

ION EXCHANGE RECOVERY AND PURIFICATION
OF STRONTIUM-90
FROM CERTAIN HANFORD WASTE STREAMS

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ABSTRACT

A cation exchange process has been developed for the selective removal and purification of strontium-90 from a Hanford waste stream containing large amounts of lanthanide group and metallic cation impurities. The process is based on (1) selectively complexing the lanthanides and metallic cations to inhibit their exchange and (2) purification of the exchanged strontium-90 by selective elution of other exchanged impurities. Greater than 99 percent recovery of strontium-90 has been demonstrated with the recovered product essentially free of lanthanide and metallic contamination in the laboratory. The process has been scaled up to an 8.5 m³ production column and is being used to process approximately 3 MCi of strontium-90. Production to date has been quite consistent with laboratory data, except for a slight lowering of product purity. The product is of sufficient purity for further purification processing in the plant, and product purity has been improving as production experience is gained. This technology has the potential to greatly reduce the cost of producing strontium-90-containing materials for beneficial uses.

INTRODUCTION

In 1968, the Waste Fractionization Facility (B Plant) was started at Hanford to remove heat producing strontium-90 from certain waste streams as part of an overall waste management effort. The strontium was recovered from the waste streams via a solvent extraction process and then further purified by selective precipitation. Ultimately, the purified strontium solutions were converted to a solid form (SrF₂) to be encapsulated for storage. Until 1978, wastes from the processing that contained appreciable amounts of strontium (typically >5 Ci/gal) were recycled through the solvent extraction process for additional recovery. In 1978, the last of the primary feed was processed, and solvent extraction operations were ended. Since then these secondary wastes have been concentrated and stored. By 1984, the stored wastes totaled approximately 303,000 L, which contained 3 million Ci of strontium. This represents over 20,000 W/h of thermal energy to be processed in some fashion, to allow B Plant to be modified for other uses.

Restart of the continuous solvent extraction operation to process this material was estimated to be very expensive (approximately \$3 million). This was primarily due to the small amount of material to be processed compared to the equipment sizing (less than one month of operation). Also after six years of disuse, much rehabilitation of equipment would have been required along with total retraining of the operating force.

Solvent extraction was kept as the base case process and a search was begun to find a more attractive alternative. Any viable alternative had to meet some very stringent requirements:

1. Plans to modify B Plant for other uses required that the process be ready for implementation before July 1984. This allowed approximately nine months to complete laboratory experiments through full scale-up in the plant.

2. Time and cost constraints mandated that any process would have to fit into existing equipment with minimal changes.
3. No major changes in the chemicals used in the alternative process could be tolerated as not only could this involve major equipment replacement, but the time required to have new chemicals certified for use in B Plant would be greater than that available.

Of the potential processes identified, recovery by cation exchange was considered most likely to fit the requirements. Strontium had been successfully recovered by ion exchange from a similar process stream at Hanford in the early 1960's.¹ Considerable recent work on removing strontium from very dilute waste streams by ion exchange had been done at Savannah River National Laboratory (Dupont), Pacific Northwest Laboratory (Battelle) and Hanford (Rockwell Hanford Operations).^{2,3,4}

In addition, ion exchange processing expertise and equipment were already available in-house at B Plant, where they had been used for the recovery and purification of cesium-137. The proposed cation exchange process consisted of selective loading of strontium onto an ion exchange column, scrubbing with dilute eluant to remove the unwanted ions, and removal of the strontium with concentrated eluant.

A laboratory plan was developed to investigate this possibility. As many ion exchange resins as possible were to be screened for strontium selectivity and capacity, using small-scale batch contacting. At the same time, batch tests were to be used to determine each resin's long-term stability to the process solutions and to radiation. If the batch results looked promising, then the best resin(s) were to be tested under flowing conditions to determine the operating parameters and conditions needed. At this point, if ion exchange looked attractive, the need for further scale-up data or direct installation in the plant was to be addressed. After the process was

implemented in the plant, additional laboratory work would be performed, as needed to ensure proper operation of the plant.

EXPERIMENTAL DESIGN

The composition of the feed prepared for the laboratory testing is shown in Table I. The large amounts of lanthanide group (rare earth) ions in the feed simulate plant solutions where they were added as carriers to reduce strontium losses during concentration processing. The primary lanthanides present are lanthanum (75 percent) and neodymium (25 percent). Trace quantities of other metals were present in the actual feed but were eliminated from the test solutions, as the concentrations were under 5×10^{-4} molar.

TABLE I

Feed Composition

Ion	Molarity x 1,000
Sr	4.1
Ca	42.6
Mg	5.3
Al	8.2
Cr	1.9
Fe	9.8
Mn	37.2
Ni	1.0
Rare earths	128.0
Pb	0.8
Na	580.0

The strontium levels were monitored by using strontium-85 as a gamma-emitting tracer. This allowed for rapid screening of strontium capacity. The other components were monitored using inductively coupled plasma spectroscopy. The resins chosen for testing are shown in Table II. Resin selection was limited to those showing previously demonstrated selectivity to strontium and other resins of similar composition.

TABLE II

Resins Chosen for Testing

Amberlite IRC 718	Rohm & Haas Co.
Dowex 50X8	Dow Chemical Co.
Duolite ES 286*	Diamond Shamrock**
Duolite ES 278	Diamond Shamrock

*Formerly C26.

**Diamond Shamrock has since sold their ion exchange line to Rohm & Haas Co.

Batch Testing

For the contacting tests, weighed samples of the resins (0.1 to 5.0 gm) were equilibrated with 12.5 mL of feed solution. Component ion uptakes by the resin were determined by analysis of the solution at equilibrium, compared to the feed composition. Samples of the resins were allowed to soak in simulated process fluids, after which component ion uptake was measured by batch contacts and compared with fresh resin. Thermal analysis (differential scanning calorimetry) was performed on treated and untreated resins to determine if any physical changes had occurred on extended contact with process solutions.

Other samples of the resins were exposed to approximately 1×10^8 rad of gamma radiation. These were then tested by ion uptake and subjected to thermal analysis. That data and percent water retention (test of resin degradation) were compared with unexposed resins.

Column Testing

Column testing consisted of multiple load-elute-regenerate cycles on a 20-mL ion exchange column. Samples of the column effluent were collected in one-column volume (CV) increments (volume of liquid treated per volume of resin) and then analyzed for component ions.

EXPERIMENTAL RESULTS

Batch Testing

The results of the batch contacting tests indicated that all of the resins tested showed good strontium capacity and selectivity. The optimum feed pH was found to be approximately 8. Due to the presence of large amounts of metal cations in the feed, adjusting the original feed solution to pH values of greater than 3 resulted in the formation of copious quantities of metal hydroxide precipitates. Under processing conditions, these solids would be intolerable as they would rapidly plug the ion exchange bed. Additionally, the solids could entrap strontium by occlusion, causing significant losses from the feed. In order to maintain a stable feed solution at the optimum pH, the addition of an organic metal complexant to "tie up" the metals was investigated. N-hydroxyethylethylenediaminetriacetic acid (HEDTA), already in use at B Plant, was found to stabilize feed solutions to a pH greater than 9 when added at a 20 percent mole excess of the total metal ion concentration. A further benefit of the complexant addition was the suppression of metal ion exchange. All of the resins showed good stability to the process fluids expected to be encountered during processing, and only the Dowex resin showed detectable degradation due to radiation.

Duolite ES 286 was chosen as the resin for further experimentation. It exhibited the best combination of strontium selectivity and capacity of the resins tested. Table III shows the expected product purity from this resin in projected column operation. This product would be suitable for further reprocessing at B Plant.

TABLE III

Column Performance from Batch Results

	Cation/Sr
Ratio of Cation Impurity to Sr in Feed	
Ca	10.4
Mg	1.3
Metals	13.5
Rare earths	31.2
Ratio of Cation Impurity to Sr in Product	
Ca	6.6
Mg	0.5
Metals	0.1
Rare earths	7.3
Bed Volumes of Feed Treated to Column Exhaustion	12.0

Column Testing

The first set of column runs confirmed the predictions of the batch results. Selectivity was even better than predicted, as actual rare earth exchange turned out to be minimal. A summary of the column runs is shown in Table IV.

TABLE IV

Laboratory Column Performance
(Fifteen Complete Column Cycles)

	Lab
Ratio of Cation Impurity to Sr in Feed	
Group IIA/Sr	11.7
Metals/Sr	13.5
Rare earths/Sr	31.2
Percent of Cation in Feed Loaded on Column	
Sr	100%
Ca	25%
Mg	70%
Metals	0%
Rare earths	0%
Percent of Cation Loaded Removed During Scrub Step	
Sr	1%
Ca	36%
Mg	100%
Na	100%
Ratio of Cation Impurity to Sr in Product	
Group IIA/Sr	1.1
Metals/Sr	0
Rare earths/Sr	0

During the work done at Hanford in the 1960's, it had been found that diluting the feed stream to the ion exchange column greatly increased the column's capacity for strontium.¹ A similar effect was found in the present study. Fourfold dilution of the feed with water resulted in a tenfold increase in the number of CVs treated before column exhaustion occurred. This represents an effective 2 1/2-fold increase in absolute column capacity, with no effect on product selectivity. One possible explanation of the effect is that the absolute sodium concentration is lowered by the dilution. Sodium competes with strontium for the exchange sites on the resin.

A limited study of the effect of flow rate strontium capacity and selectivity was completed. In the range of one to three CVs of feed per hour flow, no effects on column performance were noted.

Elution of the strontium from the column with both ammonium nitrate (NH_4NO_3) and nitric acid (HNO_3) was studied. Both effectively removed the exchanged ions from the column bed. Nitric acid was chosen for further scale-up because concentration of the product could be achieved by evaporation, forcing HNO_3 overhead and allowing its recycle for reuse. Product removal from the resin is a function of the eluant concentration, and it was found that additional product decontamination could be achieved by "scrubbing" the column with 1M HNO_3 . A fifteen CV, 1M HNO_3 scrub removed all of the exchanged sodium and magnesium ions and between 25 percent and 50 percent of the calcium ions from the bed. Strontium losses during this scrub

were typically less than 1 percent. At the end of the scrub, the strontium and remaining calcium ions were eluted from the column using 3M HNO_3 . Both downflow (flow in the same direction as the feed in the column) and upflow (counterflow) elution were studied. Upflow elution required less than ten CVs for complete elution of strontium, while downflow required approximately fifteen CVs.

Elution of the bed with HNO_3 required the addition of a resin conversion step to the original flowsheet to remove the hydrogen ions contained in the ion exchange bed prior to the next load cycle. Attempts to load the resin in the hydrogen form were not attractive because as feed ions exchanged with the resin, hydrogen ions were released, lowering the solution pH. Below pH 4, the complexing ability of HEDTA for the metal ions was inhibited, and a significant amount of metal ion exchange occurred. Prior to each load step, the resin was converted to the sodium form using a sodium nitrate (NaNO_3) solution.

PROCESS IMPLEMENTATION IN B PLANT

Based on the success of the laboratory studies, the decision was made to directly implement the process in the existing ion exchange facility in B Plant. This represented a scale-up factor of over 4.3×10^5 to a production column of 8.5 m³ volume. No equipment changes were needed to run the new process. The old cesium production resin was changed to Duolite ES 286, and provisions were made to use HNO_3 as the eluant.

The strontium recovery flowsheet, based on laboratory studies, is shown in Fig. 1. The major process steps are as follows:

1. Feed Preparation - complexant addition, pH adjustment, and dilution to a strontium concentration of approximately $1 \times 10^{-3}\text{M}$
2. Column Loading - twenty CV (91,000 L) of feed or until 5 percent column breakthrough (i.e., the concentration of strontium in the column effluent reaches 5 percent of feed concentration)
3. Scrub - fifteen CV (68,000 L) 1M HNO_3
4. Elution - fifteen CV of 3M HNO_3
5. Regeneration - eight CV of 3M NaOH

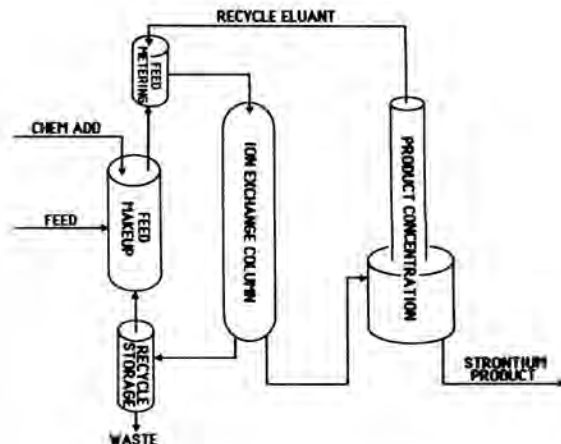


Fig. 1. Strontium Ion Exchange Flowsheet.

Sodium hydroxide was chosen for use as the regenerant in the plant because it was more readily available and less expensive than sodium nitrate. Loading and scrub wastes can be recycled if necessary. The product cut is concentrated to a volume of less than 1,900 L, recovering the HNO₃ eluant for reuse. The strontium product is forwarded for further processing in B Plant.

The use of existing facilities introduced some unique processing constraints that would not have been present in a new plant designed for strontium recovery. The feed makeup tank size is limited to (15,000 L) less than four CV capacity. This requires stopping the flow to the column while the feed tank is refilled. Extended periods of "static flow" in the column degrade performance by allowing vertical diffusion of exchanged component ions through the bed. The configuration of the ion exchange column in B Plant is not the optimum for maximum efficiency of strontium removal. The relatively short, squat column was sufficient for the simpler cesium recovery operation. A narrower, deeper bed would be more suitable for optimum strontium recovery. An additional problem with reusing equipment is the potential for cross-contamination with residual material left from previous processing. The shielded, remote operation required of a plant processing highly radioactive materials makes total cleanout of equipment nearly impossible. Cross-contamination from one process to another has been a problem at B Plant in the past.

The first column load was begun on July 9, 1984; to date, eight full cycles have been completed. Each load/scrub/elute/regenerate cycle takes approximately one week of processing time. There have been several long periods of shutdown for the ion exchange tests due to the need to perform maintenance and other processing operations at B Plant. Over one megacurie of strontium-90 has been loaded and recovered from the column. Operation has been reasonably smooth, and each cycle has shown improvement as personnel gain experience. A few laboratory results have been "reinvented" on a production scale; attempts to load the resin from the hydrogen form were just as unsuccessful in the plant.

Major changes in the laboratory-developed flow-sheet have not been needed, but some fine tuning of the process has taken place. Reducing the flow rate of the feed to the column to 0.5 CV/h (from 1-2 CV/h in the laboratory) improved strontium loading efficiency. Strontium losses during the scrub step have been reduced by cutting the concentration of the scrub solution in half (0.5M HNO₃). Both of these are very likely the result of the shallow bed configuration in the plant. It was also found that regeneration of the resin with sodium hydroxide caused the pH of the next load cycle to increase beyond the optimum value for efficient strontium exchange. The regeneration step was changed to a two-part process, with a shortened sodium hydroxide treatment followed by several CV of 2M sodium nitrate to flush the hydroxide ions from the bed.

One problem that has not been completely solved is the monitoring of strontium breakthrough (evidence of strontium in the effluent) from the column. Initial plans were to use an existing gamma radiation detector (from the cesium processing where it worked very well) on the column effluent. Strontium-90 is not a gamma emitter

(pure beta), but a beta detector was not available; and it was felt that beta Bremsstrahlung radiation (x-ray) present would allow use of the gamma radiation detector. Unfortunately, the strontium decay daughter, yttrium-90, is not exchanged on the column; and its presence in the effluent stream completely masks the strontium breakthrough. On-line determination of strontium in the effluent has not been possible. This has resulted in processing delays while samples are taken and sent to the laboratory for analysis.

Table V presents the results of a production run compared to the laboratory averages. Typically, 0.25 MCi of strontium are loaded on the production column. Total losses of strontium for the load/scrub portions of the cycle are less than 10 percent, and the strontium scrubbed from the column can be recovered by recycling. The present overall plant performance is quite close to that predicted by the original batch laboratory runs, and operations continue to improve with each cycle.

The final product metal ion/strontium ratio (2.0) shown in Table V is not consistent with that obtained from a mass balance across the column load/scrub portion of the cycle (0.69). It appears that the product was cross-contaminated from residual material in the product concentrator. The product is suitable for feed to B Plant's strontium purification processing, and additional decontamination via a second pass through the ion exchange cycle will be investigated.

TABLE V
Plant and Laboratory Performance

	Plant	Lab
Ratio of Cation Impurity to Sr in Feed		
Group IIA/Sr	7.7	11.7
Metals/Sr	2.0	13.5
Rare earths/Sr	9.7	31.2
Percent of Cation in Feed Loaded on Column		
Sr	97%	100%
Ca	62%	25%
Mg	5%	70%
Metals	5%	0%
Rare earths	25%	0%
Ratio of Cation Impurity to Sr in Product		
Group IIA/Sr	4.5	1.1
Metals/Sr	2.0	0
Rare earths/Sr	1.7	0

CONCLUSIONS

A process has been developed and implemented in production equipment to recover and purify strontium from a waste stream generated from previous strontium processing at Hanford. The process was developed within a very limited time frame and for a minimal cost. Overall development work required less than nine months and less than \$30,000. Implementation in the plant was rapid, with the major expense being the cost of the replacement resin (\$30,000). Product purity is acceptable for further processing at B Plant and may be further purified with a second pass through the ion exchange cycle. The recovery and purification of strontium by ion exchange should be applicable to other strontium-containing streams.

If this is successful, then the overall cost for recovery of strontium-90 for beneficial uses could be greatly reduced.

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