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STATUS OF FISSION PRODUCT RECOVERY AT HANFORD

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HANFORD ATOMIC PRODUCTS OPERATION
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STATUS OF FISSION PRODUCT RECOVERY AT HANFORDABSTRACT

The recovery of fission products was initiated at Hanford in August, 1960 with the production of strontium-90 and cesium-137. The program has since included production of custom quantities of cerium-144 and promethium-147. The current program involves separation of strontium and rare earths from Purex acid waste by lead carrier sulfate precipitation and subsequent separation of rare earths from strontium by oxalate precipitation. Strontium is further purified by di(2-ethylhexyl)phosphoric acid solvent extraction. Cesium-137 is recovered from aged alkaline wastes by processing the alkaline supernatant solution through a bed of alumino-silicate resin.

Several other processes have been demonstrated with full level process solutions in plant equipment. Cesium has been recovered from alkaline wastes by zeolite ion exchange and nickel ferrocyanide precipitation and from acid wastes by phosphotungstic acid precipitation. Technetium-99 has been recovered and purified by anion exchange. Cerium-144 has been separated from the rare earths by di(2-ethylhexyl)phosphoric acid solvent extraction using silver catalyzed persulfate oxidation of cerium(III) to cerium(IV). Promethium-147 was subsequently separated from the cerium-free rare earths by chromatographic ion exchange.

Future plans include the recovery of megacurie quantities of Sr, Cs, Ce, and Pm in a waste processing plant scheduled for startup in 1967.

INTRODUCTION

A major portion of the fission products in the world has been generated at Hanford as by-products of the production of plutonium-239 for use in atomic weapons. Fission product chemistry has been studied extensively by Hanford scientists and engineers for the two-fold purpose of confining the fission products in the Hanford separations wastes for radiological safety and to exploit the potential of fission products for beneficial use. As early as 1955 research and development work was started on the recovery of selected fission products. Shortly thereafter development of a waste management improvement program was started for which current plans⁽¹⁾ include extraction and high integrity storage of the long-lived heat emitters, strontium-90 and cesium-137, and the solidification of the short-lived fission products and bulk salt wastes in underground storage tanks following 6 to 8 years' aging. The two development programs proved to be complementary and although the objectives are different the end result of each is a technology for the recovery of the long-lived heat emitters from the separations plant wastes. In 1967, the waste management program will be implemented and at that time the recovery of large quantities of fission products will be realized by the waste extraction processes. Meanwhile, an interim fission product recovery program is part of the Hanford production effort.

The current fission product recovery program at Hanford began in 1960 when a crash program was instituted to supply approximately one megacurie of strontium-90 to fuel prototype thermoelectric devices which were being developed for the AEC's Division of Reactor Development. At about the same time the shipment of multi-kilocurie quantities of cesium-137 to Oak Ridge National Laboratory was initiated. In 1963 the program was expanded to

include the recovery and stockpiling of strontium-90 crude and a rare-earth crude containing cerium-144 and promethium-147. Since then custom quantities of cerium-144 and promethium-147 have been isolated and shipped to Battelle Northwest Laboratory and Oak Ridge National Laboratory. In addition, promising flowsheets for the recovery and purification of these and other potentially valuable fission products have been field tested in full scale plant equipment.

This paper will discuss the fission product recovery activities currently being conducted at Hanford and describe the processes used. Production plant flowsheet performance will be discussed for the individual fission product recovery processes. Full level plant tests of fission product recovery and purification flowsheets not currently used in the production operation will be reviewed.

CURRENT RECOVERY ACTIVITIES

The fission product recovery program at Hanford now includes the recovery of strontium-90, promethium-147 and cerium-144 from currently generated Purex plant separations wastes and the recovery of cesium-137 from Purex stored alkaline waste supernatant solutions. The strontium and rare earths, including cerium and promethium, are removed from the Purex acid waste by a lead carrier sulfate precipitation process. The rare earths are subsequently separated from the strontium by oxalate precipitation. The strontium fraction is then purified by di(2-ethylhexyl)phosphoric acid (D2EHPA) solvent extraction or stored as strontium crude. Purified strontium is stored or loaded into filter casks for shipment to user sites. The rare-earth crude fraction, containing cerium and promethium, is stockpiled to provide an inventory of well aged promethium-147 for future AEC programs. Periodically, promethium is further

purified and shipped to a user. Cesium-137 is recovered from aged Purex alkaline waste supernatant solution directly into shipping casks containing alumino-silicate ion exchange media as needed to meet AEC shipping schedules.

Special fission product loadouts are made on demand and process flowsheets are tested in the fission products recovery equipment during shutdown periods in the operating schedule. Cerium has been separated from other rare earths by batch solvent extraction of short cooled feed and shipped to a user site in a filter cask. Technetium-99 has been recovered from Purex alkaline waste supernatant solutions by anion exchange. Cesium has been recovered from the supernatant solutions by zeolite ion exchange and by nickel ferrocyanide precipitation and from Purex acid waste by precipitation with phosphotungstic acid.

RECOVERY EQUIPMENT

Fission product recovery is conducted in large scale separations facilities. Precipitation equipment in the Purex plant is used for the initial separation of strontium, and the rare earths from the Purex acid waste. The strontium-rare earth crude is accumulated in an underground vault facility from where it is fed to precipitation and concentration equipment in the B-Plant, a partially remodeled former separations plant. The strontium is separated from the rare earths in the B-Plant equipment and the crude fractions are stored in B-Plant storage tanks. Strontium crude is transferred via the vault facility to the Strontium Semiworks, a former pilot plant for the Redox and Purex processes, for purification and subsequent storage or loadout of the purified strontium. A cesium loadout station is located near a waste storage tank farm for loading cesium shipping casks. Former waste storage tanks are used for the cesium loadout station feed tank and waste receiver.

STRONTIUM AND RARE EARTH RECOVERY

SULFATE PRECIPITATION

OXALATE PRECIPITATION

FIGURE I

LEAD CARRIER SULFATE PRECIPITATION

Strontium-90 and the rare earths, which include cerium-144 and promethium-147, are recovered from the Purex acid waste in Purex plant centrifugation equipment originally used for dissolver solution clarification and subsequently made available for this purpose through Purex process improvements. The Purex acid waste stream from the waste concentrator is centrifuged to remove solids, primarily silica and sulfates, which carry fission products. The solids are leached with nitric acid to recover the carried fission products and the leachate is combined with the solids-free supernatant solution for processing.

A lead-carrier sulfate precipitation process^(2,3), shown schematically in Figure I, is used to recover strontium, cerium and the rare earths. The cerium and rare earths are precipitated as the sodium sulfate-rare earth sulfate double salt by adjusting the sulfate concentration to one molar and the solution pH to 1.0. Lead nitrate is added to carry strontium sulfate. Iron precipitation is avoided by the addition of a chelating agent such as glycolic acid. The precipitate is metathesized with a mixture of sodium hydroxide and sodium carbonate to remove lead sulfate and to convert the strontium, cerium and rare earths to acid-soluble carbonates. The precipitate is dissolved in dilute nitric acid and transferred to interim storage prior to separation of strontium from the cerium and rare earths.

In typical plant flowsheet performance only about 70 percent of the strontium and rare earths in the acid waste are made available to the sulfate precipitation process due to limited leaching of the fission products from the acid waste solids. Recovery of the isotopes in the sulfate precipitation flowsheet, however is greater than 90 percent. Decontamination factors greater

than 100 have been measured for iron and nearly quantitative separation of aluminum from the product isotopes has been demonstrated in the plant with the sulfate process. Supporting pilot plant studies⁽⁴⁾ have shown similar decontamination from iron, aluminum and other metal ions including manganese and magnesium. The removal of manganese and magnesium is of particular importance since these two ions are chemically similar to strontium in the subsequent solvent extraction purification process.

OXALATE PRECIPITATION OF THE RARE EARTHS

The rare earths, cerium and lead are separated from strontium by the addition of oxalic acid to the crude fission product feed as illustrated in Figure I. The solution is made about 0.35 molar in oxalic acid while holding the nitric acid between 0.25 and 0.5 molar. This acid side oxalate process precipitates the cerium, rare earths and lead, leaving the strontium in the supernatant solution. The strontium-bearing solution is concentrated and stored for stockpiling or to await further processing. The oxalate precipitate is slurried from the centrifuge with four molar nitric acid, concentrated and transferred to storage tanks for aging. The oxalate in the solution is destroyed in a few days by radiolysis leaving soluble rare earth nitrates in storage.

Plant experience with this process has shown good separation of strontium and the rare earths. The fraction of strontium lost to the precipitate and the rare earths to the supernatant solutions are typically five percent and two percent, respectively. Any losses due to poor separation in the precipitation step are potentially recoverable by recycle.

STRONTIUM PURIFICATION BY SOLVENT EXTRACTION

The strontium fraction from the B-Plant is transferred to the Strontium Semiworks via the storage vault for final purification and loadout or storage. The purification is performed in two Strontium Semiworks pulse columns and associated tankage by solvent extraction using di(2-ethylhexyl)phosphoric acid (D2EHPA) extractant in a hydrocarbon diluent with tributyl phosphate as a modifier⁽⁵⁾. The process is illustrated in Figure II.

Strontium, calcium and a small amount of cerium are extracted into the solvent in the first column (HA) effectively separating strontium from the majority of the metal ion and fission product contaminants. An aqueous phase chelating agent, sodium diethylenetriaminepentaacetate (DTPA), is used to reduce the extractability of the contaminants. The pH during extraction is maintained in the desired range, between 4.5 and 5.0, by sodium acetate buffering. The strontium is partitioned from calcium and the remainder of the cerium by selective stripping in the second column (HC) under carefully controlled pH conditions made possible by the use of citric acid as a stripping agent. The cerium and calcium are then washed from the solvent with nitric acid in a batch contactor and the solvent is prepared for recycle by a batch water wash to remove excess acid. The citric acid in the strontium product solution is continuously destroyed during the processing by boiling with nitric acid and hydrogen peroxide to avoid solids and tar formation associated with radiolytic degradation of citrate. Following analyses to confirm that the strontium meets customer specifications and the citrate ion is adequately removed, the product solution is stored in the Strontium Semiworks in a vault.

STRONTIUM SEMIWORKS

D2EHPA PURIFICATION OF STRONTIUM

FIGURE II

The D2EHPA solvent extraction process has proven highly efficient for the production scale purification of strontium. Typical decontamination factors for metal ion and fission product contaminants are shown in Table 1 for several purification runs. The contaminant removal efficiencies have been adequate to provide strontium product with less than ten percent by weight metal impurities, excluding alkali metals, and less than five curie percent fission product impurities.

TABLE 1TYPICAL DECONTAMINATION FACTORS IN STRONTIUM PURIFICATION

	<u>1</u>	<u>2</u>	<u>3</u>
Ca	20	10	25
Ba	20	3.5	5
Pb	>1000	7500	800
Fe	-	1300	400
Ce	1600	500	7000
Zr-Nb	8000	100	1200
Ru	> 700	35	400

STRONTIUM LOADOUT INTO FILTER CASKS

Purified strontium product is periodically loaded out into filter casks for shipments to off-site customers. Strontium carbonate is precipitated by the addition of potassium bicarbonate following partial neutralization with sodium hydroxide. The solution is adjusted to a final pH of 10 with excess potassium carbonate and digested at 90 C to assure complete precipitation of strontium. The use of carbonate rather than sodium hydroxide in the final

pH adjustment avoids the precipitation of the strontium decay daughter zirconium-90⁽⁶⁾ which builds up to significant quantities during prolonged storage of strontium-90. After cooling, the slurry is transferred into a filter shipping cask. The strontium precipitate collects on the filter where it is dried at temperatures up to 150 C to stabilize the filter cake for shipment. The cask is checked for leaks, purged with helium and monitored to determine rate of pressure buildup. When the cask meets shipping requirements it is released to the AEC for shipment off-site.

SEPARATION AND PURIFICATION OF CERIUM AND PROMETHIUM

In preparation for cerium-promethium separation, metal ions, primarily lead, are removed from the rare earth fraction by either batch or continuous solvent extraction with the D2EHPA solvent used for strontium purification. The aqueous rare earth feed is adjusted to pH 2.0 to 3.0 after the addition of a chelating agent, N-hydroxyethylethylenediaminetriacetic acid (HEDTA), to complex the lead and other metal ions and render them less extractable. The rare earths are stripped from the solvent with nitric acid providing a relatively pure feed for cerium-rare earth separation.

Cerium is separated from promethium and other rare earths by batch solvent extraction^(7,8) as illustrated in Figure III using the same D2EHPA solvent. The cerium is oxidized to cerium(IV) by silver catalyzed sodium persulfate oxidant. Cerium(IV) is extracted into the organic from an acid solution leaving the remainder of the rare earths (trivalent) in the solution. The cerium is stripped from the solvent with nitric acid containing a trace of nitrite ion to accelerate the reduction of cerium(IV) to cerium(III). The rare earth fraction is separated from the silver and sulfate reagents used in

SSW SEPARATION OF RARE EARTHS - PROMETHIUM FROM CERIUM BY D2EHPA BATCH SOLVENT EXTRACTION

FIGURE III

the oxidation step by either batch or continuous extraction with D2EHPA solvent in a pH range of two to four after addition of HEDTA to solubilize rare earth sulfates.

Promethium has been isolated on a pilot plant scale⁽⁹⁾ from the relatively cerium-free rare earth fraction by chromatographic ion exchange⁽¹⁰⁾. The rare earths are loaded onto a column of cation exchange resin. The rare earths are then eluted with a chelating solution (diethylenetriaminepentaacetic acid (DTPA) is favored) through subsequent columns where the rare earths are distributed in bands in an order established by the equilibrium between the cation resin and the chelating agent. After moving through several columns the promethium band is sufficiently isolated to permit the collection of a pure promethium fraction.

About 500 kilocuries of cerium-144 were isolated from short cooled feed for shipment to Oak Ridge National Laboratory in an early cerium-promethium test run. The cerium was loaded onto a slurry filter cask as a sodium sulfate-cerium sulfate cake^(11,12) in a manner similar to a strontium carbonate loadout. The cerium cake was removed from the cask with nitric acid at the user site.

Rare earth fractions have been separated from cerium in several plant scale runs. Full level tests have been conducted to investigate the process parameters. Isolated rare earth fractions have been shipped to Oak Ridge National Laboratory and Battelle Northwest Laboratory for research and development studies pointed toward the development of promethium as a heat source. Rare earth feeds essentially free of cerium were provided for the pilot plant scale tests of final promethium purification by chromatographic ion exchange conducted by the Hanford Chemical Processing Department.

The plant scale performance of the cerium-promethium separation flowsheet has exhibited the typical plant startup problems for flowsheets scaled up

directly from laboratory data. Problems associated with the use of plant equipment in the presence of high radiation fields, which could not be anticipated from laboratory tests, have been encountered and methods for overcoming them have been developed as a cooperative effort between the plant engineers and laboratory personnel. Despite startup difficulties, significant separations have been achieved between cerium and promethium to meet the requirements of the users.

CESIUM RECOVERY BY ION EXCHANGE

Cesium is recovered from aged Purex alkaline waste supernatant solution by ion exchange with beds of alumino-silicate gel, Decalso*, loaded in shielded shipping casks^(13,14) as shown in Figure IV. The alumino-silicate is highly selective for cesium which is present in only trace quantities in the concentrated sodium nitrate waste. Cesium selectivity is best at low temperatures and a cooler is therefore used to reduce the feed temperature at the inlet to the ion exchange bed. The quantity of cesium that can be shipped in a cask is maximized by loading the bed to near 100 percent breakthrough using a recycle line, not shown in the illustration, to route the effluent back to the feed tank after initial breakthrough is observed. Cesium is eluted from the casks at the user site with ammonium nitrate.

The production scale recovery of cesium by ion exchange has been highly efficient. Cesium losses are very low due to the recycle of effluent to the feed tank after initial breakthrough. Decontamination factors for sodium are estimated to be greater than 300 during loading. Some incentive exists however, to increase the amount of cesium that may be loaded on the cesium shipping casks

* Trade name of Pfaudler Permutit

CESIUM AND TECHNETIUM RECOVERY

FIGURE IV

in order to reduce the number of rail shipments required to meet AEC schedules. A recently tested commercial zeolite, Linde AW-500*, has more than double the capacity of Decalso for cesium loading^(15,16), providing a potential for cesium shipping economies through cask resin changeout.

TECHNETIUM RECOVERY

Technetium has been recovered from aged Purex alkaline supernatant solutions in kilogram quantities by an anion exchange process⁽¹⁷⁾. A cask filled with anion exchange resin was connected in series with a cesium shipping cask at the cesium loadout station as shown in Figure IV to recover the trace quantities of technetium present in the waste. The technetium was eluted from the cask with nitric acid solution which was then concentrated and denitrated as shown in Figure V. Final purification prior to preparation of technetium metal was done by a second anion exchange cycle.

Two plant tests were conducted with the recovery of about a kilogram of technetium in each test. The technetium from the first recovery test was transferred to Hanford Laboratories, now Battelle Northwest Laboratory, for final purification and reduction to metal for use in a NASA research program. Final purification of the technetium from the second recovery test was conducted by the Hanford Chemical Processing Department. In each case decontamination from the major contaminants was excellent.

* Trade name of Linde Division, Union Carbide Corporation

SSW TECHNETIUM PROCESSING

WASHING

ELUTION

FIGURE V

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