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THE EBR-II SKULL RECLAMATION PROCESS

*PART I. GENERAL PROCESS DESCRIPTION
AND PERFORMANCE*

by

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FOREWORD

This report is the first of a series that will be issued under the general title The EBR-II Skull Reclamation Process. This first report of the series is a general description of the process flow sheet and the individual steps involved. Subsequent reports will deal with the laboratory and pilot-plant development work on various aspects of the process.

THE EBR-II SKULL RECLAMATION PROCESS

Part I. General Process Description and Performance

by

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ABSTRACT

A general description of the EBR-II skull reclamation process and a flowsheet showing the individual process steps are presented. The skull reclamation process complements the melt refining process in the EBR-II fuel cycle. After the enriched uranium-fissium alloy used in the first core loading of EBR-II has been processed by melt refining, approximately 10% of the fuel remains in the crucible as a residue of unpoured and oxidized metal. This residue constitutes the "skull." The objectives of the skull reclamation process are: (1) to recover the uranium from the skull, and (2) to remove fission products from the uranium. A large fraction of the fission products removed in the EBR-II fuel cycle are removed in the skull reclamation process.

Liquid metals and molten salts are used as the processing media. Separation of fission products from the fuel is effected primarily by selective reduction of compounds of relatively noble fission product elements by zinc and extraction of the reduced fission product elements into zinc for disposal, and by selective precipitations of a uranium-zinc intermetallic compound and uranium metal from liquid metal solutions. Fission product elements are retained in the supernatant solutions and these are discarded to waste. The precipitated uranium is recovered by removing the supernatant liquid metal and retorting to vaporize the residual solvent metals.

Because the skull constitutes only a small sidestream of material in the overall fuel cycle, only modest uranium recoveries are required. A uranium recovery of about 95% is adequate. The requirements for fission product removal are also modest, particularly for the noble fission product elements, which are deliberately used in the fuel material as alloying elements. Removals of as low as 50% are sufficient for these alloying fission product elements. For other fission product elements, removals of about 90% are adequate. These recovery and purification requirements have been shown to be readily achievable in the skull reclamation process.

Future reports in this series will include more detailed descriptions of the development work underlying the process steps and information on equipment design, materials, and scale-up studies.

I. INTRODUCTION

Pyrometallurgical processes for the recovery of fertile and fissile materials from discharged reactor fuels are being developed with the objective of reducing substantially the fuel costs associated with nuclear power production. Such processes are characterized by high-temperature separation procedures in which the fuel is usually maintained in the metallic state, although in some instances conversions to oxides or halides are employed. Several characteristics of pyrometallurgical processes render them particularly suitable for potential use with power reactors: (1) Since the materials used are stable in very high radiation fluxes, they can accommodate fuels shortly after discharge from the reactor, thereby reducing fuel inventory costs. (2) The procedures are relatively straightforward, with a minimum of operations and process vessels. (3) The processes are compact, and the equipment is of a modest size. (4) The fission product wastes are in a concentrated, dry form which contributes to ease of disposal.

Pyrometallurgical separations do not provide highly efficient decontamination from fission products. As a result of their radioactivity, remote refabrication of the fuel is necessary. This is not a serious disadvantage, however, since the buildup of certain isotopes of the fissile and fertile materials (uranium-237, for example) also precludes direct refabrication of the fuel, especially after extensive recycling. The principal disadvantage of pyrometallurgical processes in the past has been the lack of suitable corrosion-resistant, high-temperature materials for use in process equipment. Recent developments in commercially available refractory metals and ceramics have largely eliminated this problem.

The first plant-scale application of pyrometallurgical fuel reprocessing techniques is for the Experimental Breeder Reactor No. 2 (EBR-II) at the National Reactor Testing Station in Idaho. The EBR-II is a fast power breeder reactor designed to establish the feasibility of fast reactors for central power stations. The EBR-II complex consists of the reactor, a sodium boiler plant, power-generation facilities, and an integrated fuel reprocessing plant.[1] Although the EBR-II reactor will ultimately employ plutonium as the core fuel, an enriched uranium alloy will be used as the fuel in the initial core loading.

Several pyrometallurgical schemes are being developed for use in the EBR-II fuel cycle. Of these processes, melt refining[2] is the most advanced, and it will be used to process the first (enriched uranium) core (see Figure 1). The fuel pins are about 0.144 in. in diameter and are clad with stainless steel thermally bonded by sodium in the annulus. In the melt refining process the fuel pins are declad mechanically, chopped to convenient lengths (about 2 in.), and charged to a lime-stabilized zirconia

crucible. The charge is melted, held at 1400°C for about 3 hr, and then poured into a mold to form a product ingot. This treatment removes approximately two-thirds of the fission products through volatilization of some fission product elements and selective oxidation of others, by the zirconia crucible, to form a dross. Noble metal fission products such as zirconium, niobium, molybdenum, and ruthenium are not removed by melt refining. Thus, the recycled fuel becomes a uranium-noble metal alloy, designated as "fissium" alloy. To avoid a fuel of changing composition, inactive noble metals have been alloyed with the initial fuel in their approximate equilibrium concentrations.* The presence of noble metals has proved to lend desirable irradiation stability to uranium.

Figure 1

SIMPLIFIED FUEL CYCLE FOR THE
FIRST CORE LOADING OF EBR-II
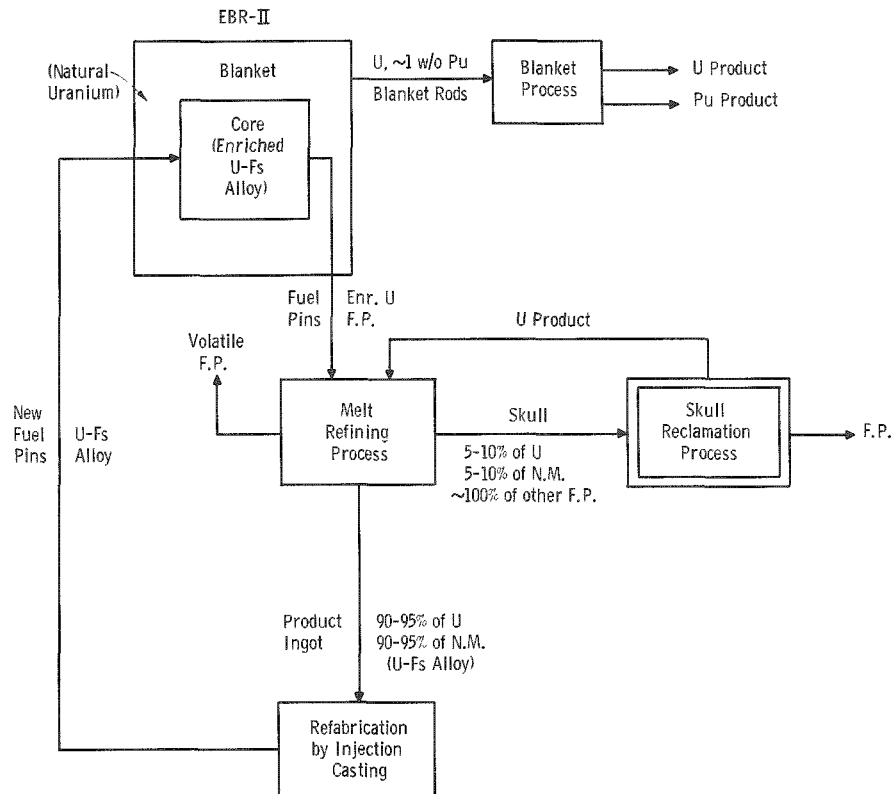
Note: For convenience, the following abbreviations are used occasionally throughout this report:

F.P. = fission products

N.M. = noble metals

Fs = fissium

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*Uranium-5% fissium alloy selected for the initial EBR-II core fuel has the following composition (w/o): Zr (0.1), Nb (0.01), Mo (2.46), Ru (1.96), Rh (0.27), Pd (0.19), balance uranium.

When the product ingot is poured in the melt refining process, about 5 to 10% of the uranium remains in the crucible as a skull constituting a mixture of dross and unpoured metal. In addition to uranium, the skull contains 5 to 10% of the original noble metal content and nearly all of the more electropositive fission product metals, such as yttrium, the rare earths, barium, and strontium. A liquid metal process, named the skull reclamation process, has been developed for processing melt refining skulls with three objectives to be achieved: (1) recovery of the uranium fuel in the skull, (2) removal of a sufficient fraction of the noble metal fission products from the recycled uranium to maintain a desired equilibrium concentration of fissium in the primary fuel cycle, and (3) removal of the more electropositive fission product elements which are concentrated in the skull material. Furthermore, it must produce a product suitable for reintroduction into a melt refining charge.

The percentage of noble metals which must be removed depends upon the fuel burnup and the fraction of the discharged fuel that enters the skull reclamation process. In the EBR-II fuel cycle, noble metals are removed only in the skull reclamation process. Therefore, to maintain any particular fuel composition, the removal of noble metals must be equivalent to the amount generated in the reactor. For a skull fraction of about 7% of the fuel charge, to melt refining, and a fuel burnup of 2%, complete removal is required to maintain the present fissium alloy composition with respect to all alloying elements except zirconium. If the skull fraction exceeds 7% or if the fuel burnup is lower than 2%, the required removal of noble metals is proportionately reduced. For example, if the skull fraction is 10% of the fuel charge (at a burnup of 2%), noble metal removals of only about 70% are required. If fuel burnups higher than 2% are achieved or if, at a 2% burnup, skull fractions are less than 7%, the concentrations of alloying elements would gradually increase to a higher equilibrium value even if completely removed in the skull reclamation process. Because metallurgical scrap is also likely to be processed in the skull reclamation process, thereby effectively increasing the fraction of the fuel going through the process, it is possible that noble metal removals as low as 50% will suffice.

Zirconium is present in the initial fissium alloy at a concentration much lower than its equilibrium concentration (0.1% as compared with about 3.5%), and its concentration in the fuel will simply increase a total of about 0.25% with each fuel cycle (e.g., from 0.1 to 0.35% after the first cycle). The rate of increase in zirconium content is relatively unaffected by zirconium removal in the skull reclamation process, since only 10% or less of the fuel is handled in this process. At equilibrium, the required zirconium removal is the same as that for other noble metals as discussed in the previous paragraph.

Rare earth fission products, and to some extent alkaline earth fission products, are concentrated in the skull material and must be largely

removed in the skull reclamation process. The required removal is some-
what arbitrary, since some recycle back to melt refining could be tolerated
Therefore, a 90% removal of these elements is regarded as adequate

An overall fuel recovery of about 99.5% is sought in the EBR-II fuel
cycle. If 10% of the fuel passes through the skull reclamation process, the
required uranium recovery is 95%; if the fraction is 5%, the required re-
covery is only 90%. These are modest recovery requirements.

Although the skull reclamation process has been developed as an
adjunct to melt refining, it is also considered to be a back-up procedure
capable of processing EBR-II fuel directly in the event of difficulties with
melt refining. In this case, the required fuel recovery would be 99.5%.

It is the purpose of this report to provide a general description of
the skull reclamation process and to indicate its capabilities and limitations.
This is the first of a series of reports on the skull reclamation process. In
succeeding reports, the research and development work on individual steps
materials of construction, process demonstrations, and process scale-up
will be discussed in detail.

II. PROCESS DESCRIPTION

The skull reclamation process is illustrated schematically in Figure 2. The basic steps of this process are:

(1) Oxidation of the skull within the melt refining crucible to convert the skull to a freely flowing powder which can be readily poured from the crucible.

(2) Selective reduction with zinc at 800°C of noble fission product element compounds from a suspension of the oxidized skull material in a molten halide salt flux, and extraction of the noble metals into zinc. The zinc phase is discarded to waste.

(3) After removal of the zinc phase, reduction at 800°C of the uranium oxides contained in the molten flux suspension by magnesium, present in an approximately 5 w/o Mg-Zn alloy. On reduction, the uranium dissolves in the magnesium-zinc alloy.

(4) Precipitation of the uranium as a uranium-zinc intermetallic compound by cooling the alloy solution from 800°C to about 525°C, after which the supernatant phase is removed.

(5) Decomposition of the intermetallic compound and precipitation of uranium metal by addition of magnesium to about a 50 w/o concentration, followed by removal of the supernatant liquid.

(6) Dissolution of the uranium metal product in a zinc-magnesium alloy.

(7) Transfer of the resulting solution of uranium (containing about 12 w/o uranium) to a retort where the solvent metals are vaporized. The product uranium metal is then recycled by adding it to a melt refining process charge.

A. Skull Oxidation

The purpose of the skull oxidation step is to provide a method for essentially completely removing skull material from the zirconium oxide melt refining crucible. The skull oxidation may be carried out at 700 to 800°C in an approximately 20 v/o oxygen-argon atmosphere. As the oxidation proceeds, the oxygen concentration may have to be increased to maintain the desired oxidation rate. Under these conditions the skull oxidation proceeds smoothly and is usually complete within 8 hr.

Iodine is expected to be the major activity evolved during skull oxidation. Special off-gas-handling procedures are required which either trap the iodine, hold it up for decay, or accomplish controlled dispersal into the

Figure 2

EBR-II LIQUID METAL PROCESS FOR RECLAMATION OF MELT REFINING SKULLS

DILUTE O_2-ARGON MIXTURE

OXIDES OF URANIUM AND FP'S

CHLORIDE FLUX

ZINC

DILUTE Mg-Zn ALLOY (5 w/o Mg)

WASTE CHLORIDE FLUX (~IgU) Ba, Sr

URANIUM OXIDE-FLUX LAYER

NOBLE METAL FP'S IN ZINC

U-Mg-Zn

NOBLE METALS Ru, Mo, Rh, Pd, Ag IN ZINC (<IgU)

MELT REFINING CRUCIBLE CONTAINING SKULL MATERIAL (~IKg U)

SKULL OXIDATION AT 700°C

NOBLE METAL EXTRACTION 700°-800°C (VESSEL A)

URANIUM OXIDE REDUCTION 800°C (VESSEL A)

Mg TO DECOMPOSE INTERMETALLIC

Zn and Mg

Mg-Zn CONDENSATE

U PRODUCT SOLUTION

Mg-RICH SUPERNATANT PLUS RARE EARTHS (~I0g U)

WASTE Mg-Zn SUPERNATANT PLUS Zr (~20g U)

RETORT (600°-850°C) TO REMOVE RESIDUAL Mg & Zn (VESSEL B)

DISSOLVE U CONCENTRATE TO GIVE 12 w/o U-12 w/o Mg-Zn ALLOY (800°C) (VESSEL A)

CONVERT U-Zn INTERMETALLIC TO METAL PPT. (800°C). COOL TO 425°C FOR PHASE SEPARATION (VESSEL A)

COOL TO 525°C TO PPT. U-Zn INTERMETALLIC (VESSEL A)

~960g U PRODUCT RETURN TO MELT REFINING

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atmosphere. The disposal of the oxygen-containing combustion atmosphere also requires special gas-handling techniques, since it is not permissible to contaminate the inert argon blanketing gas in the EBR-II processing cell with oxygen.

After oxidation, the oxidized skull material is dumped from the crucible. Carefully designed mechanical equipment will be necessary for this operation in which it will be necessary to prevent fragmentation of the zirconia crucible and the escape of oxide dusts.

B. Noble Metal Extraction

The purpose of the noble metal extraction step is to effect a separation of the noble metal fission product elements from uranium. The noble metal elements consist mainly of molybdenum, ruthenium, rhodium, and palladium, along with small quantities of silver, cadmium, and antimony. Although several metals are capable of reducing oxides or other compounds of the noble elements without reducing the uranium oxides to uranium metal, zinc is the logical choice because it is a constituent of the magnesium-zinc alloy used in the subsequent reduction step.

A chloride flux is employed to suspend the skull oxides (approximately 20 w/o skull oxide concentration) and to make possible a clean separation of the extractant metal phase. The skull oxides are preferentially wet by the flux and therefore remain suspended in it. As a result, there is no oxide contamination of the metal phase.

The flux composition is dictated largely by the requirements of the subsequent step for reduction of uranium oxide. The flux most likely will consist of 47.5 m/o $MgCl_2$, 5 m/o MgF_2, and 47.5 m/o $CaCl_2$ or LiCl Approximately a 1-to-1 volume ratio of flux to metal is employed. Good mixing of the flux and metal phases is required for efficient extraction of the noble metals. Satisfactory extraction of noble metals has been achieved within 4 hr at 800°C. Operation at lower temperatures is feasible, but longer extraction times would probably be necessary.

The phases will be separated by freezing the flux phase (m.p., ~600°C) and siphoning off the zinc phase (m.p., 420°C). This separation is complicated by the fact that the larger particles of oxide, wetted by flux, settle to the bottom of the crucible. Since the zinc phase is thereby displaced upward to a position slightly off the bottom of the crucible, a special technique is necessary to effect removal of the molten zinc. In effect, this technique consists of back-blowing argon through the transfer tube during solidification of the salt to maintain a zinc sump around the tip of the transfer tube.

To provide the necessary corrosion resistance to the molten metal and flux phases, a tungsten crucible will be used for the noble metal extraction and succeeding steps up to the final retorting step

Zinc chloride will be employed as an oxidizing agent in the flux phase. The presence of $ZnCl_2$ would prevent loss of any uranium metal which might not have been oxidized in the skull oxidation step. In the absence of $ZnCl_2$, any such uranium would be dissolved by the zinc and ultimately be lost in the zinc waste stream. The $ZnCl_2$ will also oxidize uranium and magnesium present in the crucible heel remaining after removal of the uranium product solution. This heel results from present plans to use the same tungsten crucible for the noble metal extraction through uranium product dissolution steps. Consequently, it is necessary to consider the effects of heels and their compositions on the succeeding operations.

The quantity of $ZnCl_2$ employed may be adjusted to meet the needs of a particular situation. Because $ZnCl_2$ is fairly volatile, the oxidation of uranium and magnesium will be conducted at as low a temperature as is practical, i.e., around 650°C. The concentration of $ZnCl_2$ may be kept low by adding it incrementally.

Through the use of $ZnCl_2$ in the noble metal extraction step, it is possible that non-decannable EBR-II fuel pins (warped pins or pins broached by uranium) can be handled in this step. The uranium would be oxidized and extracted into the flux phase while the relatively noble metal constituents of the stainless steel can (iron, nickel, and chromium) would be expected to remain in the zinc phase. This possibility has received some preliminary experimentation with results about as indicated.

C. Uranium Oxide Reduction

In the uranium oxide reduction step, uranium oxides suspended in the flux phase are reduced at 800°C to uranium metal by magnesium present in an approximately 5 w/o Mg-Zn alloy. As the reduction proceeds, the uranium metal dissolves in the magnesium-zinc alloy. At complete reduction of the uranium oxides, the uranium concentration in the metal phase is about 4 w/o. The solubility of uranium in the metal phase at 800°C is about 5 w/o. The uranium oxide reduction is effected at 800°C within 4 hr with good mixing. The volume ratio of flux to metal is around 1.

Following the reduction step, the flux phase is removed by pressuring it out through a dip tube. Some consideration is being given to postponing the removal of flux until after the final uranium precipitation step. The MgO byproduct of the reaction is suspended in the flux phase and reaches a final concentration of about 10 w/o. Reduction of uranium oxides is hampered by MgO concentrations above about 12 w/o.

Under the conditions employed in the reduction step, the rare earth oxides, most of the zirconium oxide, and any plutonium oxide which is present are also reduced. Barium, strontium, and cesium remain in the

flux. Rare earths and zirconium are, therefore, the principal contaminants accompanying uranium at the conclusion of the reduction step.

D. Precipitation of Uranium-Zinc Intermetallic Compound

By cooling the uranium-magnesium-zinc solution produced in the uranium reduction step from 800 to 500°C, essentially complete precipitation of the uranium as a uranium-zinc intermetallic compound occurs. After the precipitate has settled to the bottom, the supernatant phase is removed and discarded.

This step serves a two-fold function: (1) volume reduction, and (2) uranium decontamination. By precipitation of the uranium and removal of the supernatant liquid metal, the uranium is concentrated from 4 w/o to 12-15 w/o. Zirconium is the only major fission product removed in the supernatant phase. The other fission products, including the rare earths, and plutonium coprecipitate extensively with the uranium. However, removal of zirconium in this step is important, since no other step in the process provides for sufficient zirconium removal.

Two uranium-zinc intermetallic compounds have been identified in the uranium-zinc-magnesium system: (1) a compound designated "delta," having the formula U_2Zn_{17}, and (2) a compound called "epsilon," which has the approximate composition U_2Zn_{23}. The phase-diagram boundaries for these compounds have not yet been fixed, particularly in the ternary system.

From a process standpoint, it is desirable to precipitate the epsilon phase because it possesses much better settling characteristics than does the delta phase, and thus provides a better opportunity for clean and maximum separation of the supernatant phase. Experience has shown that there is a likelihood of precipitating the delta intermetallic compound if the magnesium concentration is much above 5 w/o. Therefore, to insure formation of the delta compound, the magnesium concentration is held below 5 w/o, generally in the region of 3 to 5 w/o.

E. Intermetallic Compound Decomposition and Uranium Metal Precipitation

Uranium metal is liberated by extracting the zinc from the intermetallic compound with magnesium. During the course of the intermetallic compound decomposition, the uranium metal sinters and clumps into aggregates of various shapes having fairly high uranium densities. These settle very well, thus permitting efficient removal of the supernatant phase.

Magnesium is added to the intermetallic compound concentrate to produce a 50 w/o magnesium-zinc alloy. This composition is near that of a eutectic in the magnesium-zinc system at about 47 w/o magnesium. The

eutectic melts at about 350°C, and although the eutectic valley is fairly narrow, on cooling to about 425°C, a latitude of about -10 and +4% in the magnesium concentration is available. Outside of this permissible concentration variation, magnesium or a magnesium-zinc compound will begin to precipitate. By cooling to 425°C, the uranium solubility is reduced to approximately 0.03 w/o. At 800°C, the uranium solubility is in the neighborhood of 0.3 w/o.

In experimental work to date, magnesium has been added as a solid to the intermetallic concentrate and both have been heated to 800°C to effect the intermetallic compound decomposition. Stirring has been ' employed above about 700°C.

Alternative procedures are now under investigation. The reaction of the solid phases is slow, so the minimum temperature for the decomposition will probably be 650°C, the melting point of magnesium. In addition to temperature, the method of magnesium addition (whether as a solid or a liquid), the digestion time, and rate of cooling are yet to be established.

The rare earth elements and plutonium do not coprecipitate with uranium metal. Therefore, in the course of the intermetallic compound decomposition, they are liberated and dissolve in the eutectic phase. Separation of these elements from uranium is then effected by removal of this supernatant phase. It is expected that at least a 90% removal of the supernatant phase can be realized. Separation of these elements to an extent greater than that provided by the particular percentage removal of the supernatant phase would require washing of the uranium product.

F. Dissolution of Uranium Product Metal

The uranium product is dissolved in a 14 w/o magnesium-zinc alloy at 800°C to give a final solution containing about 12 w/o uranium, 12 w/o magnesium, and the balance zinc. This solution will be transferred out of the crucible into the retorting vessel or cast into a mold for later transfer to the retorting vessel.

It may be necessary, prior to transfer of the product solution, to immobilize a flux heel which remains after the transfer of the flux phase to waste. This flux carries through the two uranium precipitation steps but causes no difficulty since it is solid at the temperatures at which the supernatant phases are transferred. However, it is molten at 800°C, the temperature at which the product solution is transferred, and, therefore, could be transferred with the product. This is highly undesirable, since the MgO and other oxides which are present in the flux would contaminate the final uranium product. To assure removal of a clean metal phase, the flux heel can be solidified by adding, prior to transfer of the product solution, all of the MgF_2, a high-melting-point constituent of the flux, required

in the flux phase for the succeeding step for noble metal extraction. This step is the first step to be performed on the next batch of skull oxide.

G. Retorting

A retorting operation is used to remove the residual magnesium and zinc associated with the uranium metal product after the intermetallic compound is decomposed. The vaporization of the magnesium and zinc can be effected under a variety of conditions, e.g., atmospheric pressure at temperatures in the range from 900 to 1100°C, or at lower pressures and correspondingly lower temperatures.

The uranium product may be poured from the crucible as a liquid or solidified and dumped from the crucible, but to avoid tipping a rather large crucible, it is more likely that it will be solidified and removed by tongs or some other suitable mechanism.

III. GENERAL OPERATING PROCEDURES AND
ENGINEERING EQUIPMENT CONCEPTS

Development work on the skull reclamation process has progressed through a series of small-scale (100 g of uranium) process demonstrations and preliminary operation of a pilot plant (1.5-kg-uranium scale, which is about 1/3 full plant scale). Although still in an evolutionary stage, operating procedures and equipment concepts are described below.

In order to oxidize the skull material in a melt refining crucible, the crucible is first placed in a tight-fitting stainless steel can which holds the fragile, and possibly cracked, crucible together during the oxidization operation. The crucible will be lowered into a narrow cylindrical tank which is closed at the top by a cover or flange sealed in place by a liquid metal freeze seal. A "Calrod" type of electric heater coil, of about 1.5-kW capacity, is suspended from the cover and fits into the crucible when the cover is in place. The heater is employed to heat and maintain the crucible at the oxidation temperature of about 700°C.

Subsequent process steps up to the retorting step are, according to the presently favored operating procedure, to be conducted in a single tungsten crucible. Previous to operation in a single tungsten crucible, the 4 w/o-uranium solution produced in the reduction step was transferred from a tungsten crucible to a beryllia crucible where the uranium-precipitation steps were performed. The use of a single tungsten crucible was suggested relatively late in the development of the process, mainly because of the poor performance of large beryllia crucibles, but has proved to be an attractive procedure since it eliminates one crucible and an entire furnace unit required for housing and heating the crucible.

The design concept of the pilot-plant equipment for the liquid metal process steps is shown in Figure 3. The equipment consists essentially of a large (12-in. OD by 19-in. high) tungsten crucible which is positioned centrally within a metal bell jar (about 30 in. in diameter by 40 in. high). The bell jar cover will be tightly sealed for maintenance of a high-purity inert atmosphere within the bell jar. Heating will be effected by means of a graphite susceptor heated by uncooled induction coils. Solution removal for the necessary phase separations will be effected by pressuring the liquids out through dip tubes, a procedure known as pressure siphoning. Although it is thought that the full plant-scale equipment will be similar to the pilot-plant equipment, the induction coils may be located outside the bell jar in the plant equipment. This would require the use of a more tightly fitting bell jar or container around the crucible than that shown in Figure 3.

AGITATOR
MOTOR

PORTS FOR TRANSFER
LINES, SAMPLERS, AND
LIQUID-LEVEL MEASUREMENT
DEVICES

REMOVABLE
BELL COVER

FUME TRAP

INDUCTION
COIL

METAL FREEZE
SEAL

WASTE CONTAINER
OR PRODUCT
SOLUTION RECEIVER
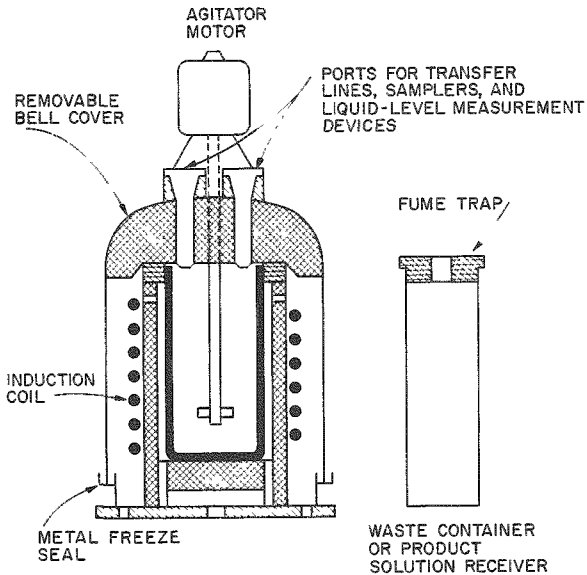
Figure 3

PREPLANT VERSION OF
SKULL RECLAMATION
PROCESS EQUIPMENT

The major operations for phase separation are:

1) Separation of molten zinc containing noble fission elements from the flux containing the skull oxide after noble metal leach in the first crucible. This separation is made by cooling to about 500°C, which freezes the flux but leaves the zinc molten. The zinc is then pressure siphoned from beneath the solidified flux to a waste container.

2) Removal of the flux phase after the reduction step by pressure siphoning molten flux at 800°C to a waste container. The pressure employed is sufficient to transfer the flux phase but not the underlying, more dense metal solution. During transfer of flux, the transfer tube is slowly lowered into the flux phase. The transfer of material stops when the transfer tube enters the metal phase. Consideration is also being given to postponing the removal of the flux phase until after removal of the metal supernatant solution of the final uranium precipitation step. This would permit removal of all liquid materials, the flux and metal waste solutions, and the final uranium product solution through a fixed transfer tube having its open end near the bottom of the crucible. The use of a fixed transfer tube would simplify remote operations.

3) Separation of a 5% magnesium-zinc supernatant solution from the precipitated uranium-zinc intermetallic compound at about 525°C by pressure siphoning the zinc to a waste container.

4) Separation of the 50% magnesium-zinc supernatant from the precipitated uranium. The separation is made at about 425°C by pressure siphoning the magnesium-zinc solution to a waste container.

5)   Removal of the uranium product solution, an approximately 12 w/o uranium-12 w/o magnesium-zinc solution, by pressure siphoning the solution at 800°C to a mold or to the retorting crucible.

6)   Removal of the solvent metals, magnesium and zinc, from the uranium by vaporizing them in a retorting operation.

As pointed out above, the uranium will be removed from the tungsten crucible by dissolving it to a 12 w/o concentration in a 14 w/o magnesium-zinc solution and transferring the solution to a mold or directly to a retorting crucible. Vaporization of the solvent metals in the retorting step will be effected at a low pressure, probably less than 10 torr. It is presently planned to perform the retorting operation in a melt refining furnace unit by placing a radiation-cooled condenser above the retorting crucibles. The retorting crucible will probably be a beryllia crucible or a crucible of another material which has been internally coated with beryllia. Considerable work is required before a definite selection of crucible materials can be made.

It has also not yet been decided whether the uranium metal product should be removed from the retorting crucible as a sintered cake or whether it should be further consolidated by melting it. If the uranium product is melted, it may be poured from the crucible and cast in a mold.

Materials of Construction. The only metallic materials which have good resistance to attack by the molten metal and halide salt systems of the skull reclamation process are tungsten and certain tungsten alloys. Tungsten, which is virtually unattacked by these systems, has been selected for the crucible material for the steps involving liquid metals. Because tungsten is difficult to machine, auxiliary items, such as agitators and transfer tubes, will be fabricated from a 30 w/o tungsten-molybdenum alloy. This alloy, although less resistant to corrosion than tungsten, appears suitable for these purposes.

It is intended to use a beryllia or beryllia-coated crucible for the retorting operation since beryllia is not significantly attacked or wetted by molten uranium.

Bell jars and other enclosing vessels will be fabricated of a 300 series stainless steel. Internal stainless steel surfaces which are exposed to attack by metal and salt vapors may have to be protected by tungsten coatings or tungsten shields.

IV. FLOWSHEET AND PROCESS PERFORMANCE

A detailed flowsheet indicating stream compositions, fates of uranium and fission products, activity levels, and fission product heating values is given in Tables 2 through 8 beginning on page 19.* In Table 1 useful design information derived from the detailed flowsheet is summarized.

Table 1

SUMMARY OF PERTINENT DESIGN INFORMATION FOR SKULL RECLAMATION PROCESS

(Basis: approximately 10 kg of uranium)

Operation or Steam	Stream No.	Handling Temp (°C)	Weight (kg)	Volume (liters)	Activity Level (Curies)	Fission Product Heating [Btu/hr (β + 10% γ)]
Ten Melt Refining Skulls and Crucibles	1	~700	104.3	50	1.8×10^6	16,000
Oxidizing Gas	2	30	1.9	1334	0	0
Skull Oxidation Off-gas	3	30	0.04	24	~2000	0
Waste Gas	4	30	0.04	24	0	0
Ten Separate Oxidized Skulls	5	~700	11.9	4	1.3×10^6	11,500
Crucible Waste	6	~100	94	50	4.9×10^5	4,460
Zinc to Noble Metal Extraction	7	30	143	23	0	0
Flux to Noble Metal Extraction	8	30	39.5	20	0	0
Total Charge to Noble Metal Extraction	-	800→500	200	50	1.3×10^6	11,500
Excess ZnCl$_2$	9	~30	0.8	146	0	0
Zinc Waste from Noble Metal Extraction	12	500	132	21	2.3×10^{-3}	86
Flux Heel from Product Solution Step	13	800	2.2	1	1.1×10^4	100
Noble Metal Extraction Flux Product	10	500→800	52	29	1.3×10^6	11,600
Metal Heel to Reduction	11	800	14.7	3	2520	10
Zinc-5% Mg to Reduction	14	30	198	37	0	0
Total Charge to Reduction Step	-	800	264	65	1.3×10^6	11,600
Flux Waste from Reduction	15	800→50	42.3	20	2.0×10^5	1,815
Zinc Product Solution from Reduction	16	800	220	39	1.1×10^6	9,700
Intermetallic Compound Pptn Step	-	800→525	22	39	1.1×10^6	9,700
Zinc Waste from Int Compound Ppt Step	18	525→~50	147.1	27	1.5×10^5	1,100
Intermetallic Compound Cake	17	500	73.1	12	9.6×10^5	8,600
Magnesium Charge to Uranium Ppt	19	30	60.9	39	0	0
Total Charge to Uranium Ppt	-	800→425	133	51	9.6×10^5	8,600
Metal Waste from U Ppt	20	425→~200	119	48	8.4×10^5	8,000
Supernatant Metal to U Solution	21	425	6.2	2	4.4×10^4	415
U Product to Solution	22	425	8.8	0.5	7.4×10^4	190
Product Solution Step	-	800	75	15	1.2×10^5	610
Metal to Product Solution	23	30	58.8	12	0	0
Product Solution Heel to Noble Metal Extraction	25	800	3.7	0.8	6.5×10^3	40
U Product to Retorting	24	800	69	15	1.1×10^5	570
Retorting Step	-	700→900	69	15	1.1×10^5	570
Metal Condensate	26	900→50	60.6	14.5	Nil	Nil
U Product	27	900→~50	8.4	0.5	1.1×10^5	570

*In order to facilitate material balance calculations, many more figures are shown than are significant.

Table 2

EQUILIBRIUM MATERIAL BALANCE AROUND THE SKULL OXIDATION STEP

Flow diagram: (4) Waste Gas → Fiberfrax Trap ← (3) Skull Oxidation Off-gas ← Skull Oxidation (10 batches) 700-800°C, 4 hr/batch. (1) 10 Melt Refining Skulls and Crucibles[a] → box. (6) Crucible Waste. (5) Skull Oxide (97.5% Transfer[d]). (2) Oxidizing Gas – O₂ and Argon[b].

1 — Ten Melt Refining Skulls and Crucibles[a]

Constituent	Grams
U	7,760.7
UO₂	979.5
Pu	95.1
PuO₂	12.0
Kr	~0.0
Rb₂O	1.1
SrO	79.5
Y₂O	44.5
Zr	137.1
ZrO	70.4
Nb	5.7
Mo	212.9
Tc	32.9
Ru	165.6
Rh	27.1
Pd	17.4
Ag	0.1
In	0.1
Sn	0.3
Sb	0.2
Te	21.3
Cs₂O	8.6
BaO	93.9
(RE)₂O₃	682.1
I (5000 Curies)	2.0[c]
ZrO₂	
Crucibles	93,775.7
Total	104 179.1
Curies	1,819,477
Btu/hr	15,984
Volume	~50 liters

2 — Oxidizing Gas[b]

Constituent	Grams
O₂	1887.0
Ar	34.0
Total	1921.0

3 — Skull Oxidation Off-gas

Constituent	Grams
O₂	7.0
Ar	34.0
Kr	0.0
Xe	0.0
I (2000 Curies)	0.8
Total	41.8

4 — Waste Gas

Constituent	Grams
O₂	7.0
Ar	34.0
Kr	0.0
Xe	0.0
I₂	(?)
Total	41.0

5 — Skull Oxide (97.5% Transfer)

Constituent	Grams
U₃O₈	9,928.0
PuO₂	116.8
Rb₂O	0.2
SrO	15.9
Y₂O	35.5
ZrO₂	204.2
(Fission Product)	
ZrO₂	119.0
(Crucible Fragments)	
Nb₂O₅	12.4
MoO₃	251.7
TcO	43.5
RuO₂	216.3
RhO₂	35.3
PdO	22.6
Ag₂O	0.1
In₂O	0.1
SnO₂	0.4
Sb₂O	0.2
TeO	25.0
Cs₂O	1.2
BaO	18.8
(RE)₂O₃	613.9
I (3000 Curies)	1.2[d]
Total	11,692.6
Curies	1,328,132
Btu/hr	11,528
Volume	~4 liters

6 — Crucible Waste

Constituent	Grams
U₃O₈	255.0
PuO₂	3.0
Rb₂O	0.9
SrO	63.6
Y₂O₃	9.0
TeO₃	1.7
Cs₂O	7.4
BaO	75.1
(RE)₂O₃	68.2
ZrO₂	
Crucibles	93,881.0
Total	94,364.9
Curies	489,345
Btu/hr	4,456
Volume	~50 liters

[a]Bases: Fuel burnup 2% of heavy atoms in 135 days. Fission product concentrations are those of 10th pass. Total skull weight – 10 kg, i.e., 10 skulls each weighing about 1 kg. In accumulating 10 skulls for processing, the cooling times would become approximately 15 days for the last skull, 15 days for the preceding one, etc.

[b]Argon used as oxygen diluent in oxidation furnace; oxygen supplied as required to sustain reaction.

[c]Based on 1/16th of iodine in melt refining charge plus decay corrections.

[d]It was assumed that no loss of iodine would occur in oxide handling; however, an iodine loss of as much as 0.5% may occur.

Table 3

EQUILIBRIUM MATERIAL BALANCE AROUND THE NOBLE METAL EXTRACTION STEP
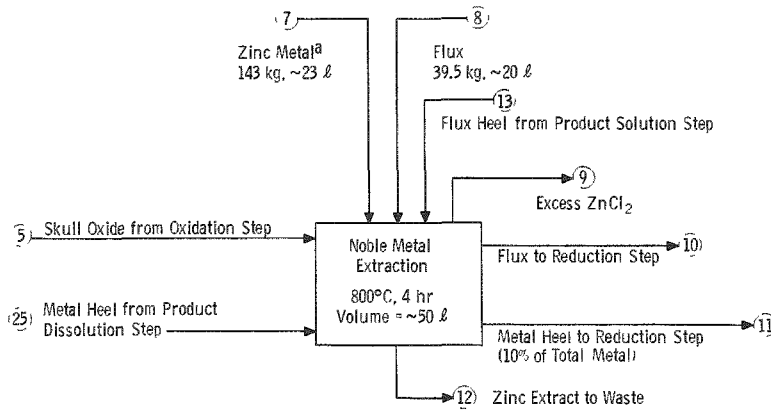
Stream						
(5)	(7)	10	(11)	(13)	25

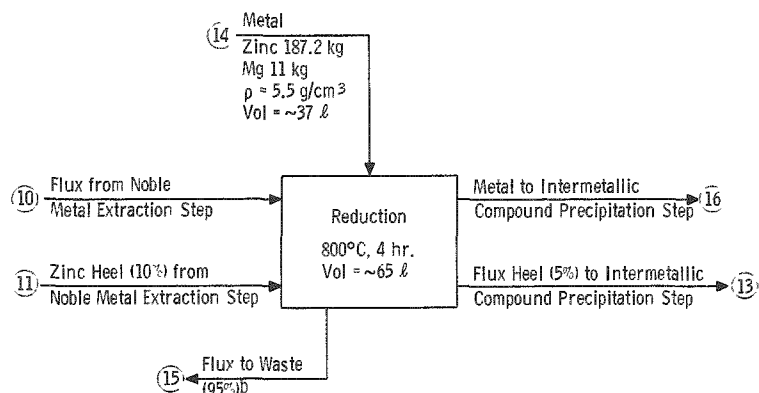| Skull Oxide from Oxidation Step		Zinc Metal		Flux to Reduction Step		10″ Metal Heel to Reduction Step		Flux Heel from Product Solution Step (5 % of total flux)		Metal Heel from Product Dissolution Step	
Constituent	Grams	Constituent	Grams	Constituent	Grams	Constituent	Grams	Constituent	Grams	Constituent	Grams
U_3O_8	9,928.0	Zinc	143,400	$CaCl_2$	21,263.2	Zinc	14,692.0	$CaCl_2$	1,063.2	Mg	436.0
PuO_2	116.8	ρ 6 3 g/cm^3		$MgCl_2$	17,075.2	Mo	19.2	$MgCl_2$	862.7	Zn	2,816.5
Rb_2O	0.2			MgF_2	1,263.2	Tc	2.9	MgF_2	63.2[b]	U	436.0
SrO	15.9	Volume - 22.8 liters		MgO	235.6	Ru	14.2	U_3O_8	2.6	Pu	0.3
Y_2O_3	35.8			ZnO	734.0	Rh	2.4	MgO	235.6	Y	0.1
ZrO_2	204 2	(8)		U_3O_8	9,930 6	Pd	1.7	Rb_2O	~0.0	Zr	2.3
(Fission Product)				UCl_3	632.0			SrO	0.8	Nb	0.1
ZrO_2	119.0	Flux		PuO_2	116.8	Total 14 732.4		Y_2O_3	0.2	Mo	0.9
(Crucible Fragment)				$PuCl_3$	0.4			ZrO_2	1.1	Tc	0.1
		Constituent	Grams	Mole %	Rb_2O	0.2	Curies	2,519	TeO_2	1.3	Ru	1.3
Nb_2O_5	12.4				SrO	16.7	Btu/hr	9	Cs_2O	0.1	RE	1.2
MoO_2	281.7	$CaCl_2$	20,200	51.2	Y_2O_3	36.0	Volume	~3 liters	BaO	1.0	Total	3,694.8
TcO_2	43.5	$MgCl_2$	14 456	36.7	YCl_3	0.2			$(RE)_2O_3$	3.1		
RuO_2	216.3	MgF_2[b]	1 200	3.0	ZrO_2	207.2	(12)		MgI_2	~0.1	Curies	6,592
RhO_2	35.3	$ZnCl_2$	3,600	9.1	(Fission Product)				Total	2,235.0	Btu/hr	37
PdO_2	22.6				ZrO_2	119.0	Zinc Extract (90 % Metal Transfer)[a]				Volume	0.8 liter
Ag_2O	0.1	Total	39,456	100.0	(Crucible Fragment)				Curies	11,099		
In_2O_3	0.1				Nb_2O_5	12.5	Constituent	Grams	Btu/hr	99		
SnO	0.4	ρ - 2.0 g/cm^3			MoO_2	28.5			Volume	~1 liter		
Sb_2O_3	0.2	Volume - ~20 liters			TcO_2	4.7	Zinc	132,227.5				
TeO_2	25.0				RuO_2	23.0	Mo	173.0				
Cs_2O	1.2	(9)			RhO_2	3.5	Tc	26.5				
BaO	18.8				PdO_2	2.3	Ru	127.4				
$(RE)_2O_3$	613.9				TeO_2	26.3	Rh	22.0				
(3000 Curies)	1.2	Excess $ZnCl_2$			Cs_2O	1.2	Pd	15.7				
Total	11,692.6	Constituent	Grams		BaO	19.8	Ag	0.1				
					$(RE)_2O_3$	617.0	In	0.1				
Curies	1,328,132	$ZnCl_2$	780		$(RE)Cl_3$	2.1	Sn	0.3				
Btu/hr	11,528				MgI_2 (3000 Curies)	1.5	Sb	0.2				
Volume	~4 liters				Total	52,373.1	Total	132 592.8				
					Curies	1,320,019	Curies	23,285				
					Btu/hr	11,569	Btu/hr	86				
					Volume	~25 liters	Volume	~21 liters				

[a] The amount of zinc employed was based on the desirability of a 90% metal transfer and on the assumption that the heel volume would be 3 liters. This heel volume is equivalent to a 1-in.-thick layer of metal remaining in the crucible. If the heel volume can be reduced, e.g., by use of a crucible with a sloping bottom or built-in sump, the weight of zinc metal charged and of the zinc extract could be correspondingly reduced. Achievement of a 1-liter metal heel would reduce these amounts by a factor of three.

[b] All of the MgF_2 may be charged just before dissolution of the uranium product in order to immobilize the flux heel by producing a salt phase with a melting point higher than that used for dissolution of the uranium (800°C). This would increase the amount of MgF_2 in Stream 13 to 1263 grams and would eliminate MgF_2 from Stream 8.

Table 4

EQUILIBRIUM MATERIAL BALANCE AROUND THE REDUCTION STEP[a]

(14) Metal
Zinc 187.2 kg
Mg 11 kg
$\rho = 5.5$ g/cm^3
Vol = ~37 ℓ

(10) Flux from Noble Metal Extraction Step

(11) Zinc Heel (10%) from Noble Metal Extraction Step

Reduction
800°C, 4 hr.
Vol = ~65 ℓ

Metal to Intermetallic Compound Precipitation Step (16)

Flux Heel (5%) to Intermetallic Compound Precipitation Step (13)

(15) Flux to Waste (95%)[b]

---

(10) Flux from Noble Metal Extraction

Constituent	Grams
$CaCl_2$	21,263.2
$MgCl_2$	17,075.2
MgF_2	1,263.2
MgO	235.6
ZnO	734.0
U_3O_8	9,930.6
UCl_2	632.0
PuO_2	116.8
$PuCl_3$	0.4
Rb_2O	0.2
SrO	16.7
Y_2O_3	36.0
YCl_3	0.2
ZrO_2 (Fission Product)	207.2
ZrO_2 (Crucible Fragments)	119.4
Nb_2O_5	12.5
MoO_2	28.5
TcO_2	4.7
RuO_2	23.0
RhO_2	3.5
PdO_2	2.3
TeO_2	26.3
Cs_2O	1.2
BaO	19.8
$(RE)_2O_3$	617.0
$(RE)Cl_2$	2.1
MgI_2	1.5
Total	52,373.1

Curies	1,320,019
Btu/hr	11,569
Volume	~25 liters

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(11) Zinc Heel (10%) from Noble Metal Extraction

Constituent	Grams
Zinc	14,698.0
Mo	19.5
Tc	3.0
Ru	14.9
Rh	2.4
Pd	1.6
Total	14,739.4

Curies	2,519
Btu/hr	9
Volume	~3 liters

(13) Flux Heel (5%) to Intermetallic Compound Precipitation Step

Constituent	Grams
$CaCl_2$	1,063.2
$MgCl_2$	862.7
MgF_2	63.2
U_3O_8	2.6
MgO	235.6
Rb_2O	~0.0
SrO	0.8
Y_2O_3	0.2
ZrO_2	1.1
TeO_2	1.3
Cs_2O	0.1
BaO	1.0
$(RE)_2O_3$	3.1
MgI_2	~0.1
Total	2,235.0

Curies	11,099
Btu/hr	99
Volume	~1 liter

---

(14) Metal

Constituent	Grams
Zinc	187,172.0
Mg	10,940.0
Total	198,112.0

ρ 5.5 g/cm^3
Volume   ~37 liters

(15) Flux Heel to Waste (95%)

Constituent	Grams
$CaCl_2$	20,200.0
$MgCl_2$	16,390.5
MgF_2	1,200.0
U_3O_8	50.6
MgO	4,713.0
Rb_2O	0.2
SrO	15.9
Y_2O_3	3.4
ZrO_2	21.9
TeO_2	25.3
Cs_2O	1.1
BaO	18.8
$(RE)_2O_3$	58.7
MgI_2	1.4
Total	42,700.8

Curies	201,296
Btu/hr	1,815
Volume	~24 liters

---

(16) Metal to Intermetallic Compound Precipitation Step

Constituent	Grams
Mg	8,090.0
Zn	202,460.5
U(4 w/o)	8,804.4
Pu	103.4
Y	25.5
Zr	228.1
Nb	8.8
Mo	40.5
Tc	6.6
Ru	32.5
Rh	5.1
Pd	3.4
RE	477.1
Total	220,287.9

Curies	1,110,143
Btu/hr	9,664
Volume	~39 liters

---

[a]Bases of reduction operation are: (1) 99.6% reduction of uranium oxides, (2) maximum uranium concentration of 4 w/o in magnesium-zinc solution, and (3) 95% transfer of flux to waste.

[b]The flux transfer may be delayed until after the intermetallic precipitation step, but its composition would be nearly the same as above.

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Table 5

EQUILIBRIUM MATERIAL BALANCE AROUND THE
INTERMETALLIC COMPOUND PRECIPITATION STEP[a]
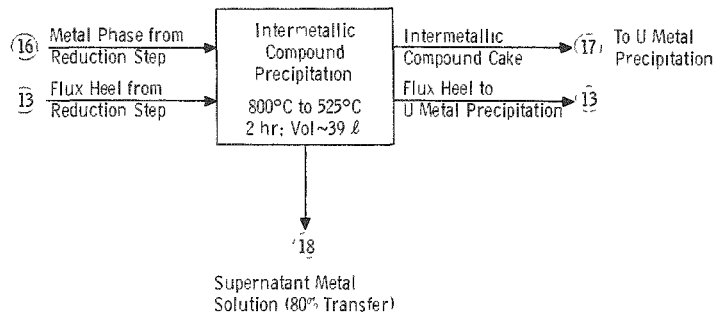
Flux Heel from Reduction or to Uranium Metal Precipitation Step		Metal Phase from Reduction Step		Intermetallic Compound Cake (12% U)		Supernatant Metal Solution (80% Transfer)	
Constituent	Grams	Constituent	Grams	Constituent	Grams	Constituent	Grams
$CaCl_2$	1,063.2	Mg	8,090.0	Mg	1,390.0	Mg	6,700.0
$MgCl_2$	862.7	Zn	202,462.5	Zn	62,321.3	Zn	140,141.2
MgF_2	63.2	U(4 w/o)	8,804.4	U	8,774.4	U(0.002%)	30.0
U_3O_8	2.6	Pu	103.4	Pu	102.4		(0.34 w/o U loss)
MgO	235.6	Y	25.5	Y	18.7[b]	Pu	1.0
Rb_2O	~0.0	Zr	228.1	Zr	45.6	Y	6.8[b]
SrO	0.8	Nb	8.8	Nb	1.8	Zr	182.5
Y_2O_3	0.2	Mo	40.5	Mo	18.8	Nb	7.0
ZrO_2	1.1	Tc	6.6	Tc	1.3	Mo	21.7
TeO_2	1.3	Ru	32.5	Ru	25.5[d]	Tc	5.3
Cs_2O	0.1	Rh	5.1	Rh	1.0	Ru	7.5[d]
BaO	1.0	Pd	3.4	Pd	0.7	Rh	4.1
$(RE)_2O_3$	3.1	RE	477.1	RE	466.8[c]	Pd	2.7
MgI_2	~0.1	Total	220,287.9	Total	73,168.3	RE	10.3[c]
Total	2,235.0					Total	147,120.0
		Curies	1,110,143	Curies	956,150		
Curies	11,099	Btu/hr	9,664	Btu/hr	8,576	Curies	153,993
Btu/hr	99	Volume	~39 liters	Volume	~12 liters	Btu/hr	1,088
Volume	~1 liter					Volume	~27 liters

[a]Basis: 80% transfer of supernatant solution with U_2Zn_{23} as the precipitated uranium phase. This results in an overall U concentration in the intermetallic cake of 12%.
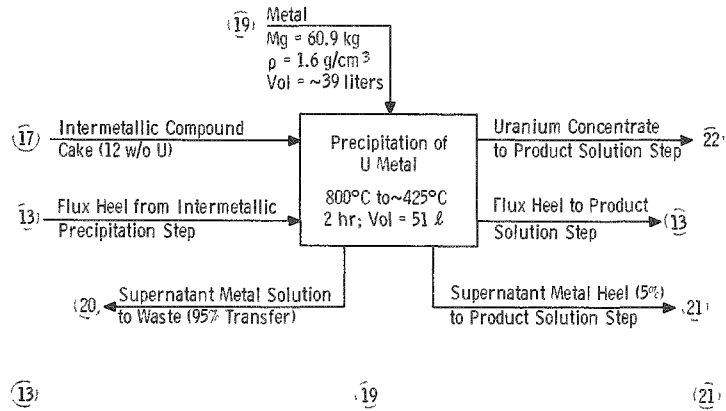
[b]Based on an assumed Doerner-Hoskins coprecipitation coefficient of 0.2.

[c]Based on a Doerner-Hoskins coprecipitation coefficient of 0.66 (see ANL-5924, pp. 135-136).

[d]Based on an assumed ruthenium solubility of 0.005 w/o in zinc in the presence of precipitated uranium. This value agrees with experimental data obtained in pilot-plant-scale runs.

Table 6

EQUILIBRIUM MATERIAL BALANCE AROUND THE URANIUM PRECIPITATION STEP[a]

(19) Metal
Mg = 60.9 kg
ρ = 1.6 g/cm^3
Vol = ~39 liters

(17) Intermetallic Compound Cake (12 w/o U) →

(13) Flux Heel from Intermetallic Precipitation Step →

Precipitation of U Metal
800°C to ~425°C
2 hr; Vol = 51 ℓ

→ (22') Uranium Concentrate to Product Solution Step

→ (13) Flux Heel to Product Solution Step

(20) ← Supernatant Metal Solution to Waste (95% Transfer)

→ (21') Supernatant Metal Heel (5%) to Product Solution Step

(13)

Flux Phase from Intermetallic Compound Precipitation and to Solution Step

Constituent	Grams
CaCl$_2$	1,063.2
MgCl$_2$	862.7
MgF$_2$	63.2
U$_3$O$_8$	2.6
MgO	235.6
Rb$_2$O	~0.0
SrO	0.8
Y$_2$O$_3$	0.2
ZrO$_2$	1.1
TeO$_2$	1.3
Cs$_2$O	0.1
BaO	1.0
(RE)$_2$O$_3$	3.1
Mg	~0.1
Total	2,235.0

Curies	11,099
Btu/hr	99
Volume	~1 liter

(17)

Intermetallic Compound Cake (12 w/o U)

Constituent	Grams
Mg	1,390.0
Zn	62,321.3
U	8,774.7
Pu	102.4
Y	18.7
Zr	45.6
Nb	1.8
Mo	18.8
Tc	1.3
Ru	25.5
Rh	1.0
Pd	0.7
RE	466.8
Total	73,168.3

Curies	956,150
Btu/hr	8,576
Volume	~12 liters

(19)

Metal

Constituent	Grams
Mg	60,931.3

ρ = 1.6 g/cm^3
Volume = 39 liters

(20)

Supernatant Metal Solution to Waste (95% Transfer)

Constituent	Grams
Mg	59,205.3
Zn	59,205.3
U	60.8
Pu	97.3
Y	17.8
Rh	1.0
Pd	0.7
RE	443.5
Total	119,031.7

Curies	838,199
Btu/hr	7,970
Volume	~48 liters

(21)

Supernatant Metal Solution Heel (5% of Total)

Constituent	Grams
Mg	3,116.0
Zn	3,116.0
U	3.2
Pu	5.1
Y	0.9
Rh	~0.0
Pd	~0.0
RE	23.3
Total	6,264.5

Curies	43,702
Btu/hr	415
Volume	~2 liters

(22)

Uranium Concentrate to Solution Step

Constituent	Grams
Mg	–
Zn	–
U	8,710.4
Zr	45.6
Nb	1.8
Mo	18.8
Tc	1.3
Ru	25.5
Total	8,803.4

Curies	74,249
Btu/hr	191
Volume	~0.5 liter

[a]Basis: 95% transfer of metal supernatant solution.

Table 7

## EQUILIBRIUM MATERIAL BALANCE AROUND THE PRODUCT SOLUTION STEP

(13)
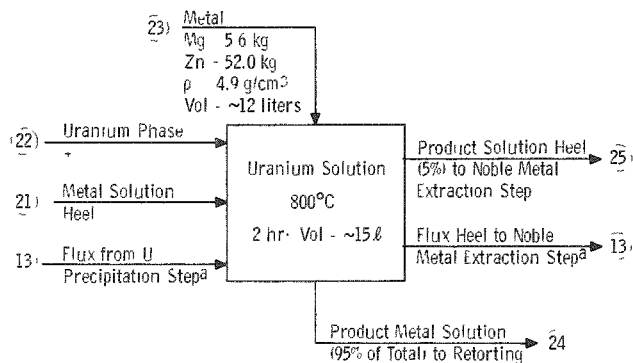
Flux from Uranium Metal Precipitation or to Noble Metal Extraction

Constituent	Grams
$CaCl_2$	1,063.2
$MgCl_2$	862.7
MgF_2	63.2
U_3O_8	2.6
MgO	235.6
Rb_2O	~0.0
SrO	0.8
Y_2O_3	0.2
ZrO_2	1.1
TeO_2	1.3
Cs_2O	0.1
BaO	1.0
$(RE)_2O_3$	3.1
Mg	~0.1
Total	2,235.0

Curies	11,099
Btu/hr	99
Volume	~1 liter

(21)

Supernatant Metal Solution Heel (5% of Total)

Constituent	Grams
Mg	3,116.0
Zn	3,116.0
U	3.2
Pu	5.1
Y	0.9
Rh	~0.0
Pd	~0.0
RE	23.3
Total	6,264.5

Curies	43,702
Btu/hr	415
Volume	~2 liters

(22)

Uranium Phase

Constituent	Grams
U	8,710.4
Zr	45.6
Nb	1.8
Mo	18.8
Tc	1.3
Ru	25.5
Total	8,803.4

Curies	74,249
Btu/hr	191
Volume	~0.5 liter

(23)

Metal

Constituent	Grams
Mg	5,597.6
Zn	51,989.3
Total	57,586.9

$\rho = 4.9 \text{ g/cm}^3$
Volume = ~12 liters

(24)

Product Metal Solution (95% of Total) of Retorting Step

Constituent	Grams
Mg(12%)	8,277.6
Zn(76%)	52,288.8
U(12%)	8,277.6
Pu	4.8
Y	0.8
Zr	43.3
Nb	1.7
Mo	17.9
Tc	1.2
Ru	24.2
RE	22.1
Total	68,960.0

Curies	111,359
Btu/hr	569
Volume	~15 liters

(25)

Product Metal Solution Heel (5% of Total to Noble Metal Extraction Step

Constituent	Grams
Mg(12%)	436.0
Zn(76%)	2,816.5
U(12%)	436.0
Pu	0.3
Y	0.1
Zr	2.3
Nb	0.1
Mo	0.9
Tc	0.1
Ru	1.3
RE	1.2
Total	3,694.8

Curies	6,592
Btu/hr	37
Volume	~0.8 liter

[a] In order to immobilize the flux heel and prevent its transfer with the metal product solution, all of the MgF_2, a high-melting-point constituent of the flux, required in the flux in the succeeding noble metal extraction step (see Table 3), may be added prior to transfer of the metal solution.

Table 8

EQUILIBRIUM MATERIAL BALANCE AROUND THE RETORTING STEP
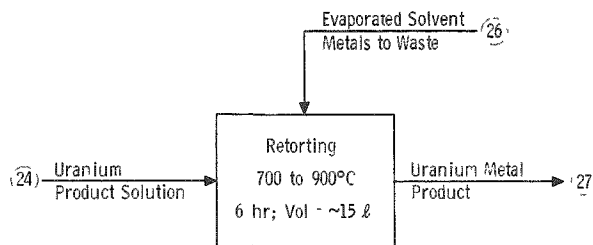
(24) Uranium Product Solution		(26) Evaporated Solvent Metals to Waste		(27) Uranium Metal Product	
Constituent	Grams	Constituent	Grams	Constituent	Grams
Mg	8,277.6	Mg	8,277.6	U	8,277.6
Zn	52,288.8	Zn	52,288.8	Pu	4.8
U	8,277.6			Y	0.8
Pu	4.8	Total	60,566.4	Zr	43.3
Y	0.8			Nb	1.7
Zr	43.3	Volume	~14.5 liters	Mo	17.9
Nb	1.7			Tc	1.2
Mo	17.9			Ru	24.2
Tc	1.2			RE	22.1
Ru	24.2				
RE	22.1			Total	8,393.6
Total	68,960.0				
				Curies	111,359
Curies	111,359			Btu/hr	569
Btu/hr	569			Volume	~0.5 liter
Volume	~15 liters				

Minimum processing losses of uranium based on solubility in waste streams are as follows:

Step	% Uranium Loss
Skull Oxidation	2.5
Noble Metal Extraction	<0.1
Reduction	0.5
Intermetallic Compound Precipitation	0.4
Uranium Metal Precipitation	0.7
Total	4.1

Losses in the intermetallic compound precipitation and uranium metal precipitation steps will be increased by the entrainment of uranium precipitates in the supernatant solutions removed in these steps. Actual losses may be as much as two to three times higher than the minimum losses of 0.4 and 0.7%. The detailed flowsheets are based on the minimum loss values.

Potential fission product decontamination factors as represented by the estimates on which the calculations for the detailed flowsheet are based are as follows:

Fission Product	Percent Removal	Decontamination Factor
Strontium	>99	>100
Yttrium	98	44
Zirconium	82	6
Niobium	81	5
Molybdenum	92	12
Technetium	96	27
Ruthenium	85	7
Rhodium	>99	>100
Palladium	>99	>100
Tellurium	>99	>100
Barium	>99	>100
Rare Earths	96	26

These fission product removals are satisfactory and, in fact, exceed the requirements for skull reclamation.

ACKNOWLEDGEMENT

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