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TREATMENT OF HANFORD NUCLEAR FUELS PROCESSING

WASTES TO PERMIT LONG-TERM STORAGE

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TREATMENT OF HANFORD NUCLEAR FUELS PROCESSING
WASTES TO PERMIT LONG-TERM STORAGE

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INTRODUCTION

The chemical processing of irradiated uranium fuels for the recovery of plutonium, uranium and other nuclear products generates a diversity of radioactive wastes. The waste solutions consist of a wide variety of chemical species including some solids, contain up to 5000 curies of fission products per gallon, and generate up to 130 Btu per hour per gallon. Plant operations originating these wastes include chemical fuel decladding, solvent extraction processing, solvent washing, and plant flushes. The solvent extraction processing waste, Current Acid Waste (CAW), generated from operations which separate plutonium and uranium from the fission products and other impurities contains greater than 99 percent of the heat producing fission products from the irradiated fuel.

It was recognized from the time of the first plutonium production in 1944 that the safe containment of radioactive wastes involved many new problems not previously encountered by industry. A very conservative approach was adopted where essentially all radioactive wastes were stored as neutralized slurries in underground storage tanks. These storage systems were viewed as interim methods of waste handling while research and development efforts proceeded in search of safe, long-term confinement techniques and systems.

Based on technology developed over the last several years, a waste management program has been adopted for immobilizing essentially all of the Hanford radioactive wastes. This program contains the following elements:

- Remove and encapsulate long-lived heat emitters for long-term, on-site storage as salts in capsules; and
- Evaporate residual salt waste to solid cakes in existing waste tanks after allowing short-lived heat emitters to decay.

Strontium and cesium removal is required to reduce the fission product decay heat content of the bulk salt cakes to prevent excessive salt temperatures. To accomplish this an obsolete chemical processing plant, B Plant, which previously recovered plutonium from uranium fuels by bismuth phosphate precipitation was reactivated at a cost of approximately \$14,000,000. Existing facilities and equipment were used to the greatest extent possible to reduce capital expenditures..

This paper describes waste processing technology for removal of cesium and strontium from bulk salt wastes producing cesium and strontium product suitable for final purification and encapsulation, and waste residues amenable to in-tank solidification to salt cakes.

WASTE PROCESSING PROGRAM

Current Acid Waste - Current Acid Waste (CAW) from the Purex irradiated fuels separations plant has the composition shown in Table I.

TABLE I
CURRENT ACID WASTE COMPOSITION

<u>SUPERNATANT</u>	
<u>Chemical</u>	<u>M</u>
H ⁺	0.5 - 2.0
Na	0.4 - 0.7
K	Trace
Ca	0.002
Mn	Trace
Mg	0.002
Al	0.24 - 0.35
Fe	0.20 - 0.35
Zr	0.0 - 0.03
Cr	0.002
Ni	0.001
SO ₄	0.3 - 0.6
NO ₃	2.0 - 3.0
PO ₄	0.01
Fission Products:	
Cs	100%
Sr	70 - 85%
Others	

SOLIDS

1 - 3 volume percent

Fission Products: Cs - Negligible
Sr - 15 - 30%

The waste consists primarily of sodium, iron and aluminum nitrates and sulfates in a nitric acid solution. It is transferred to B Plant for cesium-137 and strontium-90 removal (Figure I). The associated solids, containing from 15 to 30 percent of the strontium

FIGURE 1

HIGH LEVEL LIQUID WASTE MANAGEMENT FLOW DIAGRAM

in the waste stream, are treated by a caustic-carbonate metathesis for strontium removal. The cesium is removed from the supernatant solution as a phosphotungstate by precipitation and is purified further by ion exchange. The solids treatment product and cesium-free solution are combined and processed through solvent extraction for strontium recovery.

The strontium and cesium are presently being stored as solutions pending construction of an encapsulation plant. When the encapsulation plant is available in about 1974, the cesium will be further purified by a second ion exchange cycle, converted to a chloride and encapsulated in high integrity containers for long-term storage. The strontium will be purified by a second cycle of solvent extraction, converted to a fluoride and encapsulated similarly to the cesium. The short-lived fission products remaining in the wastes after B Plant processing will be stored from 4 to 6 years to reduce the decay heat generation rate before solidification as salt cake in underground waste storage tanks.

Stored Alkaline Waste - Prior to the startup of B Plant in 1968, CAW from fuels processing operations was neutralized and stored as a slurry in carbon-steel lined, reinforced concrete tanks. Gradually a solid sludge layer formed containing about 99 percent of the strontium and about 5 percent of the cesium. The balance of the cesium remains in solution. As part of the program, cesium is removed from the supernatant solution by ion exchange, and the solids are mined from the tanks by hydraulic sluicing. The solids are subsequently dissolved

in acid. After pretreatment using a lead-carrier sulfate precipitation flowsheet with a carbonate metathesis step to remove the bulk of non-radioactive cations, the strontium is recovered by solvent extraction processing similar to that for CAW.

Non-Boiling Waste - Wastes such as those generated from fuels de-cladding and organic wash waste from the Purex plant are directly converted to immobile salt cakes in underground storage tanks. Other stored waste solutions generated from discontinued processing operations will be similarly solidified.

CURRENT ACID WASTE PROCESSING

Solids Treatment - The CAW contains from 1 to 3 percent solids by volume with which 15 to 30 percent of the total strontium is associated. These solids consist primarily of hydrated silica and metal silicates, sulfates and phosphates. The predominant metal ions on the solids are iron, zirconium, aluminum and sodium. It is presently believed that the strontium exists primarily as a sulfate in the solids.

A caustic-carbonate metathesis process has been devised to remove the strontium from the solids. The CAW is pumped from a lag storage tank to a B Plant receiving tank (Figure II). The supernatant liquor is decanted, after solids settling, through a centrifuge. The solids are then washed with water to remove the mother liquor and to prevent subsequent iron and other cation precipitation which could hinder further solids processing. After the water wash decantation and combination with CAW solution, a 1.0M sodium

FIGURE II

B PLANT SOLIDS TREATMENT FOR CURRENT ACID WASTE

carbonate - 1.5M sodium hydroxide metathesis solution is added at 50 C to convert strontium on the solids (sulfate) to a carbonate. After digesting with agitation for one hour, the metathesis supernatant solution is decanted to an underground storage tank. The solids are washed with 0.2M sodium carbonate - 0.2M sodium hydroxide for sulfate ion removal. After decanting the wash solution to waste, the carbonate is dissolved in nitric acid to yield a final acid concentration of about 0.3M.

Process development work shows that a strontium recovery of greater than 95 percent can be achieved from the solids. Inadequate separation of the CAW mother liquor from the solids reduces the recovery efficiency by allowing post precipitation. The precipitate incorporates the solids in a metal hydroxide gel and decreases metathesis efficiency. Intimate solids-liquid contacting and washing residual sulfate ion from the metathesis cake are essential for good recovery.

Cesium Removal by Phosphotungstate Precipitation - The CAW supernatant and water wash solutions from solids processing are decanted to another tank for removal of cesium by phosphotungstate precipitation (Figure III). Sodium phosphotungstate is added to a final concentration of about 0.002M at ambient temperature to precipitate greater than 98 percent of the cesium as the phosphotungstate. The phosphotungstate ion is added in a 280 percent excess of the stoichiometric amount required to precipitate the cesium as pure cesium phosphotungstate. The

FIGURE III
B PLANT CESIUM REMOVAL FROM CURRENT ACID WASTE

product slurry is decanted through a centrifuge for solids product removal, and the strontium bearing supernatant solution becomes feed for the solvent extraction system. The solids in the centrifuge are washed with 1M nitric acid to displace the mother liquor. The cesium solids are dissolved in 1.0M or 2.0M sodium hydroxide and are routed to the ion exchange system for further purification.

Plant testing of this process has resulted in 99 percent cesium removal with good resulting product purity. Decontamination factors for iron, aluminum, zirconium-niobium-95, ruthenium-rhodium-106, strontium-90, cerium-praseodymium-144, and ruthenium-103 were greater than 1000, and decontamination factors for calcium and magnesium were 10.

Strontium Removal by Solvent Extraction - The strontium bearing supernatant solutions from cesium phosphotungstate recovery and the solids treatment product are processed for strontium recovery. Operations are performed in a battery of four pulsed solvent extraction columns. The contacting section of the columns consists of a stainless steel cartridge of nozzle plates with 0.125 - 0.187 inch diameter nozzle openings on a 0.375 inch triangular pitch with 2 - 4 inch plate spacings. The cartridge sections are from 10 - 14 feet high and 15 - 20 inches in diameter. One or more louvre plates are incorporated in each column to avoid solution channeling and to promote solution mixing.

Feed to the first extraction column (1A) is prepared by adding sufficient citric acid to the CAW supernatant solution to complex iron, aluminum, and other undesirable metal cations on a one to one mole ratio (Figure IV). A 10 - 15 percent citrate excess is used to assure adequate

FIGURE IV
STRONTIUM REMOVAL-B PLANT SOLVENT EXTRACTION

complexing. The solids treatment product solution is added to the feed makeup, and the pH is adjusted with 19M sodium hydroxide to 4.7. The sodium hydroxide must be added slowly to the makeup with agitation after complexant addition to prevent localized iron precipitation. The citric acid also acts as a buffering agent in the 1A Column for pH control. During the makeup the pH must remain in the range 2 to 6 to prevent strontium precipitation as the sulfate at low pH and metal hydroxide precipitation at high pH.

The feed is pumped to the 1A Column where it is contacted with an organic liquid ion exchanger, di-(2-ethylhexyl)phosphoric acid. The extractant has the following composition:

0.4M Di-(2-ethylhexyl)phosphoric acid (HDEHP)
0.3M Tributylphosphate (TBP)
Diluent normal paraffin hydrocarbon (NPH)

The HDEHP is partially neutralized to the sodium salt for pH control before entering the 1A Column. The TBP acts as a solvent modifier to increase the solubility of the HDEHP sodium salt in NPH, and it also has a synergistic effect on increasing the strontium distribution ratio under desired contacting conditions. The NPH diluent decreases the extractant specific gravity and increases the volume. It promotes intimate two-phase contacting and counter-current flow.

In the 1A Column strontium, calcium, manganese, magnesium, yttrium, rare earths, and uranium are extracted into the organic phase with trace amounts of other cations. The bulk of the cations and the other fission products remain in the aqueous phase and are sent to

interim waste storage. The organic is transferred to the 1S Column where the sodium and trace iron and aluminum are stripped from the organic with 0.75M glycolic acid (HAcOH) - 0.005M trisodium hydroxyethylethylenediaminetriacetate (HEDTA) solution at an initial pH of 2.4. After passing through the 1S Column, this scrub solution is routed to the top of the 1A Column. The organic is pumped to the bottom of the 1B Column where the strontium, about 25 percent of the calcium, and the balance of divalent cations are stripped with a 0.03M nitric acid solution. The organic flows to the 1C Column where the rare earths and the balance of calcium are stripped from the organic with 2.5M nitric acid. The organic is finally batch-washed with 2M sodium hydroxide - 0.15M sodium tartrate to remove yttrium, uranium, and other tightly held ions from the organic. The strontium product from the 1B Column is concentrated and stored. All other aqueous streams are routed to interim waste storage.

Pilot plant experience has demonstrated strontium removals of greater than 95 percent. Plant measured strontium losses from the 1A Column have been less than 4 percent and losses to the 1C Column have been less than 1 percent. Excessive 1A Column waste losses and strontium losses to the 1C Column have been experienced when difficulties were encountered in monitoring and controlling the 1A Column and 1B Column operating pH's. These pH meters are remotely installed in-line monitors. They were changed to continuous operation instead of intermittent checks and agreement with analyses obtained from the analytical laboratory improved

significantly from ± 0.7 of a pH unit to ± 0.2 of a pH unit. A control pH range in the 1A Column of 4.2 - 4.9 is required for good product recovery.

Typical decontamination factors obtained for the strontium product from other CAW cations are as follows:

<u>Element</u>	<u>Decontamination Factor</u>
Na	400
Fe	2000
Al	1000
Ca	3
Mg	1
Cs-137	700
CePr-144	600
RuRh-106	6000

The greatest product contaminants have been sodium and divalent cations such as calcium, magnesium, and manganese.

STORED WASTE PROCESSING

Cesium Ion Exchange Purification - Supernatant solutions from stored wastes and the product from phosphotungstate precipitation are processed by ion exchange for cesium recovery and purification (Figure V). These solutions contain up to 250 curies per gallon of cesium-137 with the molarity of sodium exceeding that of total cesium by a factor range of 65 to 10,000.

FIGURE V
CESIUM-137 REMOVAL-B PLANT ION EXCHANGE

Clarified cesium-bearing solutions at 20-30 C are pumped down-flow through the ion exchange column at a rate of 1-2 bed volumes per hour. A 1500-gallon bed of 20-50 mesh Linde AW-500^R zeolite molecular sieve with a bed length to diameter ratio of 1.3 to 1 is used. Loading is terminated at about 5 percent instantaneous breakthrough for stored supernatant wastes. The CAW cesium product of high cesium concentration is loaded on the exchanger in small batches with negligible breakthrough. The feed is displaced from the column with a 4-bed volume water wash, and greater than 95 percent of the sodium that is loaded onto the bed is removed with 4-bed volumes of 0.25M ammonium carbonate solution. The cesium is eluted upflow with 7-bed volumes of 3M ammonium carbonate - 2M ammonium hydroxide at 50 - 55 C. The column is finally washed with another 4-bed volumes of water to displace the remaining eluent in preparation for the next cycle. The cesium product is concentrated to about a 250-gallon volume and routed to storage. The ammonium carbonate is thermally decomposed, and the ammonia and carbon dioxide are absorbed in the concentrator condenser and an absorber. About 75 percent of the ammonia and carbon dioxide is recovered for reuse.

For stored Purex solvent extraction supernatant solutions containing 16 curies cesium-137 per gallon, about 25,000 gallons of solution are passed through the column before 5 percent breakthrough is reached. The complete time cycle takes about 36 hours. Cesium recovery of 92 percent has been achieved in the plant, and the product sodium to cesium mole ratio in the product is about 6 to 1 representing a decontamination factor of about 1500.

Problems may be encountered if the feed pH is not between 10.5 and 12. At low pH, aluminum, which is about 0.01M in the feed, may precipitate in the column and cause pluggage. If the pH is greater than about 12 there is a tendency to dissolve the zeolite beads. If necessary, the feed pH is controlled by chemical additions.

Strontium Recovery from Stored Sludge - After waste storage tank supernatant solutions are removed, the stored sludge will be processed through Waste Management facilities for strontium recovery (Figure VI). The sludge will be sluiced with high-pressure, warm water and slurried to processing facilities. After solids settling, the supernatant solution containing 2 to 5 curies per gallon of cesium-137 will be decanted to lag storage for subsequent cesium recovery by ion exchange. The sludge will be dissolved in 12M nitric acid to a final acid concentration of 0.1 to 1M. The residual solids from dissolution will be recycled to the caustic process feed solution for additional strontium removal treatment. The strontium bearing solution containing from 90 to 95 percent of the strontium on the solids will be transferred to lag storage to await processing in B Plant.

In B Plant, the Purex acidified sludge will be treated by lead-carrier sulfate precipitation and carbonate metathesis to separate the strontium from expected high iron and aluminum concentrations. The acid solution will be adjusted to 0.02M lead and 1M sulfate concentrations at a pH of 1 with lead nitrate, sodium bisulfate

FIGURE VI
SLUDGE PROCESS - B PLANT

and sodium carbonate for strontium precipitation. Use of sodium carbonate in place of sodium hydroxide will inhibit iron precipitation during the pH adjustment. Iron and aluminum will remain in the supernatant waste solution. The sulfate cake will be treated, similarly to the CAW solids, by a 5.0M sodium hydroxide - 0.5M sodium carbonate metathesis solution and acid dissolution for strontium recovery. The higher sodium hydroxide concentration will increase the lead precipitate solubility.

The product solution will be processed through solvent extraction similarly to CAW solutions for strontium recovery. Trisodiumnitrilotriacetate (NTA) will be used as the complexant instead of citric acid to chelate lead and other undesirable cations. Lead is not complexed by citric acid. Hydroxyacetic acid will also be added to the feed as buffer for pH control in the LA Column.

Laboratory and present sludge dissolution experience indicates that about 85 percent of the strontium can be removed from the solids in the first sludge acidification and an additional 10 percent can be removed on succeeding solids recycle treatment. Laboratory studies have shown that the acidified solution may form a siliceous gel if allowed to stand over long periods, but this gel may be eliminated by a mild caustic then acid treatment.

Testing of acidified sludge processing in B Plant has recently been initiated. Measured losses have been about 10 percent in the waste streams. Process decontamination factors from strontium have

been as follows:

<u>Element</u>	<u>Decontamination Factor</u>
Fe	50
Al	100
Ca	9
Mg	6

Laboratory and pilot plant studies indicate that an over-all strontium recovery of 85 percent should be attainable from the solids through solvent extraction.