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CHEMISTRY — SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM

UNITED STATES ATOMIC ENERGY COMMISSION
PURIFICATION OF NUCLEAR FUELS BY MELTING
IN REFRACTORY OXIDE CRUCIBLES. Interim
Report.

By
H. M. Feder
N. R. Chellew
M. Ader

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Lemont, Illinois

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Chemistry-Separation
Processes for Plutonium
and Uranium

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

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REFRACTORY OXIDE CRUCIBLES

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H. M. Feder, N. R. Chellew, M. Ader

CHEMICAL ENGINEERING DIVISION

~~March 15, 1954~~

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For The Atomic Energy Commission

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4
INTERIM REPORT
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ABSTRACT

Redistribution of fission elements and plutonium between metal and metalloid phases occurs during the melting of pile-irradiated uranium. This report discusses the use and properties of refractory oxide crucibles and presents the experimental data obtained in an investigation into this phenomenon.

The crucible materials acting as solid oxidants effect considerable concentration of certain fission elements by incorporating them into an oxide slag layer. In addition, impurity concentration is effected by crystallization of uranium monocarbide, -nitride and -oxide solid solutions and volatile impurities are lost by diffusion. Photomicrographs and x-ray data were used to characterize and identify the slag and inclusion layers. Theoretical considerations of the thermodynamic stabilities of oxides and of the kinetics of slag formation are correlated with observations on the surface oxidation of liquid uranium by the refractory oxides.

The data thus far obtained on melting uranium at 1200°C in an helium atmosphere show that: (1) plutonium, rare earths, strontium, cesium, tellurium, zirconium and niobium are concentrated to varying extents in the slag layer, whereas ruthenium is not; (2) all the radio-elements are removed from the ingot interior to some extent, although this removal is small in the case of plutonium, ruthenium, niobium and molybdenum; (3) the removal of radio-elements is independent of the use of thoria, urania, magnesia or alumina as crucible materials; (4) the tendency for loss by diffusion, in order of decreasing tendency, is cesium > strontium > rare earths > tellurium, niobium, zirconium, plutonium and ruthenium; (5) significant amounts of radio-elements diffuse into the crucible materials, whereas negligible amounts diffuse to the furnace atmosphere and walls. The removal of fission elements is also found to be affected by interrelated factors such as time at temperature, starting concentration, charge size and average minimum diffusion distance.

The separation of oxide slag from uranium metal can be made chemically, as by acid etching, or physically, as by pouring. The application of oxide slagging as a purification process for reactor fuels, particularly the enriched cores of fast neutron piles such as the proposed Power Breeder Reactor, is considered.

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I. SUMMARY

This report presents the results of a partially completed investigation of the phenomena occurring during the melting of irradiated uranium in refractory oxide crucibles. It is shown that under favorable circumstances certain fission product elements are separated to a considerable extent. Some of the separations achieved have been correlated by theoretical considerations.

Application of this process to reactor technology is considered. Its use in connection with the enriched core of a fast neutron pile appears to be particularly attractive.

II. INTRODUCTION

A. Review of Earlier Work

The idea of removing fission products from irradiated uranium without converting the metal from its metallic state is almost as old as the Metallurgical Project itself. Late in 1942, the group at Ames under Dr. Spedding investigated the diffusion of volatile fission elements away from uranium maintained at elevated temperature.¹ It was observed that cyclotron-bombarded uranium kept molten at 1800°C. for 2 hr in vacuo in a beryllia crucible lost the rare gases, iodine, barium and strontium quantitatively and cerium to the extent of 94%. At lower temperatures in graphite crucibles less quantitative but still considerable removals were obtained. In the course of these latter experiments, moreover, a very significant discovery was noted, namely, that the surface scale formed between the metal and graphite on being removed by filing showed a strong concentration of certain fission elements. The results of analyses are given in Table I.

The conclusion drawn from these and similar experiments was that "most of the fission elements other than molybdenum and tellurium² and the volatile rare gases and iodine were concentrated in a very small volume of scale and slag between the uranium and graphite surfaces." However, the methods tried removed only a small percentage of the plutonium and neptunium. Presumably, these investigations were not intensively pursued beyond this point because the primary interest at that time resided in recovery of the transuranic elements.

¹Spedding, F. H., Johns, I. B. et al., MUC-NS-3068.

²Niobium and ruthenium activities were not followed.

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Table I

CONCENTRATION OF ACTIVITIES IN THE REACTION LAYER
BETWEEN THE METAL AND GRAPHITE

(Data from MUC-NS-3068)

Element	$\frac{d/m/g \text{ scale}}{d/m/g \text{ original}}$	
	1200°C., 1-3/4 hours	1400°C., 2 hours
Ba	3.58	14.9
Sr	3.25	14.3
Te	5.93	2.32
Mo	0.90	0.67
Zr	6.12	12.8
Ce	7.30	6.2
La, Y, Pr	13.30	15.4
Np	---	0.88

By 1945 sufficient thermodynamic data on uranium compounds at high temperatures were available to permit Brewer³ to consider the theoretical feasibility of high temperature processes which "would keep uranium in the same state as it is used in the pile." From thermodynamic equilibrium considerations the following results were reasoned to be sufficiently probable to warrant further investigation:

1. Maintenance of uranium at a high temperature would remove the volatile fission products: Xe, Ba, Sr, Cs, I, Rb, Kr, Br, Sn, Cd, and Sb.
2. The addition of carbon to the molten uranium would cause the removal of zirconium and niobium and possibly some rare earths as a light carbide scum. The plutonium would remain with the uranium.
3. Addition of nitrogen would be less effective than addition of carbon.

³Brewer, L., UCRL-314

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4. Addition of oxygen as the gas or in the form of solid uranium trioxide would probably remove all the rare earth metals including yttrium and possibly also plutonium in an oxide layer, which would separate as a floating scum or on the walls of the container.

5. The use of uranium sulfides or halides would produce essentially the same results as uranium trioxide except that removal of plutonium would be more effective.

6. A combination of steps would result in the separation of plutonium and all of the major fission products except molybdenum and ruthenium.

The speculations of Brewer were not put to extensive experimental test. Consideration of the possibilities inherent in such high temperature processes was practically neglected until late in 1952. The reawakened interest stems mainly from a growing realization of the need for greater economy in fuel reprocessing methods.

The present report will be confined to results obtained by oxide slag formation. It is very natural to consider oxide slagging as one of the most desirable attacks on the problem. The technique of slagging off the oxide of a more electropositive element - either as a solid oxide dross or as a molten silicate - in order to leave behind the nobler element in purified form is older than metallurgy as a science itself. The removal of silicon and manganese from iron, of iron from copper, of iron, copper and tin from lead, of various impurities from tin, of lead from silver are examples of this technique as presently applied in its various forms on a technological scale. Occasionally these industrial purification processes are also enhanced by the simultaneous volatilization of an undesired element, e.g. zinc from lead, and this feature also plays a role in the present work.

B. Thermodynamic Data

It will be useful to review some relevant thermodynamic data before proceeding to a discussion of the theory of the effects encountered and the experimental results. In Table II are listed the free energies of formation of the oxides of the chief elements of interest over a useful temperature range. The values are from Glassner's recent compilation.⁴ The precision of the data is not stated in this reference. It may vary considerably, depending on the adequacy of the heat capacity data at the higher temperatures.

The vertical order in Table II is that of decreasing stability of the oxides at 1500°K, a temperature near that at which the present experimental work was done. For elements with more than one oxide there is listed the oxide considered most likely to be encountered in this work.

⁴Glassner, A., ANL-5107

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Table II

FREE ENERGY OF FORMATION OF OXIDES,
KILOCALORIES PER GRAM-ATOM OF OXYGEN

Compound	$-\Delta F_f^\circ$		
	1000°K.	1500°K.	2000°K.
ThO ₂	125.5	115.0	104.5
CaO	131	114	99.3
La ₂ O ₃	123.3	112	100.3
BeO	123.3	111.6	99.5
Ce ₂ O ₃	120.3	107	94
Pr ₂ O ₃	120	106.7	94.3
MgO	119	103	78.9
Al ₂ O ₃	112	102	93
SrO	116	102	80.4
UO ₂	109	99	88.5
ZrO ₂	108	97	86.5
Li ₂ O	112	96.1	66.0
BaO	111	95	80
PuO ₂	100	95	85
B ₂ O ₃	81.3	73	65.7
SiO ₂	82.5	72	61
NbO	76	66	57
CO	47.9	58.4	68.5
H ₂ O	46.0	39.3	32.3
MoO ₂	46.5	38	30
TeO ₂	15.8	4.7	-7.3
Cs ₂ O	35.1	3.6	-15.7
RuO ₂	6.0	-2.7	-10

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It may be noticed that Table II contains information which permits the selection of possible refractory oxides for the melting of uranium (M.P. = 1406°K.). Thus, the relative stabilities indicate, and experimental results confirm, the possible utility of thoria, calcia, beryllia, magnesia, alumina, urania and zirconia. Likewise, the unsuitability of refractories containing large amounts of borates and silicates is indicated by the table and confirmed by experiment.

C. Properties of Refractory Oxides Suitable for Uranium Melting

Whereas the suggestion of Brewer regarding oxide slagging was couched in terms of addition of the oxygen either as gas or as uranium trioxide it was recognized at the outset of this investigation that the reaction of liquid uranium with a refractory oxide container was likely to give the same net result. The chemical and technological properties of these refractories^{5,7} and prior experience with them in uranium melting⁶ are therefore of considerable interest. These are examined in the following paragraphs.

1. Thoria - This is the highest melting and most inert of the refractory oxides. It has a low vapor pressure and is stable in oxidizing atmospheres and in contact with carbon up to 2200°C. It is also reportedly stable in contact with acidic and basic slags. Because of its high fusion point it is difficult to fire to a dense mass of high purity. Two per cent zirconia is frequently incorporated in order to aid the firing of ware. The porosity of high-fired crucibles is quite low. Crucibles may be prepared by either dry-pressing or slip-casting to apparent densities of 9.5 - 9.7. Pure thoria crucibles are very susceptible to rupture from mechanical or thermal shock because of the difficulty of sintering. At the Argonne National Laboratory, experience with thoria crucibles for uranium melting indicates that their reuse for a second or third melt is attended with great difficulty because of breakage. It has been reported that liquid uranium does not wet thoria or undergo visible reaction with it up to 1500°C. However, these reports are based on short time contacts involving induction melting. With longer contact times, as in the current work, definite surface reaction and apparent wetting were observed. The pickup of thorium by the melt has not been measured.

Thoria crucibles are not commercially available but may be obtained by special arrangement. Their cost is high.

⁵Norton, F. H., Refractories, McGraw-Hill Book Company, 3rd. Edition, 1949, pp. 304-324

⁶Schwartz, M. A., Report on Crucibles for Melting Uranium, NEPA - 674

⁷Schwartz, M. A., White, G. D. and Curtis, C. E., Crucible Handbook, ORNL-1354

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2. Calcia - Calcia has a high but attainable fusion point. Both the raw material and the fired crucibles are hygroscopic and must be constantly protected from air. Above 1750°C. lime may not be heated unshielded from graphite. Crucibles may be formed by tamping, jolting or dry-pressing. The last method gives the most uniform, dense bodies, but these still have a 10% porosity. The wetting of lime crucibles by liquid uranium is reported to be a function of particle size; erosion of calcia liners by liquid uranium has been frequently observed. At 1600°C. the reaction between calcia and uranium becomes rapid. Calcium, being volatile, is not introduced into the uranium.

Tamped or jolted lime or dolomite ($\text{CaO} + \text{MgO}$) liners are commonly used in the bomb reduction method of manufacturing biscuit uranium. Such liners are not generally reused. Lime crucibles have also been used successfully as molds in vacuum casting.

Lime of great purity may be obtained cheaply, but there are no commercial sources of fabricated crucibles.

3. Beryllia - Beryllia is one of the most stable refractories. It may be used up to temperatures close to its melting point, 2510°C., in oxidizing, reducing and neutral atmospheres. It is, however, attacked by water vapor at high temperatures. Fired beryllia is white, very hard, and may have a porosity as low as 1%. The bulk density ranges from 2.7 to 2.9. Thermal conductivity is high, and heat-shock resistance is unusually good. These properties make beryllia particularly suitable for induction heating. Crucibles of beryllia are made by either dry-pressing or slip-casting. Beryllia has been used to a small extent for melting uranium. It has been reported that quantities of beryllium larger than allowable in reactor grade fuel elements are picked up by the uranium.

Beryllia crucibles are available commercially. The health hazard connected with their handling may not be neglected, and certain special measures involving housekeeping and monitoring are required; but it should be pointed out that the common precautions taken in this laboratory in handling radioactively contaminated objects will generally also suffice to prevent trouble in handling beryllia crucibles.⁸

4. Magnesia - Electrically fused magnesia makes an excellent refractory for high temperature work. The vapor pressure of magnesia is higher than that of the previously mentioned oxides, and it may not be used in vacuum above 2000°C. The reaction with carbon to give magnesium vapor and carbon monoxide proceeds rapidly at elevated temperatures. Magnesia is sensitive to any type of reducing conditions and requires a strongly oxidizing atmosphere above 1700°C. High purity magnesia ware contains 1 or 2%

⁸Steindler, M., The Safe Handling of BeO Crucibles, Memo To File, Dec. 22, 1953

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of silica which is helpful in lowering the firing temperature. Dry-pressing or slip-casting (in absolute alcohol) methods may be used for the preparation of dense, white crucibles. With the latter method apparent porosities of 0.5 to 8.5% may be expected, depending on firing temperature in the range 1990°C. to 1850°C. The high thermal expansion of magnesia makes it rather sensitive to thermal shock, but the material is mechanically strong.

High grade magnesia ware has been one of the principal crucible materials used in the metallurgy of uranium. Surface reaction between the melt and crucible is slow, and little magnesium is introduced because of its volatility.

A spectrochemical analysis of reactor grade uranium kept for 2 hr at 1200°C in the present equipment (see Section IIIA) gave the results indicated in Table III, p. 13.

5. Alumina - This refractory (M.P. 2050°C) is very widely used in melting pure metals. The cheaper grades are clay-bonded, less refractory, and have porosities ranging from 35 to 50%. However, they have the advantages of usability up to 1885°C. and of good thermal shock resistance. Recrystallized alumina of very high purity is relatively easy to vitrify and ware may be formed into very hard, nonporous (0.2%), translucent bodies with excellent mechanical and electrical properties. Such crucibles have good resistance to acid and basic attack and are nearly inert under varying furnace conditions. Inorganic salts high in alkalis, halides, phosphates or silicides may be fused in alumina without appreciable contamination of the melt. Ware may be formed by dry-pressing, slip-casting or even by actual melting and casting.

The resistance of alumina to liquid uranium has apparently not been fully investigated. In this laboratory it has been observed that the obvious criteria of attack, i.e., discoloration, surface roughening, wetting, are less apparent with alumina than with thoria, urania, magnesia or zirconia. Spectrochemical analysis of reactor grade uranium kept for 4 hr at 1200°C. in the present equipment (see section IIIA) gave the results shown in Table III, page 13.

6. Urania - Urania has only recently become available for refractory crucibles.^{9,10} As such it possesses the evident advantage for uranium melting of not introducing additional foreign elements. The melting point of urania, 2875°C., is second only to that of thoria among the refractory oxides. Urania ware may be formed by dry-pressing or slip-casting,

⁹Corwin, R. E., Eyerly, G. B., J. Am. Ceram. Soc. 36, 137(1953); ANL-4855

¹⁰Eyerly, G. B., Lambertson, W. A., Kraft, R. G., Corwin, R. E., ANL-5038

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followed by firing in a purified hydrogen atmosphere at 1750°C. A molybdenum resistance furnace is used in order to eliminate carbon contamination. Dry-pressed and fired urania reaches a density about two-thirds of theoretical density. Its color varies from very dark brown to black, and its composition is very close to $\text{UO}_{2.00}$. Considerable experience has been obtained in the use of urania for the melting of high purity uranium.¹¹ The reaction of uranium with urania leads to the formation of uranium monoxide. However, this reaction¹² has been observed to proceed at a measurable rate only above 2000°C, and there is no evidence that it occurs to any appreciable extent at temperatures not far above the melting point of uranium.

7. Zirconia - Electrically fused zirconia may be formed into mechanically strong ceramic forms. Because zirconia undergoes a reversible transition at about 1000°C. with a marked volume change, the pure material cannot be used alone. The addition of lime (5 - 8%) to form a solid solution raises the transition temperature; the "stabilized" material resists the effect of rapid temperature changes. Zirconia is chemically stable in acid fusions and it is not readily reduced except by carbon at 1500°C. in a vacuum or at 1800°C. in an inert atmosphere. Zirconia becomes an electrical conductor above 1600°C. Ware having a porosity of 0.7 to 5% may be formed by slip-casting.

Although the attack by liquid uranium on stabilized zirconia is not profound, it proceeds to an appreciably greater degree than with the previously listed refractories, as might be expected from the relative stabilities of the oxides. Table III, p. 13, gives the results of spectrochemical analyses of reactor grade uranium kept molten at approximately 1200°C for 4.5 hr in the equipment described below (see section IIIA).

8. Others - Little is known about the other sufficiently stable refractory oxide crucible materials. Some possibilities include: the other alkaline earth oxides, the rare earths oxides, the spinels having the general formula $\text{M}^{\text{II}}\text{Al}_2\text{O}_4$, the zirconates $\text{M}_2^{\text{II}}\text{ZrO}_4$ or $\text{M}^{\text{IV}}\text{ZrO}_4$, and the refractory porcelains composed of mixtures of three oxides from the group ThO_2 - BeO - Al_2O_3 - MgO . The reader is referred to Norton's compilation⁵ for further discussion. An interesting and relatively unexplored field (except in connection with uranium production) is the use of refractory oxide liners for crucibles of other materials. Desirable combinations of chemical and mechanical properties might be more readily achieved by this technique.

¹¹ Blumenthal, B., ANL-5019, ANL-5124

¹² Baenziger, N. C. and Rundle, R. E., CC-1984

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Table III

**SPECTROCHEMICAL ANALYSES OF URANIUM MELTED IN
MAGNESIA, ALUMINA, AND ZIRCONIA CRUCIBLES**

Material: Reactor grade Uranium

Equipment and Procedure: See Section IIIA, p. 23

Conditions: MgO - 2 hr at 1200°C; flowing helium atmosphere, 110 cc/min.
 Al₂O₃ - 4 hr at 1200°C; flowing helium atmosphere, 110 cc/min.
 ZrO₂ - 4.5 hr at 1241 - 1151°C; flowing helium atmosphere,
 110 cc/min.

Composition of Uranium After Melting, parts per million^a

Element	Magnesia Run 15	Alumina Run 16	Zirconia Run 19B	Typical Remelted Biscut Metal ^b
Ag	< 1	< 1	< 1	1 - 2
Al	10	40	< 5	5 - 20
As	< 10	< 10	< 10	< 10
B	0.4	< 0.1	0.5	< 0.1
Be	< 0.5	< 0.5	< 0.5	< 0.2
Bi	< 1	< 1	< 1	< 1
Ca	< 20	< 20	< 20	< 20
Co	< 5	< 5	< 5	< 5
Cr	5	3	3	1 - 5
Cu	3	3	2	2 - 5
Fe	40	40	30	30 - 50
K	< 20	< 20	< 20	< 10
Li	< 1	< 1	< 1	< 1
Mg	1	1	2	2 - 10
Mn	5	5	6	2 - 10
Mo	< 20	< 20	< 20	< 20
Na	< 2	< 2	< 2	< 2
Ni	15	15	7	5 - 30
P	< 50	< 50	< 50	< 20
Pb	2	< 1	< 1	1 - 2
Sb	< 1	< 1	< 1	< 2
Si	30	40	50	30 - 50
Sn	< 5	< 5	< 5	< 5
Ti	< 50	< 50	< 50	< 50
Zn	< 50	< 50	< 50	< 20
Zr	--	--	< 400	< 10 ^c

^aThe symbol (<) represents the lower limit of detection in the samples analyzed.

^bData from B. Blumenthal, ANL Metallurgy Division

^cFrom The Reactor Handbook, RH-3, April, 1953, p. 434

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D. Oxidation of Liquid Uranium by Solid Oxidants

The mechanism and rate of the oxidation of metallic uranium by a variety of reagents (air, dry oxygen, water, steam, electrons at an anode) have been studied at temperatures up to 850°C. The results are instructive, but they are not clearly applicable to the problem under study, namely, the oxidation of liquid uranium by solid oxidants. To deal with the latter problem, the uranium-oxygen system at high temperature should first be reviewed.^{13,14}

1. Solubility of Oxygen in Uranium - The solubility of oxygen in liquid uranium is very low. Values of 0.046, 0.05 and 0.2 atomic % have been reported¹⁵ at 1133°C, 1227°C and 1727°C, respectively. Even these small values may be higher than the true solubility values. Analyses varying from 5 - 25 ppm of oxygen (0.0075 - 0.027 atom %) have been obtained¹¹ on well-liquated purified metal.

2. Uranium Monoxide - Uranium monoxide, a gray metallic-looking substance is the solid phase in equilibrium with oxygen-saturated liquid uranium. Uranium monoxide may be formed by direct union of the elements at low pressures of oxygen ($<10^{-6}$ mm) and temperatures above 800°C.¹⁶ The reaction ceases after the formation of a surface layer. The reaction to form the monoxide from uranium and uranium dioxide¹² proceeds at a measurable rate only above 2000°C. Even at 2400°C this reaction is far from complete, and the pure substance has not yet been obtained in bulk. Ordinary, i.e., not highly purified, uranium contains carbon, oxygen and nitrogen in excess of their solubility just above the melting point. On melting such uranium, even in the absence of all other reactants, a gray surface forms containing these impurities.

Uranium monoxide is a face centered cubic (rock salt) structure with a lattice parameter ($a_0 = 4.92\text{\AA}$) differing only slightly from uranium monocarbide ($a_0 = 4.96\text{\AA}$) and uranium mononitride ($a_0 = 4.95\text{\AA}$). It is very likely that these isomorphous substances form a complete series of solid solutions, U(C,N,O), and that the surface coating referred to above is this solid solution.

¹³Katz, J. J. and Rabinowitch, E., The Chemistry of Uranium, Part I, McGraw-Hill Book Co., 1951

¹⁴Seaborg, G. T. and Katz, J. J., The Actinide Elements, McGraw-Hill Book Co., 1954

¹⁵Cleaves, H. E., Cron, M. M., and Sterling, J. T., CT-2618

¹⁶Wilson, A. and Rundle, R., CN-1495

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3. Uranium Dioxide - The next higher well-characterized oxide of uranium is the dioxide. This phase varies in color from dark brown to glossy black. The solid has a face centered cubic (fluorite) structure. A second high temperature form, β , is also known. The range of solid solutions with oxygen extends¹⁷ from $\text{UO}_{2.00}$ to $\text{UO}_{2.33}$, the lattice parameter diminishing linearly with increasing oxygen content from $a_0 = 5.458\text{\AA}$ for $\text{UO}_{2.00}$. Evidence against formulating this substance as U_{1-x}O_2 is discussed by Katz and Rabinowitch.¹³

Urania is an electrical semi-conductor. The increase in conductivity with increasing oxygen content, the positive Hall coefficient, and the magnetic and light transmitting properties of its solid solutions in thoria all give evidence that a certain fraction of the uranium atoms in urania, approximately 10^{-5} , is missing. Electrical neutrality in urania is maintained by the resonance of uranium ions between the +4 and higher valence states. The lattice vacancies become increasingly mobile at higher temperatures. The oxide ions in excess of the stoichiometric composition occupy lattice vacancies; they are, presumably, also mobile at high temperatures in accordance with Tammann's rule.

The excess oxygen in UO_{2+x} is not readily removed. Thus, the oxygen pressure above $\text{UO}_{2.20}$ is only 22 microns at 1160°C ., and further decomposition leading to $\text{UO}_{2.00}$ requires temperatures much higher than 1160°C .

An experimental study of the rate of surface oxidation of liquid uranium by solid oxidants, such as the refractory oxides, has been started. Figure 1 shows a photomicrographic section through the contact layers. The 30 micron contact layer has been examined by X-ray diffraction. Two face-centered cubic lattices were identified with a_0 parameters of $5.471 \pm 0.002\text{\AA}$ and $4.952 \pm 0.001\text{\AA}$, respectively. The first structure has been identified as $\text{UO}_{2.00}(30 \pm 5\%)$; the second was stronger and was tentatively identified as $\text{U}(\text{C,N,O})(70 \pm 5\%)$.

It appears that for equal contact times at constant temperature the oxidation by magnesia and alumina has proceeded at equal rates. The lack of undercutting with thoria, magnesia and alumina shows that oxidation proceeds inward from the surface. These facts may be tentatively explained by the following hypothesis concerning the formation of urania. At the original interface (Figure 2) oxide ions are detached from the lattice of the solid oxidant and become attached to the urania lattice.

¹⁷ A single observation that it also extends down to a composition $\text{UO}_{1.75}$ may be rejected in the light of subsequent failures to repeat this observation.

Figure 1

PHOTOMICROGRAPH OF URANIUM INGOT: VERTICAL SECTION
AT CRUCIBLE (MgO) WALL

Test Conditions: 2 hr at 1200°C; flowing helium atmosphere
Photographic scale: 1 cm = 10 microns

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Figure 2

The local high concentration oxide ions and metal atom vacancies, thus created, migrate under the influence of the concentration gradients to the growing interface, where uranium atoms may be incorporated into the lattice. Designating the vacancies by the symbol $\square v$, representing a deficit of 4 electrons, the process may be written schematically as follows:

A. Net reaction of growing interface:

B. Net reaction at original interface:

It may be noted that the rate of oxide layer growth is thus supposed to be determined by the rate of diffusion of vacancies or of oxide ions through the lattice (whichever is the slowest) and is thus characteristic of the urania rather than of the solid oxidant.¹⁸ Secondly, it may be noted that the metal atoms, M, formed at the original interface are supposed to diffuse away in all directions, and the reaction, therefore, does not attain equilibrium until a sufficient concentration of such atoms is built up at the growing interface. This point is of particular importance in the phenomena under discussion. If the metal atoms, M, were liberated at the growing

¹⁸A parabolic rate law for oxidation is thus implied. Too few observations have been made to provide evidence of the rate law.

interface and remained dissolved in the liquid uranium, the reaction with, say, thoria would cease after very little oxidation because the equilibrium constant for the reaction:

is unfavorably small, i.e., about 10^{-6} at 1500°K . Indirect evidence of diffusion of metal atoms, M, through the walls of the crucibles used is provided by the following observations:

1. The crucible material was always discolored to a certain depth;
2. The quantity of aluminum picked up by molten uranium after contact with the alumina is far less than equivalent to the quantity of uranium oxidized.

In the case of oxidation by zirconia a somewhat different situation occurs, because the equilibrium constant for the reaction:

is favorable, i.e., about 5 at 1500°K . Direct attack by liquid uranium on the zirconia surface might therefore be expected to occur at rates competitive with the preceding process. That such is possibly the case is indicated (1) by the undercutting of the sides of a zirconia crucible by molten uranium; (2) by the enhanced thickness of the reaction layer - about 160 microns - in 4.7 hr at approximately 1200°C ; and (3) by photomicrographs (Figure 3) that show points of direct attack.

An additional phenomenon which takes place during the melting of all but the highest purity uranium is the tendency of excess oxygen, carbon and nitrogen to form a surface layer. The tendency of this material to float is responsible for the formation of a liquation layer which can be readily identified in Figure 4. The depth of this layer is about 300 microns. The volume fraction of inclusions in the uranium matrix is of the order of 5 to 10%. The presence of a small amount of the same inclusion material in the contact layer has already been noted.

E. Mechanisms of Impurity Removal

A number of mechanisms may account for the removal of various impurities.

1. If the proposed mechanism of oxidation by the crucible is correct, the process has the following characteristics:

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Figure 3

PHOTOMICROGRAPH OF URANIUM INGOT: VERTICAL SECTION
AT ZIRCONIA CRUCIBLE WALL

Test Conditions: 4.7 hr at 1151 – 1233°C; flowing helium atmosphere, 110 cc/min.
Magnification: 100X

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Figure 4

PHOTOMICROGRAPH OF URANIUM INGOT: VERTICAL SECTION
AT TOP OF INGOT

Test Conditions: MgO crucible; 2 hr at 1200°C; flowing helium atmosphere,
110 cc/min

Photographic scale: 1 cm = 70 microns

- a. It proceeds primarily at the urania - uranium interface.
- b. It proceeds most rapidly at the beginning and subsequently tapers off to a very slow rate.
- c. Thermodynamic equilibrium is not established because of the removal of reaction products by diffusion. With regard to incorporation into the urania lattice, the fate of an impurity atom, M, originally present in the molten uranium and free to react¹⁹ will depend on the relative rates of reactions (1) and (2):

If reaction (2) is much more rapid than (1), the impurity will be highly concentrated in the earliest urania to be formed and will be less and less concentrated toward the growing interface because of its depletion in the melt. If reaction (2) has about the same rate as reaction (1), no concentration in the slag will occur, while if reaction (2) is much slower or does not proceed at all the slag layer will actually be depleted in the impurity.

The determination of such relative rates must be done experimentally. However, it is not unreasonable to assume that they will be roughly correlated with the thermodynamic stabilities of the oxides given in Table II, page 8. For each individual type of impurity atom other factors may influence the specific rate. Some of these factors are:

- a. size of the ion with respect to the size of the vacancy;
- b. charge of the ion and possible resonance stabilization by interaction with the surrounding uranium ions;
- c. polarizability of the ion.

The fission product elements molybdenum, tellurium, cesium and ruthenium almost certainly will not be removed by this mechanism.

2. Another source of impurity removal is the migration of U(C,N,O) toward the surfaces. Because of the fine state of subdivision of the inclusions and the intimacy of contact with the melt, it may be expected that any tendency of fission product elements to concentrate in them will be very markedly felt. Qualitatively, the fission product removal by this mechanism will be the same as by incorporation in the urania lattice, except for the possible role played by carbide and nitride formation. The carbides of niobium and zirconium are more stable than uranium carbide.

¹⁹Impurity atoms tied up in the monoxide - monocarbide - mononitride inclusions are not here considered.

3. Another source of fission product removal is loss by diffusion. The extent of this loss in each individual case will be dependent on temperature, pressure, state of combination, diffusion coefficient and time.

a. Xenon and Krypton - These inert elements will diffuse out rapidly above the melting point of uranium, regardless of the use of vacuum or inert atmosphere.

b. Iodine - The vapor-pressure of uranium tri-iodide is sufficiently large at elevated temperatures (estimated 280 mm of mercury at 1200°C) to cause its volatilization into a vacuum.

c. Cesium - The vapor pressure of cesium at 1200°C is about 19 atm. Cesium does not form a stable oxide, carbide or nitride at this temperature, and its solubility in uranium is probably very small. Even in an inert atmosphere and at low concentrations dissolved cesium should diffuse away from the metal fairly rapidly. It should be remarked that diffusion into porous boundary layers and crucible materials will take place simultaneously with diffusion into the atmosphere.

d. Strontium - This element, if uncombined with oxygen, may volatilize readily into a vacuum (vapor pressure = 200 mm of mercury). The diffusion constant of strontium ions through oxide lattices at 1200°C has not been measured.

e. Rare Earths - The same remarks apply as for strontium. The vapor pressures are much lower, being in the range 10^{-4} to 10^{-5} mm of mercury at 1200°C.

f. Tellurium - The situation for tellurium is similar to that for strontium, except that the tellurium may form stable uranium tellurides which, in analogy to the sulfide and selenide, will be non-volatile. Tellurium itself, has a vapor pressure of 1.9 atm. at 1200°C.

g. Others - No other fission element likely to be present in significant concentration in this work is appreciably volatile. The diffusion constants of the corresponding cations through oxide lattices are not known.

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III. EXPERIMENTAL RESULTS

A. Equipment and Procedures

1. Equipment

The high temperature studies relating to redistribution of fission products between metal and metalloid phases were conducted in a porcelain tube heated by a Globar resistance furnace. Provisions were made for blanketing the tube with argon. Additional auxiliary systems were provided to degas the tube plus contents and to permit a purified helium atmosphere during slag formation and liquation experiments. The units were installed in a ventilated hood and the furnace was surrounded with 3 in. of steel shielding.

Figure 5, p. 24, shows the experimental furnace and the accessory system required for purging air from the system, blanketing the porcelain tube with argon, and cooling a neoprene vacuum sealing gasket. The furnace tube was an unglazed McDanel porcelain tube of 2-5/8 in. inside diameter and 1/4 in. wall thickness. Crucibles were supported in the tube on porcelain cylinders in such a way that the melt would be approximately in the center of the furnace heating zone. The 4-element Globar furnace was insulated with 4 in. of firebrick and made tight enough to contain an inert atmosphere by welding a 1/8 in. steel case around the outer surface and capping the ends. Melt temperatures (ca. 1200°C) were attained in approximately 1 hr with a 2-3 kw input. Temperature was regulated with a Minneapolis-Honeywell Pyr-O-Vane controller in conjunction with a platinum/platinum-rhodium thermocouple that touched the outside of the porcelain tube in the center of the furnace heating area. Heating tests were made on the furnace to determine the relationship of temperature indicated by the external thermocouple and one located inside the furnace tube in a well drilled in a 1-kg urania crucible. When the furnace control was set at 1300°C and then at 1200°C the lag between internal and external thermocouples was about 10 min. After the furnace had reached control temperature, the temperature differential was small, reaching 4°C at equilibrium. It is felt that charge temperatures indicated in this report are correct to $\pm 15^\circ\text{C}$.

Auxiliary systems connected to the furnace tube, which include a helium purification train and a metal vacuum system, are shown schematically in Figure 6, p. 25. Performance of the metal vacuum system used for charge and crucible degassing prior to melting in purified helium has been satisfactory. The measured leakage rate into the evacuated system of about 15 liters capacity is 12 microliters per hour. Minimum equilibrium non-condensable gas pressures of 1.5×10^{-5} mm of mercury at room temperature, and of less than 10^{-3} mm with the furnace at 1300°C, have been obtained. Although the above equilibrium pressures are satisfactory for degassing of furnace components, the ultimate vacuum obtainable in the furnace tube is

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Figure 5

HIGH TEMPERATURE MELTING FURNACE WITH ARGON COOLING AND BLANKETING SYSTEM

Key

- A Sight Glass
- B Top Flange
- C Head
- D Gasket (Argon Cooled)
- E Porcelain Tube
- F Shroud
- G Sealing Pan
- H Supporting Baffle
- I Roots-Connorsville Gas Pump
- J Crucible
- K Crucible Support
- L Globar Heating Element
- M Tantalum Pail
- N Refractory Brick
- ⊙ Pressure Gauge
- ⊗ Valve

Figure 6

EXPERIMENTAL FURNACE AUXILIARY SYSTEM

limited by tubing diameter traps, bends and mechanical and oil diffusion pump sizes. With this limited vacuum system uranium melts with clean surfaces were not formed. Satisfactory melts have been obtained with the use of a flow of helium purified in the glass train shown in Figure 6. Tests are contemplated to determine the necessity of the complex 6-component purification system. Figure 7, p. 27, is a photo of the uranium melting furnace and includes the auxiliary system used in gas purification. The steel shielding wall normally surrounding the box-like furnace has been removed to obtain a view of the furnace assembly

2. Procedure

a. Melting

The procedures followed in the slag formation and liquation studies using the apparatus shown in Figures 5-7, were as follows (1) crucibles were degassed at a minimum temperature of 1000°C and permitted to cool in either purified helium atmosphere or vacuum, (2) the charge was surface cleaned with nitric acid and dried; (3) the charge after transfer to the melt crucible was degassed in vacuum at 600°C to a pressure of approximately 10^{-4} mm of mercury, (4) purified helium at a pressure of approximately 1.1 atm absolute was introduced to the system; sparging at 100 - 150 cc/min was begun and the temperature increased to 1200°C for a predetermined time, (5) the electrical power was shut off, and the furnace tube and contents were allowed to cool overnight in an helium atmosphere. Approximately 24 hr were required for the temperature to drop to 100°C Uranium melts were removed from the furnace at temperatures of 150°C or lower

Variation of the above procedure was made in Run 12A (Table XII, p. 34) in which bottom-pouring with stopper-rod and casting of metal were carried out with crucibles arranged as shown in Figure 8, p. 28. The metal was heated to 1200°C for 3-1/2 hr and then to 1250°C for 40 min, at which time the stopper rod was raised and the molten metal was cast in a secondary tantalum crucible. By the use of this technique, approximately 2 % of the liquated metal was retained in the primary crucible as a skull.

b. Ingot Preparation for Radiochemical Analysis

Nitric acid dissolution was used to obtain analytical samples for determination of fission product and plutonium concentrations in the slag or skin sections and in the ingot interiors. The weight per cent removal of uranium from the ingot was determined by intermittent spot checks of the acid uranium concentrations. Rate of dissolution was roughly controlled by acid temperature and concentration. Separate removal of the top ingot skin (approximately 300 micron inclusion depth) or bottom and side skin (approximately 30 micron slag depth) was accomplished by painting the

Figure 7

VIEW OF URANIUM MELTING FURNACE

Figure 8

BOTTOM-POUR STOPPER-ROD CRUCIBLE AND MOLD ARRANGEMENT
(Equipment Used in Run 12A)

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surface to be protected with a benzene solution of Apiezon "W" vacuum wax. Skinning of the selected area was then carried out with dilute nitric acid (4 N to 8 N) heated to a maximum temperature of 65°C (20°C below the wax melting point). Where no attempt was made to differentiate between top, side and bottom surfaces the ingot was dissolved to a point where clean metal, i.e., free from dark oxide was obtained. After the skinning operation the remaining metal was dissolved in boiling 13 N nitric acid under reflux. Final acid concentrations of both skin and interior analytical samples were about 6 N to 8 N.

Skinning of the cast ingot was not employed when the stopper-rod type crucible was used since the greater portion of the slag or skin layer was retained in the crucible during the pouring operation. Analytical samples for determining fission product concentrations were obtained by dissolving the retained slag and the cast ingot separately.

B. Analytical Data

Tables IV - XIV contain data relevant to the observed distribution of uranium, plutonium and fission elements in each of the runs made in refractory oxide crucibles. The procedures were as described in the preceding section. The term "skin" is used in these tables rather than "slag" because the deep etching procedure cannot be controlled with sufficient delicacy to prevent undercutting the surface and dissolving some of the interior metal. However, it is not probable that any of the conclusions of this investigation would be materially altered by a more precise separation. The chemical and radiochemical analyses were performed by the analytical service section of this Division using standard methods. Rare earths, cerium, strontium, ruthenium, cesium and tellurium were counted as beta activities using a G.M. tube. Zirconium and niobium gammas were counted through a lead absorber using a scintillation counter which was adjusted to discriminate against photons of less than 0.1 Mev. energy. Molybdenum was determined by a newly developed colorimetric method.²¹ Uranium was determined either by weighing directly as metal or by the acetone-thiocyanate colorimetric method. Plutonium was followed by means of standard lanthanum fluoride carrier technique and counting in an alpha proportional counter.

The material employed throughout this work was Oak Ridge irradiated uranium slugs which had been previously decanned, sliced and cleaned of adhering bonding material. For purposes of comparison untreated slices were dissolved as nearly as possible at the same time as treated slices. In the course of examination of these control slices it was determined that there was essentially no longitudinal variation in activity along the slug. In order to increase the precision of radiochemical analyses of the controls, the fission product activities were plotted versus the decay times (semi-logarithmic paper) and best lines fitted to the data. In most cases the slopes

²¹ Crouthamel, C. E. and Johnson, C. E., ANL-5224.

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Table IV

DISTRIBUTION OF MATERIAL AFTER MELTING

Run 2A

Crucible: Funnel-shaped urania crucible. Ingot sectioned vertically into 3 sections and each section individually skinned

Slice: 7 g/t, 70.5 g, 265 days cooled. 4 hr at 1200°C

Section	Percentage of Starting Material										Total	Total
	Uranium	Plutonium	Rare Earths	Ce	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Top section, skin	4.1	6.0	69.9	59.5	86.3	3.0	41.8	83.3	12.5	67.1	63.8	28.0
Top section, int.	55.0	49.6	0.5	0.2	0.9	38.2	1.7	5.4	49.5	21.0	6.4	43.4
Middle section, skin	0.8	1.7	11.0	10.7	4.2	0.4	3.6	5.4	1.6	5.4	8.5	2.7
Middle section, int.	21.9	20.2	0.1	0.05	0.1	20.9	0.6	1.5	21.3	8.6	4.0	16.9
Bottom section, skin	2.1	2.4	4.2	4.7	0.3	1.6	0.3	1.0	1.8	1.2	3.3	1.8
Bottom section, int.	15.7	14.3	0.4	0.05	0.05	15.5	0.4	1.0	14.7	8.1	1.7	12.2
Unaccounted	0.4	5.8	13.9	24.8	8.1	20.4	51.6	2.4	---	---	12.3	---

Table V

DISTRIBUTION OF MATERIAL AFTER MELTING

Run 5A

Crucible: Thoria. Ingot skinned 3 times in succession

Slice: 7 g/t, 78.4 g, 298 days cooled. 4 hr at 1200°C

Section	Percentage of Starting Material										Total	Total
	Uranium	Plutonium	Rare Earths	Ce	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Outer skin	0.7	2.1	43.8	45.7	61.4	0.5	21.3	25.5	4.8	38.6	40.5	13.6
Middle skin	0.7	1.2	26.7	25.1	26.0	0.6	14.7	19.7	2.7	17.4	22.0	6.5
Inner skin	2.9	2.4	16.7	16.5	7.2	2.8	6.7	6.0	2.7	10.2	12.9	4.7
Interior	95.5	87.3	1.1	1.3	0.1	91.1	3.4	19.4	74.9	27.4	9.5	47.4
Unaccounted	0.2	7.0	11.7	11.4	5.3	5.1	53.9	29.5	14.9	6.3	15.1	27.8

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Table VI

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 6A

Crucible: Magnesia. Ingot skinned 3 times in succession

Slice: 7 g/t, 51.8 g, 306 days cooled. 4 hr at 1200°C

Section	Percentage of Starting Material										Total	Total
	Uranium	Plutonium	Rare Earths	Ce	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Outer skin	1.2	3.7	44.7	46.6	74.9	0.4	24.6	47.0	5.9	41.8	44.1	19.4
Middle skin	1.1	1.8	23.3	26.1	17.6	0.6	11.9	10.0	2.7	15.5	20.5	7.7
Inner skin	1.9	1.7	11.9	12.6	6.4	1.6	5.6	3.6	2.7	8.9	10.3	4.9
Interior	95.5	88.0	1.7	1.9	1.6	85.1	2.7	39.8	74.3	24.7	9.9	64.8
Unaccounted	0.3	4.9	18.3	12.8	---	12.3	55.2	---	14.5	---	15.2	3.2

Table VII

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 7A

Crucible: Urania. Skinned once

Slice: 7 g/t, 30.6 g, 314 days cooled. 30 min at 1200°C

Section	Percentage of Starting Material										Total	Total
	Uranium	Plutonium	Rare Earths	Ce	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Skin	2.8	7.2	73.4	80.6	85.7	2.2	56.4	77.1	16.0	55.9	69.3	27.9
Interior	97.2	96.6	10.3	11.8	10.6	80.6	12.9	16.2	81.0	34.8	18.2	67.4
Unaccounted	0.0	---	15.3	7.6	3.7	17.2	30.7	6.7	3.0	9.3	12.6	4.8

Table VIII

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 8A

Crucible: Alumina. Very thin disc ingot. Skinned 3 times in succession

Slice: 7 g/t, 45.2 g, 321 days cooled. 4 hr at 1200°C

Section	Percentage of Starting Material									Total	Total
	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Outer skin	1.5	1.6	35.0	92.6	13.9	44.3	85.0	23.6	57.2	41.8	31.6
Middle skin	1.6	1.5	10.8	0.8	15.0	0.7	0.9	1.7	1.4	2.5	1.4
Inner skin	3.1	2.8	0.0	0.0	3.1	0.0	0.2	2.3	0.4	0.2	1.8
Interior	93.8	83.4	1.8	0.3	86.3	1.3	7.3	69.9	12.2	9.1	54.3
Unaccounted	0.0	10.7	52.4	6.3	---	53.6	6.7	2.6	28.8	46.4	11.0

Table IX

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 9A

Crucible: Magnesia. Skinned 3 times in succession

Slice: 7 g/t, 91.4 g, 330 days cooled. 30 min at 1200°C

Section	Percentage of Starting Material									Total	Total
	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Outer skin	0.9	1.1	46.7	31.1	0.6	24.2	28.3	14.0	29.2	45.4	15.2
Middle skin	1.0	0.9	8.0	27.2	0.9	19.0	24.3	6.1	9.8	10.5	6.8
Inner skin	3.2	2.8	3.9	27.2	3.2	15.0	21.6	5.7	14.0	6.0	5.4
Interior	95.2	82.8	20.2	16.8	94.1	18.8	17.3	74.8	42.5	25.1	47.1
Unaccounted	---	12.4	21.2	---	1.1	23.0	8.5	---	4.1	13.0	25.6

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Table X

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 10A

Crucible: Thoria. Top of ingot skinned separately from sides and bottom

Slice: 7 g/t, 63.8 g, 336 days cooled. 11 hr at 1200°C

Section	Percentage of Starting Material									Total	Total
	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te ^a	Nb	Zr	β	γ
Top skin	3.3	3.7	42.3	60.6	3.3	36.9	7.1	9.7	30.2	43.6	16.8
Bottom outside skin	0.9	1.9	30.6	27.3	5.7	16.3	9.0	11.7	50.2	30.1	16.7
Interior	95.5	83.3	1.3	1.3	102.6	0.9	9.3	78.7	16.2	8.4	49.5
Unaccounted	0.3	11.1	25.8	10.9	---	45.9	74.7	---	3.4	17.9	17.0

^aThese values considered doubtful because of inadequate analysis of control.

Table XI

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 11A

Crucible: Thoria. Top of ingot skinned 2 times. Bottom and sides skinned once. Crucible leached with acid.

Slice: 7 g/t, 218.5 g, 372 days cooled. 4 hr at 1200°C

Section	Percentage of Starting Material									Total	Total
	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te	Nb	Zr	β	γ
Bottom and side skin	0.6	1.0	27.3	41.8	0.3	15.3	33.7	4.7	26.1	26.7	13.3
Outer top skin	0.8	1.3	25.1	27.4	0.7	17.2	36.8	4.1	24.7	26.1	12.1
Inner top skin	1.0	1.1	19.0	8.1	1.0	8.2	2.3	2.4	13.3	18.3	7.3
Crucible leaching	0.01	0.5	3.0	8.1	0.0	41.8	8.7	0.03	0.2	4.3	4.4
Interior	97.8	99.1	11.7	6.4	109.0	5.6	7.5	86.2	32.1	19.2	61.7
Unaccounted	---	---	13.9	8.2	---	11.9	11.0	2.6	3.6	5.4	1.2

Table XII

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 12A

Crucible: Bottom-pour with stopper-rod thoria crucible. Ingot cast in tantalum pail

Slice: 42 g/t, 263.3 g, 298 days cooled. 4 hr at 1200°C

Section	Percentage of Starting Material									Total β	Total γ
	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te	Nb	Zr		
Skull	2.0	2.0	64.0	42.1	1.6	6.0	72.5	9.2	38.3	50.9	18.3
Ingot	97.6	88.4	3.1	0.2	85.2	0.1	14.5	9.3*	39.7	9.3	21.7
Unaccounted	0.4	9.6	32.9	57.7	13.2	93.9	13.0	81.5*	22.0	39.8	60.0

*Questionable Value

Table XIII

DISTRIBUTION OF MATERIAL AFTER MELTINGRun 15A

Crucible: Lime-stabilized zirconia. Ingot skinned once

Slice: 42 g/t, 68.0 g, 323 days cooled. 4.5 hr at 1241 - 1151°C

Section	Percentage of Starting Material									Total β	Total γ
	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te	Nb	Zr		
Skin	3.2	3.4	58.4	46.7	1.7	7.2	33.1	5.4	33.8	50.2	15.2
Interior	96.7	67.0	0.8	0.1	61.7	0.5	32.5	68.2	34.4	6.8	42.4
Unaccounted	0.1	29.6	40.8	53.2	36.6	92.3	34.4	26.4	31.8	43.0	42.4

Table XIV

DISTRIBUTION OF MATERIAL AFTER MELTINGRuns 16A - 17A - 18A

Crucible: Alumina. Reused twice. Each ingot skinned once

Slice: 16A - 42 g/t, 80.3 g, 325 days cooled. 4 hr at 1200°C
 17A - 42 g/t, 83.9 g, 326 days cooled. 4 hr at 1200°C
 18A - 42 g/t, 61.8 g, 338 days cooled. 4 hr at 1200°C

Percentage of Starting Material											
Section	Uranium	Plutonium	Rare Earths	Sr	Ru	Cs	Te	Nb	Zr	Total β	Total γ
(First Use)											
Skin	4.0	4.6	37.8	53.0	2.6	5.8	26.2	7.2	34.1	36.2	14.2
Interior	96.1	73.0	0.3	0.1	71.9	0.1	31.8	75.4	46.1	6.7	47.3
Unaccounted	---	22.4	61.9	46.9	25.5	94.1	42.0	17.4	19.8	57.1	38.5
(Second Use)											
Skin	4.8	5.2	78.6	35.1	3.6	8.7	83.7	12.9	61.6	71.7	27.2
Interior	95.0	89.0	2.1	0.05	87.4	0.06	6.5	99.1	37.1	9.0	53.3
Unaccounted	0.2	5.8	19.3	64.8	9.0	91.2	9.8	---	1.3	19.3	19.5
(Third Use)											
Skin	4.1	4.7	64.7	36.3	3.1	6.1	51.6	6.0	36.0	57.3	16.9
Interior	95.7	75.9	1.0	0.2	91.7	0.07	21.1	63.2	40.2	7.0	44.3
Unaccounted	0.2	19.4	34.3	63.5	5.2	93.8	27.3	30.8	23.8	35.7	38.8

of the best lines coincided with the known half-lives. The radiochemical analyses of the treated materials could then be compared with interpolated values for the controls in order to eliminate the variation due to decay time between analyses. Separate cerium analyses were discontinued after Run 7A since total rare earth activity was found to be due almost entirely to cerium-144 in the slugs processed (about 260 - 350 days cooling).

The accuracy and precision of these results is not easy to assess. The accepted precision of analyses (relative per cent) from the service laboratory are: uranium, $\pm 2\%$; plutonium, $\pm 5\%$; total beta and gamma activities, $\pm 5\%$; individual fission elements, $\pm 20\%$. Actually the confidence limits of these precisions have not been determined, and it would not be surprising if 95 % confidence levels were more than twice these values. The accuracy of the routine determinations of individual radio-elements tends to deteriorate badly if the counting rate is low or if separation from much larger amounts of other activities is required. In such cases variations from run to run of factors of 2 for a particular activity at low levels have not been assumed to be significant. Finally, since the entry marked "unaccounted" is obtained by difference from 100 %, only major variations or consistent trends will be assumed to have significance in the following discussions. A dash has been used to indicate that the analyzed materials total more than 100 % of the starting material. These excesses range from 1 to 18 %.

C. Discussion and Interpretation

In Tables IV - XIV each entry under a radio-element which significantly and consistently differs from the corresponding entry under uranium indicates a concentration or removal of that radio-element from the given location. In regard to redistribution of plutonium and fission products:

1. Except for ruthenium every radio-element reported in Tables IV - XIV is concentrated to a greater or lesser extent in the slag. This is demonstrated more clearly by Table XV. The large variation from run to run of the slag layer concentration of some radio-elements will be shown later to be due to the interaction of several variables.

2. Every radio-element reported in Tables IV - XIV is removed from the interior of the ingot to a greater or lesser extent. This is demonstrated more clearly by Table XVI. The effect of the chief variables on the concentration of residual activities will be discussed in the following paragraphs.

- a. Crucible Material - In runs 2-5-6-8A the single important variable changed was the crucible material. With the possible exception of tellurium the residual activities do not change by large amounts from run to run. It may be concluded that urania, thoria, magnesia and alumina do not bring about radio-element removal by special mechanisms peculiar to the

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Table XV

RADIO-ELEMENT CONCENTRATION FACTORS^a IN SLAG LAYERS

Description ^b	Pu	Rare Earths	Sr	Cs	Te	Nb	Zr	Ru
Run 2A, top	1.6	18	22	11	22	3.2	17	0.77
Run 5A, outer	2.8	59	83	29	34	6.4	52	0.61
Run 6A, outer	3.1	38	63	21	40	4.9	35	0.32
Run 7A	2.8	38	33	22	30	6.1	21	0.83
Run 8A, outer	1.0	23	60	29	55	15	37	0.91
Run 9A, outer	1.3	54	34	28	33	16	34	0.73
Run 10A, bottom and side	2.1	33	30	18	9.8 ^c	13	55	0.62
Run 11A, bottom and side	1.9	49	75	27	60	8.4	47	0.54
Run 12A, skull	1.0	32	21	3.0	36	4.6	19	0.80
Run 15A	1.0	18	14	2.2	10	1.7	10	0.53
Run 16A	1.1	9.4	13	1.4	6.5	1.8	8.4	0.63
Run 17A	1.1	16	7.3	1.8	17	2.7	13	0.75
Run 18A	1.1	16	8.9	1.5	12	1.5	8.8	0.75

^aDefined as cpm/millimole uranium in slag ÷ cpm/millimole uranium in control.

^bThe skin showing maximum concentration of activities has been chosen where more than one skinning was performed.

^cQuestionable value.

Table XVI

RESIDUAL ACTIVITIES IN THE INGOT INTERIOR

Run	Crucible	Hr at 1200°C	g/t ^b Level	Charge, g	Percent of Original Concentration ^a							
					Pu	Rare Earths	Sr	Cs	Te	Nb	Zr	Ru
2A	UO ₂	4	7	70.5	90	0.9	1.7	3.0	9.7	90	38	71
5A	ThO ₂	4	7	78.4	92	1.2	0.1	3.6	20	78	29	95
6A	MgO	4	7	51.8	92	1.8	1.7	2.9	42	78	26	89
8A	Al ₂ O ₃	4	7	45.2	92	1.9	0.3	1.4	8.1	77	13	95
7A	UO ₂	0.5	7	30.6	99	11	11	13	17	83	36	83
9A	MgO	0.5	7	91.4	87	21	18	20	18	79	45	99
10A	ThO ₂	11	7	63.8	87	1.4	1.3	0.9	9.7 ^f	82	17	108
15A	ZrO ₂	4.5	42	68.0	69	0.9	0.1	0.5	34	71	36	64
16A	Al ₂ O ₃	4	42	80.3	76	0.4	0.1	0.1	33	78	48	75
17A ^c	Al ₂ O ₃	4	42	83.9	94	2.3	0.1	0.1	6.9	105	39	92
18A ^d	Al ₂ O ₃	4	42	61.8	79	1.0	0.2	0.1	22	66	42	96
11A	ThO ₂	4	7	218.5	102	12	6.5	5.7	7.7	88	33	111
12A ^e	ThO ₂	4	42	263.2	91	3.2	0.2	0.1	15	9.5 ^f	41	87

^aDefined as 100 cpm/millimole uranium in ingot ÷ cpm/millimole uranium in control.

^bThe concentration of radio-elements is roughly proportional to the plutonium content which is given in ppm in the starting material.

^cFirst re-use of crucible from 16A.

^dSecond re-use of crucible from 16A.

^eBottom-pour stopper-rod run.

^fQuestionable value.

refractory oxide. This is in good agreement with expectation inasmuch as the melt is contained in an envelope of uranium oxides soon after it is formed and the source of the oxidizing agent is then immaterial. This is further confirmed by runs 16 - 17 - 18A in which removal of activities does not change significantly although the uranium is initially exposed to different surfaces in 16A as against 17A and 18A.

The one run made in a zirconia crucible (Run 15A) is also in agreement except for ruthenium. This is more clearly demonstrated by the appropriate entries in Table XIII which shows that 37 % of the ruthenium is unaccounted for. This may indicate a possible connection with the fact that zirconia is rapidly and directly attacked by the melt.

b. Time at Temperature - If the processes involved in removal are not very rapid time will be an important variable. Examining Table XVI, direct comparison immediately reveals that rare earth, cesium and strontium removal after $1/2$ hr is less complete than after 4 hr. On the other hand after 11 hr (Run 10A) removal is not significantly different than after 4 hr. An obvious exception to this is cesium which in the 11-hr run is removed to a slightly greater degree as might be expected for continuing evaporation from the melt. One concludes that under the given experimental conditions the slagging process for the other radio-elements is nearly complete at some time between $1/2$ and 4 hr.

c. Original Concentration of Activity - Comparison of Runs 16 - 17 - 18A with Runs 2 - 5 - 6 - 8 - 10A in Table XVI reveals that cesium, certainly and strontium, possibly, are significantly better removed as activity level increases. Moreover their removal is not into the slag layer as examination of Table XV will show. A possible explanation for this is given below in section 3.

d. Charge Size - The weight of the charge melted should have no significance in itself except as it affects the geometry of the experiment, i.e. the extent of surfaces exposed to the atmosphere or the crucible or the distance a particle must diffuse to reach a boundary. Let it be assumed that the latter factor is the significant one. For convenience it will be measured by the average thickness of the ingot measured across its narrowest dimension, i.e. the average minimum diffusion distance. The radio-elements which will be subsequently shown to be most susceptible to loss by diffusion are cesium, strontium and the rare earths. In Table XVII the residual activities of these elements are shown as a function of the average ingot thickness, other variables being kept constant. Inspection of this table reveals that, with the exception of the entries marked by asterisks, the trend is well marked, increasing ingot thickness paralleling increasing activity retention. Attempts to apply the same correlation to other radio-elements meet with less success. Likewise attempts to correlate the retentions of cesium, strontium and rare earths using as variables weight, total surface area, crucible contact area or top surface area were less successful.

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Table XVII

RESIDUAL ACTIVITIES IN THE INGOT INTERIOR AS A FUNCTION
OF DIFFUSION DISTANCE

Average Thickness of Ingot, In.	Hr at 1200°C	g/t Level	Run	Per Cent of Original Concentration			
				Cs	Sr	Rare Earths	Ce
0.20	4	7	8A	1.4	0.3	1.9*	-
0.25	4	7	2A	3.0	1.7	0.9	0.4
0.48	4	7	5A	3.6	0.1*	1.2	1.4
0.53	4	7	6A	2.9*	1.7	1.8	1.9
0.96	4	7	11A	5.7	6.5	12	-
0.18	0.5	7	7A	13	11	11	12
0.63	0.5	7	9A	20	25	22	-

*See text, page 39.

3. After melting, the radio-elements present in the starting material must be recoverable in the slag layers, the ingot interior, the crucible, or the furnace atmosphere and walls. The entries marked "un-accounted" in Tables IV-XIV are, therefore, measures of the activities diffused to the crucible or to the furnace atmosphere.

The percentages under discussion are tabulated in Table XVIII.

Because the entries in Table XVIII are determined indirectly from the summation of the analyzed fractions, their accuracy is indeterminate. A rough estimate may be obtained by the following consideration. If the analyzed fractions constitute only 10 % of the starting material and if the precision of its analysis is ± 20 % (relative), then the activity lost by diffusion will be 90% of the starting material, and the precision of the value will be ± 2 % (absolute), etc. By this argument, the entries are estimated to have absolute precisions as follows:

<u>Activity Lost, %</u>	<u>Abs. Precision, %*</u>
10	18
20	16
30	14
40	12
50	10
60	8
70	6
80	4
90	2

*Divide by 4 for plutonium.

Inspection of Table XVIII with the foregoing remarks in mind leads to the observation of a definite trend toward greater diffusional losses of the radio-elements as their concentration in the starting material is augmented. On re-examining Table XV (Run 12A-18A vs. 2A-11A) it may be seen that simultaneous with their greater diffusional losses the radio-elements become relatively less concentrated in the slag layers. The phenomenon is not strongly time dependent. As a tentative explanation it may be suggested that the diffusing atoms may occupy a limited number of sites ("traps") in the boundary layers, and that passage of the diffusing atoms through the boundary layers is consequently retarded until these sites start to fill up. The number of sites available to each kind of diffusing atom may be different, depending on atomic or ionic radius or other factors. A very rough estimate of the concentration of cesium "traps" in the slag may be made if they are assumed to have been filled in these experiments. For the runs at 7 g/t level the average fraction of the total cesium found in the slag was 45 ± 5 %. The fission

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Table XVIII

ACTIVITIES LOST BY DIFFUSION^a

Run No.	g/t Level	Hr at 1200°C	Percentage of Starting Material ^b							
			Cs	Sr	Rare Earths	Pu	Te	Nb	Zr	Ru
7A	7	0.5	31	4	16	-	7	3	9	17
9A	7	0.5	23	-	21	12	9	-	4	1
8A	7	4	54	6	52	11	7	3	29	-
2A	7	4	52	8	14	6	2	-	-	20
5A	7	4	54	5	12	7	30	15	6	5
6A	7	4	55	-	18	5	-	15	-	12
11A ^c	7	4	57	16	18	-	21	6	15	-
10A	7	11	46	11	26	11	75 ^d	-	3	-

12A	42	4	94	58	33	10	13	82 ^d	22	13
16A	42	4	94	47	62	23	42	17	20	26
17A	42	4	91	65	19	7	10	-	1	9
18A	42	4	94	64	34	19	27	31	24	5
15A	42	4.5	92	53	41	30	35	26	32	37

^aDetermined by difference. Dashed entries indicate sum of analyzed fractions exceeds 100 %.^bValues rounded to nearest per cent.^cCrucible leachings included in these values.^dQuestionable value.

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yield of cesium is about 6%, and the total yield of cesium will be about 12% (33 y. Cs^{137} + 2.1×10^6 y. Cs^{134}). The slag weight averages roughly 3% of the starting weight of the uranium. Accordingly

$$\text{Concentration of cesium 'trap'} = \frac{7 \times 10^{-6} \times 0.45 \times 0.12}{0.03} = 1.3 \times 10^{-5} \text{ weight fraction}$$

At the 42 g/t level the average fraction found in the slag is $7 \pm 1\%$ and a similar calculation yields a 'trap' concentration of 1.2×10^{-5} . The calculated order of magnitude 10^{-5} is a quite reasonable value for the fraction of lattice imperfections in urania capable of accomodating the large atoms of cesium.²² If these notions are realistic one will expect that at much higher starting concentrations of cesium its removal by diffusion will be very nearly quantitative. Similar calculations for other radio-elements indicate that the trapping sites available to them were not completely filled in these experiments. This is not too surprising when one considers the pertinent ionic or atomic radii. Experiments at higher levels will be needed for testing this explanation.

In any case the data thus far obtained give a qualitative indication of the diffusional tendencies of the radio-elements. These are, in order of decreasing tendency cesium > strontium > rare earths > tellurium, niobium, zirconium plutonium ruthenium.

Mention should be made of some anomalously high diffusion losses for which no explanation is offered. These are: rare earths in runs 8A and 16A using new alumina crucibles, and niobium in the bottom-pour stopper-rod run 12A.

4. The fate of the elements lost by diffusion has been subjected to preliminary investigation. In run 11A the crucible interior was acid leached after the run to effect extraction of some of the substances diffused into its surface. Less than 0.01% of the starting uranium was thus extracted; but of the radio-elements lost by diffusion 70% of the cesium 50% of the strontium, 42% of the tellurium and 16% of the rare earths were recovered, along with negligible quantities of plutonium ruthenium, niobium and zirconium. To what extent these recoveries fell short of 100% due to the inability of the leaching to extract is not known. One conclusion, however, can be firmly stated, namely: under the given experimental conditions (1200°C, helium atmosphere) significant fractions of the radio-elements diffuse into the crucible walls.

The large exposed surface and the porosity of the crucible materials make this observation readily understandable. That the phenomenon is quite general in these experiments is further verified by the constant observation (by survey meter) of intense beta-gamma activity levels near the crucibles after the irgot has been removed.

²² The imperfection of the lattice may vary from place to place depending on its mode of formation.

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On the other hand the large losses of radio-elements which have been observed by others as a result of volatilization at higher temperatures and lower pressures are not observed in these experiments. Surveys of the furnace walls and exit gas traps after completion of a run show only slight radioactive contamination. By use of a cold finger suspended over the crucible during a run, the presence of deposited cesium plus some other activities could be picked up by gamma ray scintillation spectrometry. The quantities were inadequate for radiochemical analysis, so the following expedient was resorted to. After 7 runs at the 7 g/t level and 16 inactive runs the porcelain furnace tube was disassembled and thoroughly decontaminated with hot nitric acid. The solution was concentrated and silica removed by fuming with hydro-fluoric-sulfuric acid. Thirty milligrams of uranium were recovered in this solution. The results of the radiochemical analysis are shown in Table XIX and are compared with typical analyses of starting materials and slags from the same runs. At first glance it may seem that comparison of the deposit and the starting material indicates a strong enrichment of the former in a number of radio-elements. Closer consideration of the physical situation however indicates that comparison is more properly made with the surface layers through which the material must diffuse. On this basis it is evident that only cesium is definitely volatilized. The presence of the non-volatile elements uranium zirconium niobium and ruthenium in the deposit must be accounted for by a slight dusting up of the surface coating of the ingot (This material has been observed to dust readily.) That they are less concentrated than in the slag is due to dusting of the surface coating of inactive ingots. Tellurium in combination with uranium must be reckoned as non-volatile. The data for the remaining elements does not establish their volatility or non-volatility unequivocally.

D. Summary

The separation of radio-elements from uranium by the process of melting in refractory oxide crucibles and subsequent chemical or mechanical removal of slag has been investigated in a preliminary fashion. The knowledge gained to date may be summarized by considering the individual elements.

1. Cesium - The separation of this element is entirely a diffusional process involving atomic cesium; cesium oxide is unstable under the given experimental conditions. Diffusion takes place first to the envelope of slag, where the available sites are rapidly filled, then to the crucible and the furnace atmosphere. The gross removal of cesium from the interior metal is favored by time short distance, large concentration, and probably high temperature. The nearly quantitative removal of this element poses no special problems except for minimizing the spread of contamination due to volatility.

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Table XIX

COMPARATIVE ANALYSIS OF ACTIVITIES DEPOSITED
ON FURNACE WALLS

Activity	Specific Activity, 10^7 cpm./millimole uranium		
	Deposit	Typical Starting Material*	Typical Slag*
Cs	29	0.099	2.0
Sr	1.05	0.25	15
Rare Earths	100	2.6	97
Ce	97	2.0	78
Te	0.079	0.0055	0.22
Zr	3.3	1.1	40
Nb	4.1	2.2	11
Ru	0.02	0.19	0.062
Pu	0.046	0.013	0.041
Total β	150	3.7	140
Total γ	70	3.8	63

*Run 6A

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2. Strontium - The separation of strontium is conditioned by 2 factors: (a) a strong tendency to oxidize so as to become incorporated in the slag lattice, and (b) a moderate tendency of strontium ions to diffuse from the slag to the crucible. Nearly quantitative removal of strontium by exaggeration of the favorable factors may be expected.

3. Rare Earths - All the experimental results show the behavior of total rare earths and the rare earth cerium to be strictly parallel. The variations of behavior within the lanthanide series may be expected to be small. The remarks pertaining to strontium also apply to the rare earth elements.

4. Tellurium - The analytical data concerning tellurium are less regular than those for the other elements. If the irregularities are not due to analytical uncertainties caused by the low counting levels, other explanations must be sought. One possibility is that removal of tellurium takes place by mechanisms not akin to those operating for the previously discussed elements and hence is affected by different variables. Two likely suggestions have been proposed: (a) liquation of an intermetallic compound (UTe?), and (b) incorporation of tellurium as tellurium anions in the slag. Diffusional loss of tellurium takes place to a moderate extent.

5. Zirconium - Zirconium may be characterized as an element which is incorporated into the slag somewhat less readily than strontium or the rare earths but still much more than would be predicted on the basis of its oxide stability alone. To what extent this is due to the fact that the formation of zirconium carbide may play a role cannot be ascertained. Removal of zirconium by diffusional loss takes place to a small extent. In general, the factors that favor the removal of cesium, strontium, rare earths and tellurium do not also enhance the removal of zirconium to any marked extent. A more clean-cut separation of zirconium from uranium by chemical metallurgical means would seem to depend on the development of additional treatments, e.g., exaggerated liquation of added carbide, volatilization of zirconium fluoride, or others.

6. Niobium - The remarks made with respect to zirconium apply with still more force to niobium. It will be of special interest to ascertain whether or not the excellent separation of niobium encountered in the stopper-rod run can be duplicated and, if so, to determine the causative factors.

7. Plutonium - Plutonium behaves in a fairly predictable manner. It is miscible with liquid uranium and forms an ideal solution therein.²³ Extensive, and probably nearly ideal, solid solutions occur among the oxides of the 2 elements. Plutonium is less readily oxidized than uranium, and its

²³Cubiciotti, D., NAA-242.

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retention in the melt is nearly complete except for a small fraction which is lost by diffusion. At the experimental temperature and pressure used in these experiments the loss by volatilization is negligible.

8. Ruthenium - Ruthenium is an easily reduced noble metal, and its loss from the melt is quite negligible by either slagging or diffusion. The small amounts actually encountered in the slag layer can be entirely accounted for by the metal inclusions found therein. The one exceptional observation of ruthenium removal in which a zirconia crucible was employed requires further scrutiny.

9. Molybdenum - Not enough analyses for this element have been made to justify its inclusion in the tabulations. In 3 runs, analyses of starting materials and ingot interiors for molybdenum concentrations were made. The results of these analyses are given in Table XX. In each case, no change within experimental error can be detected. A very probable conclusion from these experiments and from the position of molybdenum in the periodic table and in Table II page 8, is that its behavior is completely analogous to that of ruthenium.

Table XX

ANALYSIS OF MOLYBDENUM IN INGOT INTERIORS AND
STARTING MATERIAL

Material. ORNL irradiated slugs, 300-330 days cooled

Conditions. 4 hr at 1200°C : flowing helium atmosphere, 110 cc/min.

Run	Crucible	g./t. Level	Charge g.	Molybdenum Concentration $\mu\text{g./g. Uranium}$	
				Ingot Interior	Starting Material
7A	UO ₂	7	57.9	1.1	0.8 ₇
12A*	ThO ₂	42	263.2	3.1	3.3
15A	ZrO ₂	42	68.0	3.1	3.3

*Bottom-pour stopper-rod run.

10. Total Beta and Gamma Activities - The gross activities were followed in the experimental work because they afforded an excellent opportunity for cross-checking the individual analytical results. The measurement of these activities has little intrinsic interest unless the irradiation and cooling of the metal has been specified. When the removal of all the individual fission products can be predetermined by means of adequate experimentation the gross removal of fission activity will become calculable as a function of irradiation and cooling time.

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IV. APPLICATION TO NUCLEAR FUEL PROCESSING

The nature of the chemical metallurgical manipulations under discussion does not lead to the expectation that further development can achieve the kind of fission product decontamination now required to make possible non-remote handling of the end product. This circumstance strongly mitigates against the notion that these methods will find application in the complete processing of the fuel of any existing nuclear reactor.²⁴ More likely, the appropriate applications of such new processes will be found in connection with reactors planned for the future, in which the remote handling and re-fabrication features can be made integral with the over-all design. Moreover, because the specific process investigated in this report is one in which plutonium is not separated from uranium, it seems likely that its application can be made most readily to a plutonium-enriched fuel. The Power Breeder Reactor (PBR) is one to which the process under development can be applied in a nearly ideal fashion. First, the PBR is in the planning stage, and hence the concepts of remote processing and refabrication can be integrated in the plan. Second, the fuel material presently planned is uranium enriched with 10 % plutonium. Third, the expected daily turnover of the fuel is small and so is ideally suited to the small batch operations envisioned. Fourth, the PBR operates in the fast neutron region where the nuclear cross-sections of the fission elements are monotonic functions of the atomic number. Consequently, no specific element need be removed to extreme limits, and it is necessary only to remove a gross fraction of total fission product mass; the removal need be only to such a degree that the depression of reactivity by the remainder is readily overcome. Fifth, the burnup of atoms in the PBR core is planned to be so large that the principle purposes of reprocessing are the elimination of radiation damage and the reconstitution of the nuclear components; these functions are readily served by melting, alloying and recasting.

An interim research report like the present one often tends to be written with only the more obvious goals in mind. It may well be that chemical metallurgical processing of nuclear fuels will in the future play a more significant role than is now visualized even by its advocates.

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²⁴A chemical metallurgical operation might find application as a head-end step in connection with existing processes and reactors. Such an operation would serve to effect a bulk removal of fission products in concentrated form and to reduce radiation damage in present processes such as solvent extraction.

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and construction; D. P. Krause and L. E. Ross, for conscientious efforts to meet a demanding schedule of radiochemical analyses; C. E. Crouthamel, for the development of new analytical methods for trace molybdenum and radiosamarium and radioeuropium; D. S. Flikkema for optical and X-ray diffraction analyses; H. H. Chiswick, for photomicrographic examinations; J. Faris, for spectrochemical analyses. The staff members of the Chemical Engineering Division are thanked for stimulating discussion and criticism.

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