over the loss of about 12 g in a fully restrained crucible. It was concluded that restraint of the top and bottom, as well as the sides of the crucible, was advisable.

Oxidations were conducted both with skulls which contained cerium and skulls that did not. The presence of cerium appeared to cause the formation of more and finer crucible fragments during the oxidation, because of increased crucible degradation in the reaction zone.

In general, the full-scale skull oxidations were satisfactory, with about 97.5% recovery of skull oxide, which contained 1 to 2 w/o crucible fragments.

C. Oxidation Rates

It is of prime importance to prevent the initial reaction from becoming too rapid, and to avoid actual ignition of the skull. Large initial temperature excursions cause excessive crucible fragmentation, possible equipment damage, and off-gas problems. The initial reaction rate does not depend significantly on the superficial furnace temperature above 650°C, since the rapidly oxidizing particles reach a temperature well above that of their surroundings. In the experiments with undiluted oxygen, local hot spots lasting a few seconds appeared as brilliant white flashes, indicating temperatures above 1200°C. In extreme cases, some fusion of the oxide was noted. Temperatures below 600°C proved to be unsatisfactory, since the skull had a greater tendency to ignite violently. The use of argon as a diluent, however, prevented runaway ignitions. Nitrogen proved unsatisfactory as a diluent gas, because it greatly decreased the overall oxidation rate. A skull that had been exposed to air at 600 to 800°C subsequently reacted at a slow and erratic rate in undiluted oxygen.

Since the rate of skull oxidation varies considerably from skull to skull, a rigorous correlation of rate data is not practical. The general trends of the rates with the more important variables, however, are illustrated in Figures 7 through 10. These data were obtained from small-scale experiments in static atmospheres.

The initial reaction rate decreased as the percentage of oxygen and the partial pressure of oxygen were reduced (Figure 7). The time required to reach 50% completion of the reaction is shown as a function of gas

Figure 7
EFFECT OF OXYGEN DILUTION ON OXIDATION RATE
OF MELT-REFINING SKULLS AT 850°C

Temperature: 850°C
Weight of Skulls: 25-30 g

Figure 8
EFFECT OF GAS COMPOSITION AND PRESSURE ON
OXIDATION RATE OF MELT-REFINING SKULLS

Temperature: 850°C
Weight of Skulls: 25-30 g

Figure 9
EFFECT OF OXYGEN DILUTION ON OXIDATION
RATE OF MELT-REFINING SKULLS AT 700°C

Temperature: 700°C
Weight of Skulls: ~20 g

Figure 10
EFFECT OF SKULL WEIGHT ON OXIDATION
RATE OF MELT-REFINING SKULLS

Temperature: 700°C
Atmosphere: O₂ 200 torr
Ar 400 torr

composition in Figure 8. The overall rate was not greatly increased by using undiluted oxygen. After the initial period, the rate was not influenced greatly by temperature between 700 and 850°C. This is evident upon comparison of two runs in Figures 7 and 9, in which the oxygen partial pressure was 200 torr and that of argon, 600 torr. Above 850°C, the rate appeared to decrease. This decrease in the high-temperature oxidation rate of uranium-molybdenum alloys has been noted by other experimenters⁽¹³⁾ and is attributed to a fluxing action of MoO_3 . It is believed that during the oxidation of uranium the brittle oxide layer is greatly stressed and cracks when it reaches a critical thickness, thereby exposing new surface. The MoO_3 (mp, $\sim 800^\circ\text{C}$) tends to produce a more plastic oxide layer, which is more protective.

The total weight of the small-scale crucible skulls also influenced the reaction rate to a certain extent, the larger skulls oxidizing more slowly (see Figure 10). This effect was less pronounced with the full-scale skulls, probably because the button of unpoured metal is smaller, relative to the total skull weight.

No systematic study was made of the effect of high radiation levels on the skull-oxidation rate. A few observations were made, however, during the oxidation of skulls resulting from small-scale (400-g charge), melt-refining experiments with highly irradiated uranium-fissium alloy (~ 1 total a/o burnup).⁽¹⁴⁾ The crucibles were the same size as those used in the small-scale inactive experiments described previously, but the skulls were somewhat larger (100 to 200 g) as a result of low pouring yields during melt refining. The melt-refining crucibles containing the skulls were heated under vacuum to 700°C. Then air was slowly admitted to a final pressure of about 700 torr, care being taken to avoid temperature excursions. The time required for complete oxidation of the highly radioactive skulls was 6 to 8 hr, whereas the time required for the unirradiated skulls was 10 to 12 hr. In both cases, complete oxidation converted the skull to a free-flowing granular product that could be poured from the crucible. Partial oxidation, sufficient to free the irradiated skulls from the crucibles, required about 2 hr. Although the oxidation rate appears to be somewhat faster for highly irradiated skulls, the difference is not sufficiently large to cause difficulties in controlling the reaction.

D. Nature of the Oxide Product

Particle Size

The particle size of the product should be such that it is a free-flowing material which can be easily poured from the zirconia crucible in good yield. It should also be free of very fine material that would cause excessive dusting. The material must have a large enough surface area to react at satisfactory rates in the subsequent process steps, i.e., noble

metal extraction and oxide reduction. The rate of skull-oxide reduction by zinc-magnesium alloy has been found to increase as the particle size of the oxide decreases. In practice, the material produced in routine, full-scale, skull oxidation has proved satisfactory for subsequent reduction.

The full-scale oxidation experiments have undoubtedly given more significant particle-size distribution data for process purposes, but the small-scale experiments have provided some comparative data under relatively extreme conditions. Screen analyses for ten small-scale runs are listed in Table 8. The percentage of the skull that was oxidized was calculated from the total amount of oxygen consumed and the theoretical amount estimated from the overall skull composition and weight. In general, the small-scale runs tended to produce larger particles because of the proportionally larger metal buttons which form coarser particles during oxidation. When a stream of oxygen was directed onto the skull, local hot spots were formed with temperatures estimated to be well over 1200°C. These hot spots resulted in sintering and fusion of the product into large pieces, along with losses of oxide adhering tightly to the crucible. Very mild conditions (low temperatures and high argon dilution) produced a somewhat finer product, but they also resulted in poorer uranium recoveries.

Table 8

SCREEN ANALYSES OF SKULL OXIDE FROM SMALL-SCALE EXPERIMENTS

Furnace Temperature (°C)	Percent Oxidized ^b	Product Distribution (w/o)		Size Distribution of Oxide Powder (w/o)		
		Metal Button	Oxide Powder	+60 Mesh	-60, +325 Mesh	-325 Mesh
500	20	42.3	57.7	38.9	41.0	20.1
700 ^a	90	-	-	41.3	50.4	8.3
700	90	-	-	50.4	34.9	14.7
700	60	27.2	72.8	33.4	48.3	18.3
700	85	-	-	52.9	32.9	14.2
700	65	13.2	86.8	63.3	26.8	7.9
800 ^a	90	-	-	47.5	43.2	9.3
800	80	-	-	57.0	35.1	7.9
850	55	41.5	58.5	43.1	42.9	14.0
850	60	34.8	65.2	44.7	44.8	10.5
850	30	44.5	55.5	64.9	26.0	9.1
850	100	-	-	55.7	37.1	7.2

^aOxidized in pure oxygen, 75 torr.

^bOxidations were stopped when the oxygen consumption rate became too slow to follow. Percent oxidized calculated as equivalents of oxygen adsorbed, divided by estimated metal equivalents in skull.

Two full-scale, skull-oxidation runs with 600 torr of argon and 200 torr of oxygen pressure produced the particle distribution data shown in Figure 11. The first skull had been prepared by melt-refining a uranium-cerium alloy; the second was prepared by melt-refining a uranium-fissium alloy. Further oxidations of full-scale, melt-refining skulls showed

the major portion of the particles to be in a size range between about 100 and 1000 μ . Finally, 22 full-scale skulls prepared from cerium-uranium-fissium alloy were oxidized at about 750°C, in an atmosphere of 25% oxygen and 75% argon, at 800 torr total pressure. The success of these oxidations led to considerable confidence in the operation as a practical process step that could be adapted to remote operation. Screen-analysis data on the product are shown in Table 9.

Figure 11

OXIDATION OF URANIUM-CERIUM AND URANIUM-FISSIUM SKULLS

	U-Ce Skull	U-Fs Skull
Nominal Oxidation Temp. (°C)	850	775
Hot-Spot Temperatures (°C)	875-950	875
Oxidation Time		
Reaction Appeared Complete (hr)	6	6
Total Exposure (hr)	8	10
Total Product (g)	942	716
Crucible Fragment Inclusions (w/o)	<2	~5
Uranium Recovery (%)	99.4 ^a	99.6 ^a
Uranium Loss (g)	4	2.1

^aThese values were determined by acid leaching the waste crucible. This procedure is now known to recover only about half the total uranium (see Section IV G).

To assess the amount of dusting resulting from fine particles during skull oxidation, a particle-size distribution measurement of a blend of skull oxides from 13 oxidations was extended into the subsieve range. The results are shown in Figure 12. Less than 1% of the particles were smaller than 10 μ , and the smallest particle size observed was 1 μ .

Table 9

PARTICLE-SIZE DISTRIBUTION OF COMPOSITE
SKULL OXIDE FROM 22 FULL-SCALE
SKULL OXIDATIONS

Conditions Temperature: 750°C
 Atmosphere: 25 v/o O₂, 75 v/o Ar,
 total pressure 800 torr

<u>Mesh Size</u>	<u>Amount in Fraction (w/o)</u>
+14	0.6
-14, +25	10.5
-25, +45	21.6
-45, +80	18.7
-80, +170	15.3
-170, +325	14.6
-325	18.6

Figure 12
 PARTICLE SIZE DISTRI-
 BUTION OF URANIUM-
 FISSION SKULL OXIDE

The presence of molybdenum in the skull influenced the product particle size. High molybdenum alloys gave a coarse product, probably as a result of the sintering action of MoO₃, which is liquid at the skull-oxidation temperatures.

Some additional particle-size reduction can be accomplished by alternate hydrogen reduction and reoxidation. This reaction appears to be less effective with fission alloy than with pure uranium, however, and it is not considered desirable because of the water vapor formed as a product.

Chemical Composition

Although the stable uranium oxide at temperatures below 1000°C under oxidizing conditions is U_3O_8 , oxides with compositions between UO_2 and U_3O_8 have been found by X-ray diffraction analyses of oxidized skulls. Upon further oxidation it should be possible to convert this material to U_3O_8 . Fission alloys appear to be more oxidation-resistant than unalloyed uranium. Lower uranium oxides may also be stabilized by the presence of fission-product oxides. For example, uranium and cerium zirconates have been tentatively identified by X-ray diffraction analyses of skull oxides.

The fission-product elements were distributed preferentially in various particle-size fractions, as shown by the results of the full-scale skull oxidations listed in Table 10. Cerium tends to concentrate in the fine fractions, which are formed mainly by oxidation of the reaction layer between the crucible and the skull. The ruthenium, and to a lesser extent, the molybdenum, appear to a greater degree in the coarse fractions. The uranium, being the major constituent, was distributed relatively evenly among the different particle-size fractions. The uranium content of the skull oxide, calculated as uranium metal, was about 74%.

Table 10

DISTRIBUTION OF FISSION-PRODUCT ELEMENTS IN SKULL-OXIDE SCREEN FRACTIONS

Based on composite material from
22 full-scale skull oxidations at 750°C,
25 v/o O_2 in Ar, 800 torr total pressure.

Mesh Size	Analysis (w/o)					Percent of Total Oxide
	U	Ce	Mo	Ru	Zr	
+14	74.6	0.35	0.97	1.44	2	0.6
-14, +25	72.0	1.18	2.00	1.35	4	10.5
-25, +45	75.6	0.94	1.95	1.40	2	21.6
-45, +80	74.0	1.40	1.71	1.37	1	18.7
-80, +170	74.4	1.42	1.38	1.06	1	15.3
-170, +325	74.7	1.87	0.99	0.60	1	14.6
-325	74.1	2.60	0.86	0.32	1	18.6
Average	74	1.56	1.47	1.02	~2	

Some zirconia is introduced into an oxidized skull as a result of deterioration of the crucible in the melt-refining reaction zone and at any cracks. The total zirconium content generally varied between 1 and 2 w/o in the skull oxide from the full-scale oxidation runs, whereas the amount

of zirconium added as a fissium constituent was only 0.07 w/o. Less than about 1% zirconium in oxidized skulls probably cannot be expected from the introduction of crucible fragments. This minimum amount probably comes from the reaction zone. The total amount of zirconia will vary depending upon the condition of the crucibles, because a badly cracked crucible will introduce more zirconia than an uncracked one. The zirconia crucibles currently used at the EBR-II Fuel Cycle Facility have proved to be considerably better than those used in many of the earlier melt-refining skull-oxidation tests. Therefore, since no adverse effects of irradiation were noted on small zirconia crucibles after melt-refining and skull-oxidation runs on fuel irradiated to from 0.2 to 1.8 a/o burnup,⁽¹⁴⁾ the crucible fragment content of the skull oxide will probably be closer to 1 w/o than 2 w/o at the EBR-II plant.

E. Volatilization of Fission Products

Because krypton and xenon are removed by melt refining, they are not present in significant amounts in the oxidized skull material. Iodine and cesium are also largely removed in melt refining, but significant amounts of these elements may condense on the upper wall of the crucible, which does not reach the melt-refining temperature of 1400°C. Other fission-product elements that are not separated by melt refining and might be expected to volatilize through the formation of volatile oxides include molybdenum, ruthenium, technetium, and tellurium, and possibly rhodium and palladium.

The studies were conducted with a two-fold objective: (1) to establish whether significant fission-product decontamination could be achieved through the volatilization of certain elements to simplify the separations required in subsequent process steps, and (2) to determine the requirements for handling volatilized fission products in the skull-oxidation equipment.

Iodine. A rough estimate has indicated that as much as several hundred Curies of I^{131} activity may be present in the full-scale crucible and skull when highly irradiated fuel is melt-refined under plant conditions. Since this activity is very likely present as iodides, its conversion to volatile, elemental iodine during oxidation of the skull would be expected. In a very small-scale (~7-g charge), melt-refining and skull-oxidation experiment, using highly irradiated uranium-fissium alloy, about 0.25% of the original iodine in the melt-refining charge remained in the skull and crucible after oxidation.⁽¹⁵⁾ This percentage would correspond to about 10 Curies in the plant operation, and these results suggest that most of the iodine present in the skull after melt refining will be volatilized during the skull oxidation.

Iodine tracer studies were also performed in which approximately 400-g charges of lightly irradiated uranium-fissium alloy were melt-refined and the resulting skulls were oxidized. Although reliable data were not obtained at the tracer levels involved, it was evident that significant amounts of iodine activity were released during the skull oxidation. No activities, other than iodine, were detected in the off-gases. A Fiberfrax plug proved to be relatively effective in trapping the iodine activity. Activated charcoal is considered to be a more suitable trapping material for plant use, however, as it is known to have high efficiency and capacity for elemental iodine. If a charcoal trap is used, the possible hazard of passing residual oxygen from the skull-oxidation furnace through the trap must be avoided.

Ruthenium. Ruthenium forms volatile RuO_4 under certain conditions. Although this compound is reported⁽¹⁶⁾ to be stable in oxygen at 300 to 500°C, little reliable information is available on its chemical properties. Ruthenium has also been reported⁽¹⁷⁾ to be volatilized during oxidation of the metal above 1000°C.

In three preliminary experiments, skulls were prepared by melt-refining uranium-fissium-cerium alloy spiked with Ru^{103} tracer. The 0.50-MeV gamma activity was counted with a single-channel analyzer after determining the specific activity by means of chemical analysis and counting procedures. The three skulls were oxidized in a flowing argon-oxygen atmosphere. The ruthenium behavior is shown in Table 11. The

Table 11

OXIDATION OF SKULLS CONTAINING TRACER RUTHENIUM

	Run Number								
	1			2			3		
Oxidation temperature (°C)	700			800			800		
Atmosphere	Flowing O ₂ -Ar			Flowing O ₂ -Ar			Flowing O ₂ -Ar		
Inlet O ₂ concentration (v/o)	26.3			29.2			8		
Length of oxidation (min)	330			325			260		
Weight of skull (g)	49.6			24.1			22.8		
Weight of cerium (g)	3.1			2.8			2.3		
Subsequent treatment	None			H ₂ reduction, O ₂ oxidation			Oxidation in undiluted oxygen for 90 min		
	<u>Ruthenium Balances</u>								
Total Ru in skull (g) ^a	0.925			0.384			0.388		
	<u>Ru in Oxidized Skull Fractions</u>								
	Fraction Weight (g)	Ru Content (w/o)	Weight of Ru (g)	Fraction Weight (g)	Ru Content (w/o)	Weight of Ru (g)	Fraction Weight (g)	Ru Content (w/o)	Weight of Ru (g)
Screen fraction of oxide powder									
+60 mesh	35.09	1.43	0.503	18.54	1.53	0.285	20.46	1.60	0.329
-60, +100 mesh	7.05	1.22	0.086	4.95	1.12	0.055			
-100, +200 mesh	4.60	1.23	0.056	4.29	1.16	0.049	6.29	0.86	0.054
-200, +325 mesh	2.75	0.80	0.022	2.18	1.24	0.027			
-325 mesh	4.24	0.52	0.022	2.59	1.03	0.027	1.31	0.48	0.006
Unoxidized button	8.23	2.18	0.180	-	-	-	-	-	-
Crucible			0.025	-	-	-	-	-	-
Total Ru recovered			0.894			0.443			0.389
% Ru recovered			96.7			115			100

^aMethod of estimating composition of skull described in appendix.

observed ruthenium recoveries were 96.7, 115, and 100%, which probably corresponded to actual values close to 100%. (The method used to estimate the noble metal content of the small-scale crucible skulls is described in the appendix.)

During the first two experiments, the furnace tube was lined with a thin steel sheet, which was subsequently sectioned and counted for Ru^{103} activity. No activity was found on the steel sheet or in the off-gas system. The skull oxide resulting from Run 3 (Table 13) was transferred to an alumina crucible, where it was reduced with hydrogen at 700°C and then reoxidized at 850 to 930°C in pure oxygen, which was directed into the crucible at a flow velocity of 2 ft/min. After this treatment, some activity was found on the hot portions of the furnace tube. Finally, this oxide was reduced with hydrogen at 500°C , reoxidized at 600°C , then exposed to pure oxygen flowing at 5 ft/min for $3\frac{1}{2}$ hr at 930°C . A larger amount of ruthenium had deposited on the furnace, and significant amounts were found in the cool portions. The total ruthenium removed from the skull in Run 3 in the three oxidation cycles was less than 5%.

To investigate further the behavior of ruthenium, small samples of uranium-fissium metal or skull, spiked with Ru^{103} tracer, were oxidized in Vycor tubes. The sample weights were about 0.6 g. A fixed pressure of argon was added to the tube, the sample was brought to temperature, and oxygen was admitted. The results are shown in Table 12. In only one experiment (the first at 950°C) was a significant amount of ruthenium volatilized. In this run, most of the volatilized activity deposited at the end of the heated zone.

Table 12

SMALL-SCALE OXIDATIONS OF METAL AND SKULL
SAMPLES CONTAINING TRACER RUTHENIUM

Sample Type	Sample Weight (g)	Ru Content (g)	Oxidation Conditions			Percent of Ru Remaining in Oxidized Material
			Temp ($^\circ\text{C}$)	Time (hr)	Ar Pressure (torr)	
Metal	0.620	0.0110	800	1	200	99 ^a
Metal	0.713	0.0125	800	3	200	100 ^a
Metal	0.755	0.0129	800	24	200	100
Skull	0.657	0.0093	800	1	200	98 ^a
Skull	0.550	0.0077	800	3	200	106 ^a
Skull	0.565	0.0074	800	24	200	110
Metal	0.762	0.0130	950	1	5	80 ^a
Metal	0.762	0.0128	950	3	5	105
Metal	0.574	0.0100	950	24	5	100
Skull	0.460	0.00344	950	1	5	110
Skull	0.455	0.00398	950	3	5	95
Skull	0.458	0.00346	950	24	5	94

^aIncomplete oxidation

A few additional runs using small metal and skull samples were made, using both static and flowing atmospheres. In six runs in a static system at 900°C, metal and skull samples were oxidized for two hours (1 atm O₂), reduced for two hours (1 atm H₂), and then reoxidized for two hours (1 atm O₂). No ruthenium volatilization was detected in any of the runs.

Since RuO₄ may be stable at lower temperatures (300 to 500°C), a few experiments were performed under these conditions. Small skull samples were oxidized in a static system at 750°C, reduced at 750°C, reoxidized at 900°C, reduced again at 650°C, and then reoxidized at 800°C. Each treatment lasted two hours and used one atm of oxygen or hydrogen. With the Vycor tubes filled with oxygen, the temperature was lowered gradually to 100°C, samples of oxide being removed at 400, 300, 200, and 100°C. No ruthenium was removed during the oxidation of any of the samples.

To determine the volatilization of ruthenium at higher temperatures in static atmospheres, three samples of ruthenium powder and three of skull were oxidized, reduced, and reoxidized. The oxidation (one atm O₂) was then continued for five hours at 1200°C. In all cases, the recoveries of nonvolatile ruthenium exceeded 95%. Some tracer activity was found in the cold portions of the tubes, but in no case did it exceed 3% of the original activity. The weight gains of the metal samples indicated that oxidation to RuO₂ was about 75% complete.

Three additional experiments were performed in which a flowing oxygen atmosphere passed over the samples in a porcelain boat at a gas velocity of 4 ft/sec. In the first run, oxygen passed over the samples (one of skull, and one of ruthenium metal) at 930°C resulted in ignition of the skull sample, accompanied by a brilliant white flash. After four hours, over 90% of the ruthenium was removed from the skull sample, but none was removed from the metal sample. The tracer activity was evenly spread over the cooler portions of the tube. In the second run, a 20% oxygen-80% argon mixture was passed over a skull sample under the same conditions used in the first run. No flash was seen when the oxygen flow started. After one hour, the atmosphere was changed to undiluted oxygen. About 75% of the ruthenium was volatilized. In the third run, two skull samples were accidentally ignited at ~300°C. When oxygen at 800°C was passed over the samples, a glass wool plug downstream showed the presence of ruthenium tracer. The ruthenium removal was about 35%.

Although ruthenium can be volatilized by oxidation under very severe conditions (high oxygen concentrations, flowing atmosphere, and high temperatures), apparently no appreciable fission-product ruthenium will be volatilized under the normal conditions of skull oxidation. This conclusion has been supported by various other skull-oxidation studies with inactive and irradiated material.

Molybdenum. Molybdenum trioxide (mp, 795°C; bp, 1264°C)⁽¹⁸⁾ is a volatile compound under the conditions of skull oxidation. In several of the experiments with ruthenium described in the previous section, characteristic yellowish-colored, sometimes crystalline, deposits of volatilized MoO_3 were observed in the cooler portions of the apparatus. The results of several of the small-scale experiments described earlier are summarized in Figure 13.

Figure 13
MOLYBDENUM REMOVAL RESULTING
FROM OXIDATIONS OF URANIUM-
FISSIUM METAL AND MELT-
REFINING SKULLS

108-4163

cerium in the skull, as indicated by the following results. Two skulls were prepared from uranium-fissium alloy in zirconia crucibles. Only one contained cerium (0.6 w/o in the alloy). The skulls were oxidized in a 3-in.-diameter Vycor furnace tube, which was evacuated, brought to temperature, and then filled with argon (1 atm). A flowing stream of oxygen was directed within one inch of the bottom of the crucible. Finally, the temperature was raised to 940°C, and the tube was evacuated. During the first hour of oxidation, brilliant flashes were observed. At higher gas velocities (~800 cm³/min, STP), a dense smoke was evolved from the cerium-free skull, but none from the cerium-containing skull. The smoke collected as a light yellow powder, which was identified by X-ray diffraction as MoO_3 . In both experiments, about 80% of the molybdenum was removed from the skull; but with the skull containing cerium, no MoO_3 condensed on the furnace

characteristic yellowish-colored, sometimes crystalline, deposits of volatilized MoO_3 were observed in the cooler portions of the apparatus. The results of several of the small-scale experiments described earlier are summarized in Figure 13. To achieve molybdenum removals in excess of 50%, nearly complete oxidation of the skull proved necessary, and evacuation to one torr above 900°C after oxidation was required. A flowing atmosphere was more effective than a static one.

In an experiment with a 30-gram, uranium-fissium skull, oxidation, reduction, and reoxidation twice under conditions which, in the smaller-scale experiments, would have removed over 70% of the molybdenum, resulted in only 25% removal. Although it was first suspected that incomplete oxidation of the skull in the larger-scale experiments accounted for the lower molybdenum removals, it was found subsequently that MoO_3 volatilization was inhibited by the presence of

walls until a vacuum had been applied to the furnace tube. In both cases, black deposits of RuO_2 were observed in the off-gas line, indicating that significant quantities of ruthenium had been evolved from the skulls under these severe oxidizing conditions.

Since cerium and other rare-earth fission products will be present in irradiated fuel, and because the volatilization of MoO_3 is slight even in the absence of cerium, volatilization of molybdenum in the skull-oxidation step is expected to be negligible. This result has also been borne out in other skull-oxidation studies with inactive and irradiated materials.

Technetium. Technetium forms a nonvolatile dioxide, TcO_2 , and a volatile heptoxide, Tc_2O_7 (mp, 119.5°C ; bp, 311°C).⁽¹⁹⁾ To investigate the behavior of technetium during skull oxidation, approximately 100 mg of the metal was prepared from a solution of NH_4TcO_4 by the method of Cobble et al.⁽²⁰⁾ This metal was melted with a 50-g slice of uranium-fissium alloy in a beryllia crucible to prepare an alloy which had the following composition (w/o): Zr, 0.30; Mo, 3.22; Tc, 0.19; Ru, 2.10; Pd, 0.60; balance, U.

One-gram samples of this alloy in a porcelain boat were placed in a one-inch-diameter, quartz, furnace tube which was connected to the gas manifold. To prevent the metal from igniting, the sample was brought to temperature under an argon atmosphere; then a stream of oxygen diluted with argon was passed through the furnace tube for 20 to 30 min. After this initial period, during which the sample was almost completely oxidized, pure oxygen was passed through the furnace tube. The variables investigated were: initial oxygen concentration (10 to 50 v/o), furnace temperature (650 to 870°C), gas-flow rate (static to $100\text{ cm}^3/\text{min}$ STP), total time of oxidation, and extent of oxidation. The percentage of oxidation was defined as the percent-weight gain of the oxidized sample (corrected for any volatilized components), divided by 19.1, which was the calculated percent-weight gain for this alloy upon complete oxidation.

The extent of oxidation and the duration of the experiment had the largest effect on the amount of the technetium volatilized, as shown by Figure 14. Changes in the furnace temperature had a slight effect, but the initial oxygen concentration and the gas-flow rate appeared to have little or no effect. With a static oxygen-argon atmosphere, the fraction of technetium volatilized was somewhat less than in a flowing atmosphere, but the results were erratic, since it was difficult to oxidize a sample completely in a static system. A large proportion of the technetium was volatilized when the furnace temperature was raised to 950°C and a vacuum was applied to the oxidized sample.

Figure 14
TECHNETIUM RETENTION IN URANIUM-
FISSIUM SKULL OXIDE

The behavior of technetium during the oxidation of uranium-fission alloy was what might be expected of a metal that forms a nonvolatile lower oxide and a higher volatile oxide. The relatively larger amounts of technetium volatilized while the uranium alloy was undergoing oxidation probably resulted from the sample temperature being higher than that of the furnace because of the heat of reaction. From the results obtained with one-gram metal samples containing no rare earths, it is difficult to predict the behavior of technetium during the oxidation of full-scale skulls. Because cerium inhibits the volatilization of molybdenum from skulls, rare earths might be expected to decrease the amount of technetium volatilized. Also, it was generally found that ruthenium and molybdenum were more easily volatilized from small samples than from a whole melt-refining skull. Therefore it was concluded that only small quantities of technetium would be volatilized during skull oxidation (probably less than 10%) if the oxygen is diluted with argon, the furnace temperature is kept below 850°C, and a vacuum is not applied to the oxidized skull until it has cooled.

Tellurium. Tellurium was not volatilized during the oxidation of skulls under anticipated process conditions. A 60-g, uranium-fission skull, containing 0.6 w/o cerium and about 0.06 w/o tracer tellurium, was oxidized in a static oxygen-argon atmosphere at 725°C. The tellurium remained in the oxidized material, and no evidence of any activity was found outside the crucible. The lack of tellurium volatilization is believed to have resulted from the formation of stable, nonvolatile tellurates with cerium.(21)

These results indicate that there is great difficulty in volatilizing major fission products, other than iodine, during the skull-oxidation

procedure. Therefore, skull oxidation cannot be regarded as a fission-product removal step for elements other than iodine, and it appears that special provisions for handling other volatilized fission products will not be required.

F. Oxidation of Massive Uranium-Fissium Alloy

A possibility exists that massive uranium-fissium alloy may on occasion require nonroutine handling at various points in the EBR-II Fuel Cycle. For example, molten metal spills, unpourable ingots, certain types of scrap, and other materials may not be suitable for direct introduction into the melt-refining process. In this event, these materials may be suitable for oxidation and processing via the skull reclamation procedure.

To examine the feasibility of this possibility, a 360-g melt of uranium-fissium alloy was prepared in a small zirconia crucible (inside

dimensions $3\frac{1}{2}$ in. deep, by $1\frac{1}{4}$ in. diameter). The oxidation was conducted at 750°C in a stainless steel vessel to which oxygen was added as it was consumed by the reaction. During the initial 7.5-hr period, 100 to 200 torr of oxygen was diluted with 200 torr of helium. Undiluted oxygen was then added, as indicated in Figure 15. The approximate oxidation rates after the initial period at 750°C are shown in Table 13. Preliminary examination after 7.5 hr indicated that oxidation was occurring only at the exposed metal surface. After 56 hr, the experiment was terminated, although the reaction was still proceeding. During the oxidation, the crucible was restrained by a 20-mil stainless steel jacket. The oxide did not expand upward as

Figure 15

OXIDATION OF MASSIVE URANIUM-FISSIUM INGOT (Expt. 1)

expected, but outward, breaking the crucible and wedging it and the jacket into the furnace tube. Most of the oxide was removed as a friable single piece along with an 18-g piece of metal.

In a second experiment, a 370-g ingot of uranium-7.5 w/o fissium was prepared in a small zirconia crucible. The unrestrained crucible was supported upside down over an alumina crucible, where it was oxidized at

750°C in undiluted oxygen. The progress of the oxidation is indicated in Figure 16. The run was terminated after 24 hr, but the reaction was complete after nine hours. The zirconia crucible had been split by the expanding oxide, and little or no material had fallen into the alumina crucible. The oxidation rate was considerably higher than in the first experiment, as indicated in Table 13.

Table 13

OXIDATION OF MASSIVE URANIUM-FISSIUM ALLOY

Sample: Approximately 360 g of uranium-fissium alloy prepared in a two-in. OD zirconia crucible.

Temperature: 750°C

Oxygen Pressure (torr)	Oxidation Rate (moles O ₂ /hr)	
	Experiment 1: Crucible Restrained by Stainless Steel Jacket	Experiment 2: Crucible Unrestrained, Inverted
100	0.018	-
200	0.031	0.12
300	-	0.27
500	0.13	-
700	-	0.60

Figure 16
OXIDATION OF MASSIVE
URANIUM-FISSIUM INGOT
(Expt. 2)

Massive metal apparently can be oxidized successfully for introduction into the skull-reclamation process, provided the appropriate measures are taken to handle the expanding oxide.

G. EBR-II Skull-oxidation Equipment

In view of the oxidation experiments already discussed, remotely operable skull-oxidation equipment for use with irradiated EBR-II fuel was developed. Prototype equipment was built and tested. The designs were revised slightly, and the equipment for use in the EBR-II Fuel Cycle Facility has been completed and tested and will be installed later in 1964.

The plant equipment employs oxygen feed control to regulate the rate of oxidation. The gas-control system feeds oxygen to the furnace in such a manner that a nearly constant rate of oxidation is maintained. After a skull has been heated under argon, some argon is removed and oxygen is introduced to initiate the reaction. As the run progresses, the oxygen composition of the furnace gas is increased to a final level of about 75 v/o. An oxidation rate of about 2 g of uranium per min is maintained. The effluent gas from each run will be accumulated in a small tank for disposal through the plant stack when atmospheric conditions permit. These gases are expected to contain little radioactivity but will contain a certain amount of excess oxygen and probably some nitrogen.

The oxidation furnace is a small vessel which is heated by radiation from a resistance heater suspended over the skull. The furnace to be installed at the EBR-II plant is illustrated in Figure 17. A freeze seal is provided between the lid-heater and the bottom of the furnace to permit opening of the furnace for charging and unloading of skulls.

Figure 17

EBR-II PLANT EQUIPMENT FOR SKULL OXIDATION

108-7080

crucibles as a result of improved fabrication technology. Other possible factors may be the use of an internal heater instead of a heated furnace wall, and a somewhat lower crucible temperature.

illustrated in Figure 17. A freeze seal is provided between the lid-heater and the bottom of the furnace to permit opening of the furnace for charging and unloading of skulls. If a heater fails, the entire lid would be replaced. The zirconia crucibles containing the melt-refining skulls will be supported in a stainless steel can during the handling and oxidizing operations. This can does not provide the circumferential and vertical support that was found to be helpful in earlier experiments. Such support appears unnecessary in the light of the latest series of full-scale oxidation runs in which the crucibles cracked but did not come apart. A major reason for this better performance is probably the higher quality of the newer zirconia cru-

After an oxidation, the crucible is removed with the steel jacket to a dumping apparatus. Figure 18 shows a crucible and jacket in place in the dumper, with a receiver for the oxide being placed in position over the crucible by a manipulator. The three-gallon can below the dumper is for disposal of the empty crucible after the oxide is removed through the side opening.

Figure 18

EBR-II PLANT EQUIPMENT
FOR DUMPING SKULL
OXIDE FROM A MELT-
REFINING CRUCIBLE

108-6611

In the development of the prototype equipment and testing of the plant equipment, several skulls were oxidized and dumped. The waste melt-refining crucibles from these tests were processed to evaluate the efficiency of uranium removal. A jaw crusher and ball mill were used to pulverize the crucible to facilitate sampling. Acid leaching of the samples did not extract all the uranium, but a fusion-dissolution procedure using a small (0.2-g) sample was satisfactory. The technique which proved most useful for analysis was direct X-ray fluorimetric analyses of pulverized samples. Results have been obtained by X-ray fluorescence, and spot checked by the fusion-dissolution procedure for the crucibles from eight runs. These results are presented in Table 14. Runs SOF 26 through 35 were made in the prototype equipment, and the others were done in the plant furnace. The observed loss of about 0.2% of the original melt-refining charge is acceptable for this process.

The oxidized skulls from the last six runs in Table 14 were analyzed to determine the extent of crucible fragment inclusion. The resultant zirconium ranged from 0.4 to 3.2 w/o of the skull and averaged 1.2%.

Table 14

URANIUM LOSS IN MELT-REFINING CRUCIBLES AFTER REMOVAL OF SKULL BY OXIDATION

Skull Oxidation Run No.	Weight of Original Melt-refining Charge (g)	Composition of Original Melt-refining Charge	Weight of Unoxidized Skull (g)	Uranium Loss in Waste Zirconia Crucible		
				(g)	Percent of Uranium in Skull	Percent of Uranium in Melt- refining Charge
SOF 26	8,361	U-5% fissium- 0.7% cerium	619	18	3.5	0.2
SOF 29	8,252	U-5% fissium- 0.7% cerium	510	11	2.5	0.14
SOF 30	8,888	U-1.3% fissium	634	12	2	0.14
SOF 31	9,675	U-5% fissium	834	9	1.2	0.10
SOF 32	9,532	Uranium	562	20	3.5	0.2
SOF 33	8,552	U-5% fissium	246	8	3.5	0.10
SOF 34	10,288	U-5% fissium	195	5	3	0.05
SOF 35	8,334	U-2.5% fissium	318	6	2	0.07
SOF 36	9,689	U-1.7% fissium- 0.61% cerium	642	16.0	2.8	0.17
SOF 37	9,271	U-1.7% fissium- 0.67% cerium	554	9.1	1.9	0.10
SOF 38	9,188	U-1.3% fissium- 0.67% cerium	902	22	2.7	0.25
SOF 40	7,451	U-1.3% fissium- 0.72% cerium	592	8.5	1.6	0.12
SOF 41	9,476	U-1.3% fissium- 0.66% cerium	741	9.0	1.4	0.10
SOF 42	9,693	U-1.6% fissium- 0.62% cerium	840	34	4.4	0.37

V. CONCLUSIONS

Complete oxidation of melt-refining crucible skulls is a satisfactory method for converting the material to a form that is amenable to subsequent processing. Suitable conditions are a temperature of 700 to 800°C and 20 v/o oxygen diluted with argon at a total pressure of about one atm. The material is converted to a relatively coarse, free-flowing powder which is easily poured from the crucible and does not appear to dust excessively. The only significant fission product volatilized is iodine.

It appears that oxidation procedures are also suitable for converting massive uranium-fissium alloy, as well as nitrides and carbides, to an oxide product that is suitable for further processing.

Appendix

CALCULATION OF SKULL COMPOSITIONS

The overall composition of different melt-refining skulls can vary widely, depending on the amount of uranium oxidized by reaction with the crucible, and the amounts of metal occluded in the dross and metal in the unpoured button. Because of sampling difficulties, the composition of the dross could not be determined reliably by chemical analysis. In the preparation of small-scale skulls for the study of noble-metal oxide volatilization, a standard set of melt-refining conditions was used so that a single correlation could be used to compute the composition of the skulls from readily measurable quantities. It was not determined whether the same correlation would be applicable to other melt-refining conditions. It is discussed here, since the procedure was used to evaluate the behavior of ruthenium and molybdenum during the oxidation of skulls.

The components of a melt-refining skull are defined for this discussion as

- F = weight of initial charge to melt-refining crucible,
- I = weight of poured ingot after melt refining,
- B = weight of unpoured metal (has the same composition as the poured ingot),
- D = weight of dross (consists of the reaction layer between the melt and the crucible, and occluded metal),
- z = concentration in weight percent (subscript refers to component stream).

The oxygen transferred from the crucible to the dross during melt refining is excluded in this discussion. To prepare the small-scale crucible skulls for the oxidation studies, cerium was added to the poured ingot from one melt to form the charge to the next melt. It was found that as a single alloy was remelted several times, the concentration of the noble metals, ruthenium, molybdenum, and palladium, gradually increased, but the concentration of zirconium remained constant.

Figure 19 shows the increase in the relative noble-metal concentration and the constant zirconium content for two fissium alloys as the alloys were melt-refined several times under constant conditions. Samples from the poured ingots were analyzed by methods having an accuracy of $\pm 3\%$. If it is assumed that the increase in the noble metal concentration is a constant percentage of the charge concentration, the data should fit the equation

$$\frac{z_I^{(n)}}{z_I^{(0)}} = (1 + a)^n, \quad (1)$$

where $z_I(n)$ is the noble-metal concentration in the ingot after the n th pour, and $z_I(0)$ is the concentration in the original ingot. The best fit to the data is given where the parameter $a = 0.009$, or

$$\frac{z_I(n-1)}{z_I(n)} = 0.991. \quad (2)$$

Since 0.60 w/o cerium was added to the poured ingot of one run to form the charge to the next run,

$$\frac{z_F(n)}{z_I(n-1)} = \frac{1.000}{1.006},$$

and

$$\frac{z_F(n)}{z_I(n)} = \frac{z_I(n-1)}{z_I(n)} \times \frac{z_F(n)}{z_I(n-1)}.$$

Then,

$$\frac{z_F(n)}{z_I(n)} = \frac{0.991}{1.006} = 0.985. \quad (3)$$

Substituting Equation (3) in the noble-metal material balance, which is

$$Fz_F = Iz_I + Bz_B + Dz_D, \quad (4)$$

rearranging, and recalling that $z_I = z_B$, the material balance becomes

$$z_D = \frac{[0.985F - (I+B)]z_I}{D}. \quad (5)$$

Figure 19

INCREASE OF CONCENTRATION
OF MOLYBDENUM, RUTHENIUM
AND PALLADIUM IN URANIUM-
FISSIUM ALLOYS UPON RE-
PEATED MELT REFINING

The dross weight, D , is found from a relation obtained between the dross weight and the melt weight, F , shown in Figure 20. The relation was obtained during a series of experiments in which the skulls were nitrated.⁽¹⁰⁾ This treatment effectively separated the button from the dross and the crucible. The button which reacted only superficially with nitrogen could be recovered and weighed; then the dross weight could be calculated by difference. Since the skulls to be oxidized were prepared under the same conditions as were the skulls to be nitrated, the same relationship between dross and melt weights was assumed to hold. The weight of the button could not be adequately correlated since it depended on the effectiveness of the pour, which was difficult to control.

Figure 20
WEIGHTS OF MELT
REFINING DROSSES

Substituting the relation between dross and melt weight into Equation (5), and noting that $I + B = F - D = -0.966F$, and $D = 0.034F$ (see Figure 20),

$$z_D = \left(\frac{(0.985 - 0.966)F}{0.034F} \right) z_I, \quad \text{or} \quad z_D = 0.56z_I. \quad (6)$$

Wherever analyses were taken, an average of 3% of the cerium charged to melt refining appeared in the poured ingot. It was thus assumed that the dross contained 97% of the cerium charged. The balance of the dross was assumed to be uranium and zirconium. This method of calculation is different from the cruder calculation used to estimate the number of metal equivalents to correlate the reaction rate. For the latter calculation, it was assumed that the skull contained all the cerium charged, and the remainder of the skull had the same composition as the melt.

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