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U^{233} PURIFICATION AND METAL PRODUCTION

by

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ABSTRACT

Two problems are encountered in U^{233} purification and metal production. One is high alpha activity, which requires that all operations be enclosed. The other is beta-gamma activity originating from U^{232} present in U^{233} as a contaminant. Th^{228} , the immediate daughter of U^{232} , produces a chain of strong beta-gamma emitters, which make shielding and thorium separation procedures necessary.

Chemically impure solutions of $U^{233}O_2(NO_3)_2$ from Oak Ridge Thorex product or from metal fabrication residues are separated from trace amounts of thorium isotopes by cation resin exchange in shielded equipment. The short-lived thorium daughters are allowed to decay, after which beta-gamma activity is low enough to permit chemical purification in unshielded equipment.

The U^{233} is chemically separated from nonradioactive contaminants by precipitation as $UO_4 \cdot xH_2O$, which is calcined to U_3O_8 . The U_3O_8 is reduced to UO_2 and converted to UF_4 . Pure metal is prepared by bomb reduction of the UF_4 with calcium as the reducing agent.

Residues from the chemical purification steps, reduction, metal fabrication, and general cleanup are processed into nitrate solutions, solvent extracted, and concentrated for recycle.

Ion exchange, precipitation, reduction to metal, and casting all have effect upon the thorium isotopes and their daughters, resulting in changes in the levels and growth rates of beta-gamma activity.

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1. Introduction

U^{233} was first discovered and isolated in 1942. It belongs to the neptunium radioactive series and is an alpha emitter with a half-life of 1.63×10^5 years. It is produced by the irradiation of thorium with neutrons according to the reaction:

Isolation of U^{233} from thorium is done by a solvent extraction method. When additional separation from thorium is required, an ion exchange step is added.¹

This uranium isotope has interesting and valuable fission characteristics in that it possesses a large cross section for thermal neutrons.

Once macro amounts of U^{233} became available, there was an increasing interest in obtaining certain physical data needed for the evaluation of its possible uses. Starting in 1950, Los Alamos Scientific Laboratory (LASL) was called upon to furnish metallic U^{233} fabricated into various shapes and to act as a distributor of U^{233} compounds and solutions. Until late in 1953 there were no specific facilities for processing U^{233} . All chemical, metallurgical, and residue recovery operations were carried out in two dryboxes, which were modified slightly to permit the necessary operations to be performed. However, the job was not too difficult in that the amount of material was small, and the feed solutions were mostly uranyl nitrate, and thus could be processed by conventional means. The amount of recycle was small and very intermittent, and the diversion of material to residues difficult to recover was not serious.

Early in 1952 it was learned that kilogram amounts of U^{233} would become available and that processing of U^{233} to metal might become a routine operation. LASL was assigned this task, and the decision was made to install a semiworks production facility capable of handling the necessary chemical, metallurgical, and residue recovery operations.

2. Problems in U²³³ Processing

2.1 Containment of Alpha Activity

The alpha activity of U²³³ is between that of U²³⁵ ($t_{1/2} = 7.1 \times 10^8$ y) and Pu²³⁹ ($t_{1/2} = 24,100$ y). For the isotopic mixtures usually encountered, U²³³ has a specific activity 152 times as large as U²³⁵, while Pu²³⁹ is 51 times more active than U²³³. With respect to alpha activity the precautions followed in handling Pu²³⁹ are also applicable to U²³³. The U²³³ alpha activity constitutes a serious hazard to personnel. U²³³ tends to accumulate in the lungs and in the bones, where its continued activity can be quite harmful. Accordingly, U²³³ is a health hazard due to its activity in amounts insufficient to cause heavy metal poisoning.

Because of its large mass and double charge, an alpha particle has a limited range of travel. For this reason it is easily shielded against, and control of alpha activity reduces to the prevention of ingestion, inhalation, and the spread of the active isotope.

2.2 Beta-Gamma Activity

2.2.1 Activity from U²³² Chain

In itself, the U²³³ decay chain presents no great hazard from beta-gamma activity, the majority of the daughter isotopes being alpha emitters only. Most nuclide charts show three beta emissions and three gamma emissions in the chain, the strongest being a 0.31 Mev gamma from U²³³ itself.

Nearly all of the activity stems from the U²³² chain. U²³² is present in the U²³³ as a contaminant. The quantity of U²³² present is a function of neutron flux and time of irradiation and is produced according to the reaction

at the same time that the U²³³ is produced.

The radioactive half-life of U²³² is a comparatively short 74 years, and the daughters in this chain, all with short half-lives, produce numerous gamma emissions ranging from about 0.04 Mev to about 2.62 Mev energies. Some of the stronger emissions are 0.719 Mev from Bi²¹², and 0.510 Mev, 0.582 Mev, 0.859 Mev, and the 2.615 Mev, all from Tl²⁰⁸.

The quantities of U²³² encountered in U²³³ have ranged only from 10 ppm to about 40 ppm, but the short half-lives of the daughters contribute to a rapid growth of beta-gamma activity which makes the handling of U²³³ extremely hazardous from a radiation standpoint.

2.2.2 Measurements of Activity

Listed below are the radiation readings of some typical batches, as measured by a Jordan Model AGB-10-KSR meter. Readings were first taken with the probe in contact with the U^{233} container, then at the indicated distances from the wall of the container. The same measurements were repeated with a 1/2 inch lead shield between the container and the probe.

TABLE 2.1
RADIATION FROM SOME U^{233} BATCHES

Material	Distance	Radiation Reading, r/hr	
		Unshielded	1/2" Lead Shield
700 grams U^{233} metal	Contact	0.80	0.275
	10 cm	0.25	0.125
	100 cm	0.0065	0.003
250 grams of U^{233} as U_3O_8	Contact	0.35	0.125
	10 cm	0.125	0.052
	100 cm	0.0032	0.0014
500 grams of U^{233} as UF_4	Contact	0.55	0.23
	10 cm	0.20	0.10
	100 cm	0.006	0.0028
125 grams of U^{233} metal as casting skull	Contact	4.0	1.2
	10 cm	0.95	0.495
	100 cm	0.035	0.0175
	200 cm	0.0075	Negligible

The age of the various batches was not accurately known, but all were at least a month old, allowing sufficient time for Th^{228} to reach equilibrium with its daughters. About 35 to 50% of the radiation penetrated a half inch of lead. Half-value layer figures for lead place the penetrating radiation in the range between 1.5 Mev and 2.0 Mev.²

The casting skull in the table above was previously measured with a Cutie Pie meter within a few days of casting, at which time the readings were 10 r/hr at contact with the container, 550 mr/hr through 1-3/4 inches of lead, and 160 mr/hr through 2-1/2 inches of lead. From these data, it is apparent that a significant percentage of the gamma radiation from U^{233} is from the 2.62 Mev gamma of Tl^{208} .

2.2.3 Personnel Exposures and Quantities Handled

Despite the radiation problems, it has been possible to process rather large quantities of U^{233} and still remain generally within the imposed limitations for whole body radiation.

The following table summarizes the exposures received by personnel working with U^{233} , together with figures for the quantities of U^{233} which were completely processed through the laboratories during the indicated period.

TABLE 2.2

PERSONNEL EXPOSURES FROM U^{233} (GAMMA REM)

Year	kg U^{233}	Operator Number									
		1	2	3	4	5	6	7	8	9	10
1955 ^a	9.07	3.93	6.47	0.51	1.14	c	0.03	c	0.07	0.01	0.02
1956 ^a	29.49	11.37	12.02	2.52	c	4.13	5.42	c	2.24	4.51	3.28
1957 ^b	9.57	5.19	4.60	0.85	c	c	0.36	1.54	3.81	1.39	1.52

a. Limit set at 15 rem/year.

b. Limit set at 5 rem/year.

c. No U^{233} work during the period.

Operators 1 and 2 were the only personnel regularly engaged in U^{233} work. All others were engaged in U^{233} work only on a part-time basis, the periods ranging from a week to five months per year.

It is interesting to note that the ratio of total exposures for all personnel to 1 kg of U^{233} processed was about 1.3:1 in 1955, about 1.6:1 in 1956, and about 2:1 in 1957. This increase in exposure per kilogram of U^{233} corresponds roughly to an increase in U^{232} content of the new material received during the same period. This increase in U^{232} content has been from about 20 ppm to over 40 ppm.

Because of the radiation hazard, it has been necessary to rotate some of the personnel engaged in the U^{233} work in order not to exceed exposure limits. Even with this device, careful scheduling of work loads was necessary, and the rate of throughput was usually governed by the radiation previously received by personnel.

It should be pointed out that all the work done in the period covered was essentially unshielded. For the latter half of the period, some 1/2 inch thick portable lead shields were available for placement in front of hotter work. The contribution of these to reduced exposure does not seem to have been significant.

2.2.4 Procedures for Reducing Activity

It is, of course, impossible to separate the U^{232} from the U^{233} , so the next approach is the removal of the various daughters of U^{232} as a means of reducing the beta-gamma activity.

The only effective procedure is in separation of the immediate daughter, Th^{228} . If only the thorium daughters are removed, activity returns in a very short period, since it requires only about 3 to 4 weeks for Th^{228} to grow in to equilibrium with its daughters.

However, if the Th^{228} can be quantitatively separated, activity will decline for a period ranging from several days to about three weeks, depending on the U^{232} content. The Th^{228} daughters, for lack of a parent, die off with the 3.64 day half-life of Ra^{224} . It is not until Th^{228} again grows in from U^{232} that the growth of activity is resumed.

For this reason, processing procedures have been evolved with the aim of separating thorium isotopes from the uranium and lowering beta-gamma activity, with a consequent decrease of personnel exposure.

3. Equipment

3.1 Drybox Processing Line

3.1.1 Design Philosophy

After reduction of beta-gamma activity, U^{233} can be processed in unshielded dryboxes of a fairly conventional design. Their specific design and mode of installation were governed by two considerations.

a. Nuclear Safety. Provision had to be made for nuclear safety during processing and storing of U^{233} material. Allowing for a factor of safety, this meant that two independent improbable accidents had to occur before a nuclear

hazard could arise.

The minimum parameters of a critical system of U^{233} as a homogeneous aqueous solution are recorded³ as follows: (1) mass - 588 grams, (2) volume - 3.5 liters, (3) cylinder diameter - 4.0 inches, (4) slab thickness - about 0.5 inch, and (5) concentration - 10.9 grams/liter. Any one of these limitations on mass, volume, container dimensions, or concentration will prohibit a chain reaction regardless of other conditions. A safety factor of 2 should be applied to the mass and volume restrictions in order to cover errors in analysis and in batch make-up. Uncertainties suggest that the always-safe concentration be taken as ≤ 5 grams/liter.

According to local comparisons between U^{233} and Pu^{239} , the rules for handling plutonium as metal or other hydrogen-free forms are satisfactory for U^{233} in a similar form.

Nuclear safety requirements were taken care of fairly easily in that the anticipated amount of material to be handled at any one time was to be small. Solution batch sizes were set at 250 grams. This was well within the critical limits, this amount of material was easy to handle, and much information was available on processing U^{235} in this size batch. The dryboxes in which solutions were to be processed had wells built into the floors to accommodate the necessary glassware. In the event of breakage several lots could not flow together. By having specific, limited locations for each solution handled in each box, it was possible to reduce the probability of inadvertently having more material than was nuclearly safe in any one box.

The possibility of flooding with water, with the subsequent tamping effect, was reduced by having a readily accessible main valve which was turned off when the equipment was to be left unattended for any length of time. In addition water outlets were omitted entirely from those sections of the line in which only oxides and fluorides were handled.

Although the permitted amounts of nonhydrogenous compounds that could be handled or stored were considerably higher than the quantities normally encountered, the possibility of exceeding any critical amount was lessened by having a limited storage unit for each compound. Its success was, of course, dependent on adherence to rules that no material be stored except in a prescribed location.

In the facility designed for residue recovery the largest container had a volume of 25 liters and was not geometrically safe, so that concentrations had to be limited. From past experience the maximum anticipated concentration was 1 gram/liter, which is well within the "always-safe" region. The amount of material going into this container would be known beforehand.

One section of the recovery facility was intended for nonroutine work, and as such it was difficult to incorporate any specific nuclear safety features, other than to divide the floor up into several sections such that breakage

could not lead to the combination of several batches.

b. Alpha Containment. A primary method of reducing alpha contamination is to carry out operations in gloved dryboxes which are as airtight as possible. As an added precaution the boxes are at a slight negative pressure so that in the event leaks occur, material will not be carried into the room.

The remaining important source of alpha contamination is the transfer of anything to or from a contaminated box. The philosophy was to reduce these transfers to a minimum. Air transfers of U^{233} during processing to UF_4 were eliminated by connecting the various dryboxes into a continuous train. Thus U^{233} entered the line as turnings, oxide, or solution and as a rule did not again leave until it was removed as UF_4 inside a sealed reduction bomb.

Some airlocks were installed in the drybox train where air transfers seemed necessary. An attempt was made to keep these airlocks relatively free of contamination by segregating them from the work areas by means of sliding doors.

Plastic bag ports were installed in many locations to facilitate the safe removal of discardable trash. In case of need these same ports could be used for introducing necessary apparatus or chemicals into the line.

A drain system led all the residue solutions into a common storage bottle.

No air transfers were necessary for the addition of reagent solutions, as these were piped directly into the area where they were needed.

The same techniques were employed in the recovery facility, although there the problem was simpler in that all operations were carried out in one large box.

3.1.2 Description of Enclosure Equipment

a. Metal Production Line. The metal production line is installed in a double laboratory module in the CMR Building. It consists of a train of 15 dryboxes as shown in Figure 3.1. Boxes 1, 3, 4, 6, 7, 9, 10, 11, 14 are of a standard design and essentially a stock item for use in the building. The remaining boxes are specifically designed and made for this line. All of the boxes have stainless steel bodies and Lucite windows.

This line provides facilities for processing U^{233} (in solution, as turnings, or oxide) to metal. The processing is the same as that employed in enriched uranium processing at LASL, although at times the incoming material has required different treatment.

Oxide and metal turnings are introduced into box 1 where dissolution and filtration equipment are available. Because of the pyrophoric nature of

Fig. 3.1 Enclosure equipment, U²³³ metal production line.

uranium metal turnings, provision is made for the establishment of an inert helium atmosphere in this box. This lessens the possibility of uranium fires during the handling of dry turnings. Dissolving is carried out in Pyrex dissolvers set in steam-jacketed wells. The necessary reagents are added through stainless steel tubing coming from a reservoir on the outside. The resulting solution is filtered through a glass fritted funnel and then moved to box 2.

If the uranium to be processed is already in solution, it is introduced directly into box 2. This can be done through an ordinary air lock or else by means of an airlock attached to the bottom of the drybox. This airlock encloses a container lift operated by an air cylinder.

Box 2 contains facilities for obtaining volumetric samples of the solutions entering it for processing, and for the first hydrogen peroxide precipitation.

Precipitation of uranium peroxide is carried out in a 5 liter round bottom flask which sits in a well. Stirring is done magnetically by means of a rotating magnet mounted outside, adjacent to the bottom of the well. This magnet is powerful enough to rotate a small Teflon-covered magnet placed in the precipitation flask. Reagent flow is controlled manually by small needle valves in the reagent lines. The pH is monitored continuously on an external meter connected to electrodes immersed in the precipitation flask.

The precipitate is filtered out onto a glass fritted funnel. This box has its own filtrate receiving bottle, attached to a funnel in the floor, so that initial dirty filtrates may be segregated from subsequent ones.

Ignition to UO_3 is done in box 3. The floor of the box contains two wells shaped to fit the filter funnels. These are bolted on, and a rubber gasket makes the necessary seal. Crucible furnaces are mounted on the outside so as to enclose each well. The gasket area is kept cool by means of a cold circulating water coil built into the well at that location. Mounted on a panel above the box are the instruments for controlling and indicating furnace temperature and for switching the power off at pre-set times. In the event of circulating water interruption, the furnaces are automatically turned off.

Dissolution of the UO_3 and filtration of the resulting solution are performed in box 4.

The precipitation and ignition facilities are repeated two times (boxes 5 through 10) so that, if necessary, it is possible to re-precipitate each batch two times without having a back flow of material. The precipitate from the final precipitation is filtered on platinum funnels having sintered platinum frits. Thus it is possible to ignite to U_3O_8 without having to transfer the uranium peroxide to some other container. Boxes 9 and 10 contain the same facilities as box 4, but the furnaces are operated at a much higher temperature.

Filtrates and waste solutions generated in boxes 4 through 7 are all drained into a bottle placed under box 7.

Box 11 provides space for the handling of U_3O_8 . Here the oxide is ground, sampled, and stored.

Weighings that are necessary for accountability or for processing purposes are done in box 12. Here are installed two analytical balances having capacities of 2 kilograms and 200 grams, respectively.

Reduction of U_3O_8 to UO_2 and hydrofluorination of UO_2 to UF_4 are done in box 13. The reactor consists of a nickel tube set inside a 5 inch I.D. tube furnace. The necessary meters and valves are mounted on the front in a long, shallow box completely separated from the interior of the large box. To facilitate changing of reactors a large port is installed on the rear of the right wall of this box. It is possible to remove the window covering this port and work on the rear of the reactor or the furnace through a plastic bag. Because of poor heat dissipation it is necessary to use Homolite as window material for the front of the box and for the rear accessory port. The exhaust gases are led through a soda-lime absorber and then into the building exhaust. This absorber unit is mounted on the rear of box 15 and makes it possible to load and unload the absorbent and sample it without danger of spreading contamination.

Handling of UF_4 is done in box 14. In addition to providing fluoride storage space, reduction charges are prepared here. Required amounts of iodine and calcium are weighed outside the line and introduced through a convenient air lock. Mixing of the charge is done by hand.

Loading and sealing of the reduction bomb is done in box 15. An air-operated vise built into the bottom of the box holds the bomb during the tightening of the lid bolts. Connections are provided so that the bomb can be evacuated and then flooded with argon. In order to be fired the loaded bomb has to be transferred to a separate drybox which contains an induction coil powered by an Ajax 20 kw converter. Movement of the bomb between box 15, the firing location, and the unloading area is accomplished by using a transfer can which fastens to the bottom of the boxes in question by means of a double breech lock arrangement. Thus the inside of the can is never exposed to the room, and the outside surfaces of the can are never exposed to a contaminated atmosphere.

Unloading of the fired bomb, cleaning, and sampling of the metal button are done in a section of the Recovery Box.

b. Recovery Box. This facility consists of a 15 foot long drybox providing space both for certain routine operations and for general chemical procedures, as shown in Figure 3.2.

The fired bombs are introduced into section 1 and unloaded. There are facilities here for handling of used crucibles and slag and for cleaning bombs.

Fig. 3.2 Enclosure equipment, U^{233} recovery box

Semiclean buttons are then placed in section 2. Here they are thoroughly cleaned and a sample taken. Section 3 contains a 2 kg capacity balance used in making the necessary weighings. Material can be moved between sections 2 and 3 by means of a small cart which travels in a well joining the two sections.

The bulk of the residues fall into three main types and so specific areas of the recovery box are set aside for them and contain permanent equipment for their recovery.

Reduction residues (slag and crucibles) are dissolved in a 5 gallon, steam-jacketed, stainless steel kettle installed in section 5. The residues are loaded by hand through a large opening in the kettle lid. Reagents flow by gravity from storage and measuring vessels sitting above the kettle, but on the outside of the box. Reagents are drawn by vacuum into these intermediate tanks. A large stainless steel condenser installed on the kettle lid makes it possible to reflux the solutions. The condenser outlet leads through a caustic trap in order to remove iodine vapors. A vacuum transfer is also used to charge the trap with caustic solution.

Two types of solution-handling vessels are employed. For storage, mixing, and volume measurement the vessel consists of a long battery jar with a cone-shaped bottom fitted with a stainless steel cover held on by tie rods. This makes it possible to use metal piping in their installation. Vessels used mostly to provide gravity flow of solutions are made by capping sections of large diameter Pyrex tubing with stainless steel plates that are held on by tie rods and contain a gasket groove. Tygon gaskets are usually used. These vessels are suspended from the roof of the drybox. Solutions are drawn into them by vacuum.

Parts of sections 5 and 6 contain equipment for small-scale solvent extraction recovery of the U^{233} contained in fabrication crucibles, reduction residues, peroxide filtrates, and miscellaneous solutions.

Originally, a small-scale simple batch extraction system was used, but now two modified Scheibel columns are used, one for extraction and one for stripping uranium from the organic phase. Appropriate tanks are provided for storage of feed, feed adjustment, and storage of raffinates. Aqueous product goes to the stills for concentration.

Section 6 contains two stills for the concentrating of various solutions. These are made from large bell jars covered with a stainless steel head. The head is equipped with a steam coil that reaches to the bottom of the jar. It also contains connections for vacuum, a dip tube, and a small capped opening. Vapors from the still pass through an Oak Ridge trap and then a simple condenser. Both are made of stainless steel and are an integral part of the head. Distillates are collected in calibrated tanks placed just outside the drybox.

Filtrate containers from the metal production line are brought into position just outside of section 6 and are emptied by means of a dip arrangement which permits the solutions to be vacuum transferred to a container inside the box. Gravity flow is then used for the transfer to the stills. When not in use the dip tube is drawn up into a plastic sleeve and the end is covered.

A crucible furnace is installed in section 4. This installation is the same as that used in the furnace boxes of the metal production facility. The main use of this furnace is for the incineration of combustible residues (mostly rags). A Vycor tube is used as a crucible. Gaseous products are collected in a water-filled scrubbing tower by pulling air through an inverted funnel set just above the top of the Vycor container.

Ashes from incinerations are leached and the solutions combined with other residues.

Space for general chemical operations is provided in sections 7 and 8.

A large well is built into the bottom of section 8. It is covered with sliding pans so that one can readily use it for storage. Part of the well is covered by a completely enclosed, stainless steel steam bath. In the event of the need to evaporate large quantities of liquid, a small canopy can be brought down close to the containers. This canopy is connected to a small fan which exhausts into the main exhaust system. In this manner fumes and vapors are kept from spreading throughout the box. The box exhaust, which has inlet vents along an island down the center of the box, does not have a great enough flow for this purpose.

One large airlock plus two large plastic bag ports provide a means of transferring equipment in and out of the box.

Concentrated uranium solutions can be removed by an airlock assembly built onto the bottom of section 7. A bottle can be raised into position against a seal. A hole in the seal can be uncapped and a funnel passed down to the bottle. In this manner it is possible to fill the bottle and still keep the outside surfaces free from contamination.

The various services which are needed enter the box through pipes welded into the box along the edge just below the glove ring level. All valves are outside the box, and connections inside are made onto hose cocks. When a service is needed for a definite part of some equipment or solution container, the piping is arranged so that the control valve remains on the outside of the box.

3.2 Reduction of Personnel Exposure

3.2.1 Portable Shields

With increases in the quantity of U^{233} processed and thus increase in gamma activity, it became necessary to take steps for reduction of personnel exposure. An early measure was the introduction of portable lead shields.

These shields consist of a sheet of 1/2 inch thick lead plate, mounted in a frame on wheels for portability and location where needed. The top is at average neck height and is surmounted by a square of leaded glass 2 inches thick to provide some protection to the head. The top is cut in such a way that the shield can be placed against a drybox to permit working through glove ports. This is done by cutting away the corners of the shield in the shape of the drybox glove rings.

3.2.2 Automatic Titrator

Considerable time is spent in proximity to U^{233} solutions during the peroxide precipitation step of chemical purification. In order to decrease exposure during this operation an automatic titrator is installed.

In the automatic titrator setup, two delivery units are employed, one over each regular precipitation box. These are connected to the control unit on top of one of the boxes. Signals from the solutions are fed to the control unit through one or more connector boxes using shielded cable. This makes it possible to precipitate with less exposure, the operator's presence being required only to start and stop the operation, with a resultant exposure decrease. Arrangement of the automatic titrator is illustrated in Figure 3.3.

3.2.3 Shielded Drybox

The most important item in reduction of personnel exposure is the shielded drybox built for ion exchange separation of uranium and thorium, Figures 3.4 and 3.5.

This is a standard four-section drybox converted for ion exchange work. Shielding consists of 4 inch thick boiler plate, equivalent to 2.5 inches of lead. The shielding was empirically calculated (from actual data obtained by survey meter readings) to permit an operator to handle two batches per day at 2 r/hr radiation level each. One inch of boiler plate shielding is provided overhead to protect personnel on the floor above. The windows are 2 inch thick leaded glass, equivalent to about 1 inch of lead.

Equipment within the box is designed to provide means for dissolution

Fig. 3.3 Automatic titrator arrangement, U^{233} oxide production.

Fig. 3.4 U^{233} shielded drybox-east side.

Fig. 3.5 U²³³ shielded drybox-west side.

of oxide or metal, together with evaporation of excess acid from the solutions, followed by filtration, volume adjustment, sampling, ion exchange, and the re-cycling of some residues resulting from the procedures.

This shielded box is in no sense a remote operation. However, nearly all transfers of solutions are accomplished by use of vacuum, and the routing of the solutions is accomplished by connection of appropriate semiball joints and flexible tubing. Wherever possible, one semiball joint on a container is used both to admit solutions to the container and to permit withdrawal of solutions from the container.

Normal procedure requires an operator to make a connection, then turn a valve on the outside of the box, in order to permit a chemical to flow by gravity into a piece of apparatus, after which the connection is changed and a valve turned outside the box to provide the vacuum required for transfer of the solution to the next piece of apparatus. The only time an operator need be in or near the box is while making connections or turning valves.

Figure 3.6 is an illustration of a typical setup. In the left foreground is the top of the volume adjustment box. The in-line sampler is in the right foreground, and the ion exchange reservoirs, with resin cartridges attached, are in the background. The flexible tubing from the in-line sampler carries the solution from the volume adjustment box to the ion exchangers by applying vacuum to the ion exchanger. The same line serves both ion exchangers by moving the male semiball joint to the appropriate female semiball joint on the ion exchanger. Other connections are similar.

Each quadrant of the box is equipped with necessary services through hosecocks set in the box floor in the dead space close to the front wall of the box. These are controlled by valves along the sides of the shield.

Loading and unloading of the U^{233} is done manually through an airlock, since exposure for such operations is slight. The construction of the shielded drybox, together with the chemical procedures involved, is a significant step in lowering personnel exposure.

4. Processing

4.1 Feed

4.1.1 Thorex Product

The primary feed to the U^{233} purification and metal production line has always been the product of the Oak Ridge Thorex Process. In this process the U^{233} is quantitatively separated from thorium by dissolution and solvent extraction of irradiated thorium slugs. The solvent extraction system also results in separation of fission products. The improvement of this process

Fig. 3.6 U^{233} shielded drybox connection.

over the years has resulted in a U^{233} product low in fission products and contaminating cations.¹

Several types of solutions of U^{233} Thorex product have been received and processed, including UO_2F_2 and an acetate-citrate complex. Each of these types has been successfully processed, but each created undesirable side streams. As a result, the Thorex Process was modified to make the end product a uranyl nitrate solution, ready for direct processing to metal.

4.1.2 Recycled Residues

The fabrication of specific shapes of U^{233} metal results in a number of residues. These consist of skulls, turnings, crucibles, and cleanup rags. The skull is the thin shell of metal adhering to a melting crucible. The turnings are the result of machining operations. Crucibles are largely high-fired MgO used in melting operations.

The skulls and turnings are a prime feed source, going directly into oxide production for the purpose of repurifying the U^{233} for subsequent use. Crucibles and rags require treatment to permit solvent extraction and enter the main recovery scheme by another route.

4.2 Oxide Production

4.2.1 Ion Exchange

The purpose of the ion exchange system in the shielded drybox is the decontamination of U^{233} , giving a product of lowered beta-gamma activity. Using a cation resin exchange operation, the objectionable Th^{228} is quantitatively removed from the uranium, along with some undetermined fraction of the Th^{228} daughters. The remaining daughters, having short half-lives, decay rapidly, giving in a short period a U^{233} product of greatly reduced radiation activity, capable of being processed in unshielded equipment.

Figure 4.1 shows the extent of decontamination of a typical U^{233} lot with AG50-X8 (Dowex-50) cation resin. Samples were taken from influent and effluent solutions, representing about 1 mg of uranium each, and followed by scintillation gamma counting.

The immediate decline in activity shown by the lot amounts to almost 50% of the influent activity; the activity then declines to about 20% of the original within two to three days after separation, reaching a minimum of slightly over 10%, before new Th^{228} growing in starts the activity rising again.

Similar results can be obtained with much smaller quantities of resin, but the decrease in activity is slower. The 200 ml of resin was selected as

Fig. 4.1 Decontamination of a 250 gram batch of U^{233} with 200 ml of cation resin.

the quantity giving the best decontamination in a short time for the least diversion of uranium, since the resin becomes saturated with uranium. The rapid drop in effluent activity, along with some analytical results, indicates that considerable Ra^{224} is removed with the thorium.

The following survey meter readings, made with a hard-shell Cutie Pie, are indicative of the results obtained by ion exchange. The readings were taken in contact with either the bottle of solution or the bottle of oxide, at the highest point read.

Influent solution - 1750 mr/hr

Effluent solution - 900 mr/hr

1 day after separation - 610 mr/hr

2 days after separation - 500 mr/hr

5 days after separation - 350 mr/hr

6 days after separation - 300 mr/hr

7 days after separation - 250 mr/hr

(Lot precipitated as uranium peroxide and calcined to U_3O_8)

8 days after separation - 100 mr/hr

9 days after separation - 125 mr/hr

12 days after separation - 275 mr/hr

13 days after separation - 300 mr/hr

14 days after separation - 370 mr/hr

Figure 4.2 is a drawing showing the interior of the ion exchange box and Fig. 4.3 is a flowsheet of the ion exchange procedure.

Thorex solutions, or oxide, or metal for dissolution are introduced through an airlock and put into the dissolvers (A) in approximate 250 gram lots. The HNO_3 necessary for dissolution of oxide or metal is introduced, as are all reagents, from outside the box, through plastic tubing (L), then into the dissolver through the semiball joint attached to a dip tube. Unless acid adjustment is necessary, the dissolvers are simply a point for introducing Thorex solutions into the system. The dissolver well is surrounded by a steam coil for heating.

Acid concentrations up to 3 M HNO_3 can be ion exchanged successfully. The acid concentration of dissolved lots can be held at <0.5 M by controlling the quantity of dissolving acid. Thorex lots are usually <3 M in HNO_3 . However, in case the acid concentration is high, a closed circuit ejector vacuum system is to be installed for removing excess acid.

This system, Fig. 4.4, will consist of a vented tank, a pump, and an ejector. Water will initially be pumped from the tank and recirculated to the tank through the ejector. This will provide a vacuum applied directly to the distillate receiver (B) and indirectly to the dissolvers, which are heated. Any vapors not condensed will go through the vacuum line to the ejector, to be absorbed by the circulating water-acid system. The tank will

Fig. 4.2 Ion exchange equipment, U^{233} shielded drybox.

Fig. 4.3 Flowsheet U²³³ - thorium separation.

EJECTOR - VACUUM SYSTEM

Fig. 4.4 Ejector - vacuum system.

be periodically drained. After a solution has been dried to crystals, the crystals are dissolved in 0.05 M HNO_3 .

When ready, the solutions are transferred by vacuum to a filtering apparatus (C) where insoluble material is filtered out on a fritted glass disc. The solutions are collected in a receiver under the filter before transfer to a volume adjustment box.

The volume adjustment box (D) is used to adjust volume for accountability sampling purposes.⁴ Vacuum is applied to the entire box to transfer the solution to a calibrated flask where water can be added and the solution stirred by a magnetic mixer set under the floor. The solution is removed from the flask by an adjustable-height dip tube (center) equipped with a wiper. The box is equipped with nozzles for spraying and a valved line for withdrawal from the pan in case of breakage.

Accountability sampling is accomplished by an in-line sampler (E). Figures 4.5 and 4.6 show the sampler and bottle evacuator. A narrow mouth bottle is fitted with a serum bottle stopper. The chamber of the bottle evacuator is put under vacuum, a hypodermic needle is placed on the end of the evacuator, punched through the stopper, and the valve opened to evacuate the bottle. This is done outside the dry box.

In the dry box, the solution is slowly pulled through the sampler by vacuum. The hypodermic tubing in the sampler is used to punch through the stopper, and the appropriate volume of solution pulled into the evacuated bottle.

From the sampler, the solutions go directly to the ion exchange reservoirs (F), where the ion exchange scheme is carried out, the resin having been previously conditioned.

Two ion exchange procedures are possible. Column-type operation is available, in which case the flowsheet rates apply. Other resin cartridges (G) are provided with small sidearm stopcocks in order to permit a batch type of operation. Air is admitted through the sidearm while the reservoir is under vacuum, stirring the resin through the solution, after which the solution is rapidly drained. Contacting times are 10 minutes each for conditioning solutions, and 1 hour for all others. The batch operation is the usual one.

Effluents and eluates are collected in polyethylene bottles. Effluents are removed from the box for storage and decay of activity before further treatment. HCl solutions are transferred to stills (H) by way of a vacuum reservoir (K). In the stills, the chloride is converted to nitrate by three successive distillations and treatment with HNO_3 . Part of the HNO_3 is supplied by distillates from the dissolvers and by the conditioning solutions. The remainder is fresh concentrated HNO_3 . When a convenient number of HCl eluates has been collected and converted, the lot is recycled through ion

Fig. 4.5 In-line sampler - 23 Decontamination Lab.

Fig. 4.6 Bottle evacuator - in-line sampler - 23 Decontamination Lab.

exchange for further thorium removal. HCl distillates are collected in (J).

Acetates are removed from the box and will probably be treated in the same manner as HCl in order to recover thorium isotopes, but this phase of the program is still under development.

(M) is a typical flexible line for removal of distillates to waste disposal and (N) shows location of a typical service hosecock. (P) is the valve controlling the hosecock.

4.2.2 Chemical Purification

After allowing sufficient time for decline of beta-gamma activity, the effluent solutions are returned to the main processing stream for separation from nonradioactive contaminants.

Purification is accomplished by precipitation of $\text{UO}_4 \cdot x\text{H}_2\text{O}$. The reaction vessel is a 5 liter round-bottom flask. Stirring is done by Teflon covered magnetic bars, with the magnetic mixer set under the floor of the box. The acidity of the solution is controlled by a glass-calomel electrode system and an automatic titrator.

The pH of the solution is first adjusted to 1.5 with 1:1 NH_4OH . A dissolved mixture of 2 grams of citric acid and 10 grams of malonic acid in 25 ml of water is added to inhibit decomposition of H_2O_2 by iron, and the pH again adjusted to 1.5.

$\text{UO}_4 \cdot x\text{H}_2\text{O}$ is precipitated by addition of 30% H_2O_2 . H_2O_2 is added to the uranyl solution, while the automatic titrator delivers concentrated NH_4OH to maintain a pH of 1.5. Stirring is done at the fastest rate which does not cause splattering. The H_2O_2 is added in about 20% excess, about 140 ml per 250 grams of U, at a rate between 5 and 15 ml per minute. The precipitation step is used as many times as necessary to attain a desired degree of purity, two being the usual number of precipitations.

If the precipitation step is to be repeated, the precipitate is vacuum filtered on a Buchner funnel with fritted glass disc and then washed. The $\text{UO}_4 \cdot x\text{H}_2\text{O}$ cake on the frit is set in a crucible furnace for calcination at about 300°C for 8 to 12 hours. The product is of the approximate composition UO_3 . A stoichiometric compound is not sought, as the object is simply a compound rapidly soluble in HNO_3 .

After cooling, the calcined cake is wet down, then dissolved in concentrated HNO_3 . The precipitation procedure is repeated.

The final uranium peroxide is vacuum filtered on a platinum frit in a platinum funnel, and this cake is calcined to U_3O_8 over a period of 12 to 16 hours at 800 to 900°C .

4.3 Metal Production

4.3.1 Hydrofluorination

The preparation of UF_4 for reduction to metal is accomplished in two steps, reduction of U_3O_8 to UO_2 with H_2 and the conversion of UO_2 to UF_4 with HF .

Nickel equipment is used, since the reaction atmosphere is a reducing one at all times. The uranium compounds are contained in a nickel boat within a nickel reactor. The reactor itself is simply a copper-gasketed tube set into a 5 inch hinged, resistance-type tube furnace. Appropriate inlets and outlets are provided for gases, and the exhaust gases are passed through a bed of coarse soda lime to absorb excess HF , the remaining gas going to the box exhaust system. A thermocouple well is set into the body of the reactor.

The following cycle of operation is used.

Stage	Time (hours)	Temperature (°C)	H_2 Rate (liters/minute)	HF Rate (grams/hour)
Reduction	1	660	4.0	-
Hydrofluorination	5-1/2	550	4.0	200
Sintering	2	740	2.0	200

Including times to reach temperature, change rates, and cool, a complete cycle takes about 10-1/2 hours. The cycle may be interrupted and resumed at any time with no detrimental effect on the lot. The sintering time is used to provide a better quality fluoride for reduction and to give better conversion.

It should be noted that the operation is not necessarily stopped after each stage and can be continuous. If reduction or hydrofluorination are incomplete during the allotted cycle time for the stage, the reaction is completed during the subsequent stage or stages.

Average calculated conversion of U_3O_8 to UF_4 is greater than 99%, with an arbitrarily set minimum of 98.5%. Calculations are based on the weight of U_3O_8 . Stoichiometric factors are applied to determine U, as well as theoretical UO_2 and UF_4 . It is assumed that reduction of U_3O_8 to UO_2 is complete and that any unconverted material in the hydrofluorination product is UO_2 . The calculation for conversion percentage is then

$$\% \text{ Conversion} = \frac{\text{Wt. UF}_4 \text{ (actual)} - \text{Wt. UO}_2 \text{ (theoretical)}}{\text{Wt. UF}_4 \text{ (theoretical)} - \text{Wt. UO}_2 \text{ (theoretical)}} \times 100$$

4.3.2 Reduction to Metal

Conversion of UF_4 to metal is done by the bomb reduction method.⁵ A mild steel cylinder equipped with a flanged, bolted, and copper gasket sealed lid is used. A close-fitting MgO or CaO crucible contains the reaction. The space between crucible and bomb walls is filled with fine MgO sand to help prevent crucible cracking upon firing.

A charge contains UF_4 , calcium, and iodine. Calcium is the reducing agent. The iodine is a slagging agent for better separation of metal and slag and, in addition, provides additional heat in the reaction with calcium, and starts the whole process at a lower temperature. Normally, 0.2 mole of iodine per mole of UF_4 is used. The amount of calcium is 25% in excess of the stoichiometric quantity to reduce the UF_4 and to react with the iodine.

The charge is lightly mixed, poured into the crucible in the bomb, and the crucible lid put into place. The bomb is sealed when a knife edge on the lid bites into a soft copper gasket as the lid is bolted to the flange on the bomb body. Air in the bomb is replaced by argon by evacuating to a few millimeters of mercury, then flooding with argon under slight pressure through a small screw seal in the bomb lid. The cycle is repeated three times.

The reduction itself is accomplished by heating of the bomb in an induction coil. External temperature only is recorded. At about 600 to 700°C the recorder will show a "kick" as the reduction reaction occurs.

After cooling, the bomb is unloaded and slag, liner, and sand are set aside for solvent extraction recovery. The button is pickled in dilute acetic acid to remove excess calcium. Samples for chemical and/or isotopic analysis are drilled from the button when necessary, and button and samples are weighed. Yields from CaO crucibles average greater than 98% and from MgO crucibles greater than 99%. Total impurities average less than 500 ppm. Table 4.1 shows a typical spectrochemical analysis for U^{233} metal.

TABLE 4.1
U²³³ METAL PURITY

Element	ppm in Metal
Li	<0.1
Be	<0.1
B	0.2
Na	<1
Mg	8
Al	3
Si	40
Ca	30
V	<10
Cr	4
Mn	2
Fe	100
Co	<2
Ni	20
Cu	15
C	70 (separate analysis)

4.4 Solvent Extraction Recovery

Solvent extraction recovery is fed by four main types of residues. These are fabrication crucibles, reduction residues, peroxide filtrate concentrates, and rag leaches.

Fabrication crucibles and reduction residues are dissolved according to recipe in a small steam-jacketed dissolver kettle. HNO₃ is used for dissolution and, in the case of reduction residues, to flash I₂ from the slag prior to refluxing. Aluminum nitrate is added to provide additional salting agent for extraction and also aids in dissolution of reduction residues by complexing fluoride.

Concentrated peroxide filtrates and rag leaches have been found to extract best if they are treated individually, but can be used as additions to solutions from the dissolver. When treated individually, separate feed adjustment is necessary. Rag leaches are the result of ashing and leaching the rags used in cleaning up all the enclosures.

Feed adjustment is necessary to insure optimum conditions for solvent

extraction. The solvent extraction scheme is shown in Figure 4.7.

Equipment-wise, the setup consists of the dissolver, storage tanks for solutions both before and after extraction, the two columns, and the extraction feed system. The extraction feed system consists of overhead tanks for gravity flow of feed, solvent, scrub, and strip. These consist of three glass tubes slightly off the horizontal, and one squat stainless steel tank, to maintain gravity head fairly constant. Solutions are moved up by vacuum and all flow is metered. Equipment is shown in Figure 4.8.

Other solutions are bled into solvent extraction charges as circumstances dictate.

The concentrates from solvent extraction are returned to oxide production for peroxide precipitation of the uranium present and eventual inclusion in recovery lots.

4.5 Miscellaneous Recovery

From time to time, U^{233} residues of unusual types are received for recovery or are created in processes associated with the general U^{233} recovery scheme. Each of these usually represents an individual problem to be solved as it occurs.

4.5.1 Analytical Residues

The only other source of residues for routine recovery is analytical residues. These consist of metal and oxide, rags, and the solution residues from wet chemical analyses.

Metal and oxide come from unused portions of samples, are usually clean and reliable, and go directly into lots for oxide production. Rags are treated the same as other rags, by ashing and leaching with HNO_3 for eventual solvent extraction.

The solution residues consist of unused nitrate solutions, which can be added directly to lots, together with the actual solutions resulting from volumetric and colorimetric analyses for uranium. Solutions from volumetric analyses contain sulfate. In the usual quantities, they can be conveniently bled into extraction charges for U^{233} recovery, or the uranium can be precipitated from them as ammonium diuranate, $(NH_4)_2U_2O_7$, with the filtrates discardable at less than 0.1 ppm of uranium.

Colorimetric analysis solutions contain thiocyanates and chlorides, and no completely satisfactory simple method for the recovery of the U^{233} has been developed. The bulk of the uranium is first precipitated as $Na_2U_2O_7$, NaOH being used to keep the stannous ion used in the analysis in solution.

Fig. 4.7 Flowsheet - U^{233} recovery and solvent extraction.

Fig. 4.8 U^{233} solvent extraction equipment.

The resultant precipitate is dissolved in HNO_3 , and the resultant solution is distilled until chloride free and sent to solvent extraction. The filtrates sometimes need one or more additional caustic treatments to reach discardability.

4.5.2 Discards

The recovery operation is the only one from which discards are made. Discards are made when solids or solutions contain less than 0.1 ppm of uranium and no longer lend themselves to simple recovery schemes. Aqueous raffinate, distillate, and diuranate filtrates are the common discards. Leached rag ashes are occasionally discarded in small quantities.

4.6 Removal of Thorium and Thorium Daughters

As previously stated, the method for reducing the activity of the U^{233} in order to permit processing with less personnel radiation exposure is to remove Th^{228} . When this is done, the short half-life daughters will decay and give the desired result.

Unfortunately, it has not been possible to obtain radiochemical analyses of sufficient accuracy to permit determination of the effect of the various operations on Th^{228} and its daughters. As a result, thorium material balances have not been possible. However, the results of experiments have been followed by survey meter readings and scintillation gamma counting, and give good indications of what takes place.

4.6.1 Ion Exchange

The ion exchange step has proved to be the best means for quantitative separation of the thorium. The effectiveness of ion exchange has been demonstrated by experiments using depleted uranium spiked with thorium as well as by actual U^{233} experiments. In the U^{233} experiments, the effluent activity has been followed by survey meter and by samples for scintillation gamma counting. In all cases, analyzed or indicated thorium removal is about 90%.

4.6.2 Precipitation

Peroxide precipitation seems to affect only the thorium daughters. Immediately after precipitation, the mass of uranium exhibits very low beta-gamma activity. However, regrowth of the activity begins almost immediately

and climbs rapidly when followed by a survey meter. The pattern is what would be expected from removal of the thorium daughters, since they are the strong gamma emitters. The rapid regrowth of activity comes as the thorium proceeds to re-establish equilibrium with the daughters over a 3 to 4 week period. Decontamination by peroxide precipitation is only temporary.

4.6.3 Reduction and Casting

A study made by Group W-7 showed that during reduction thorium remained in the button quantitatively, and that upon casting the bulk of the thorium remained with the skull and the casting crucible.⁶

Survey meter readings made subsequent to these findings bear out this information. Immediately after a reduction, the button shows negligible beta-gamma activity, while the slag is extremely hot. Activity in the metal rises rapidly, while that in the slag declines rapidly. It is obvious that the clean-up by reduction is only temporary.

Meter readings for cast pieces and for the skulls from the same casts indicated the thorium separation. Skulls were extremely hot, grew in activity for a very short period, and then cooled as the Th^{228} began to decay. The cast metal showed reduced activity which grew rather slowly at first, then increased rapidly as new Th^{228} grew into the metal. Casting, therefore, presents a possible method for partial decontamination of U^{233} metal. A small part of the mass can be set aside as a skull for cooling, while the greater part of the mass is reduced to a reasonable level of activity for further processing.

When ion exchange is used prior to preparation of the metal, the ion exchange is the controlling factor in decontamination, and the subsequent processing steps will induce behavior which deviates from that outlined above. It is possible to assure a continued decline in activity through the button stage by use of ion exchange.

5. Summary

The use of a combination of shielded and unshielded equipment makes possible the processing of U^{233} solutions to metal without undue personnel exposure.

No serious problems arise in the chemical purification procedure, as the chemistry of the process is well established for the production of U^{233} metal of reasonably high purity.

The only difficulties lie in the beta-gamma activity from the U^{232} daughters in the U^{233} . If Th^{228} from this decay chain can be removed, un-

unshielded processing becomes possible. The ion exchange separation scheme offers a very simple means of overcoming these difficulties.

Two major areas of the work are not yet complete, and additional development work is in progress. Thorex nitrate solutions have given erratic results with ion exchange decontamination. Some have behaved in the ideal pattern expected from development work, while others have given extremely poor results. It is believed that the thorium in the Thorex lots sometimes exists in a form which is not absorbed by the cation resin. Work on a means of insuring consistent behavior from Thorex lots is continuing.

The other area is in the recovery of thorium isotopes after ion exchange. The Th^{228} and Th^{229} from the decay of U^{232} and U^{233} , respectively, are in demand for various physical measurements. These isotopes are removed from the cation resin in the acetate solutions. Because of the value of these isotopes, it is important that a scheme for further concentration and recovery of the isotopes be evolved.

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