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THE RECOVERY OF FISSION PRODUCT RARE EARTH SULFATES

FROM PUREX 1WW

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Chemical Research and Development
HANFORD LABORATORIES OPERATION

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I. INTRODUCTION

A research and development program aimed at devising processes for the economical recovery of the potentially valuable long-lived fission products from Purex waste has been under way at Hanford for several years. When this work was begun, the concentrated waste was primarily a nitric acid solution (6 to 10 $\underline{M}$ HNO_3) containing the fission products and relatively small concentrations of iron, sulfate, and other corrosion products. Flowsheets based on classical separation schemes and rather similar to processes used by the Isotopes Division at the AEC's Oak Ridge operation served to separate the desired fission products from one another and from the corrosion products [1,2,3]. These separation schemes employed careful step-wise pH adjustment to precipitate first the iron and then to separate the desired fission products from one another. The flowsheets were demonstrated on a pilot-plant scale with full-level plant waste. However, since the earlier work was completed, plant operations have been modified. The plant waste is now more concentrated and is a high salt solution with nitric acid actually a minor constituent. The previously developed flowsheets are not satisfactory with the new waste. The exact composition of the Purex 1WW waste is variable; however, Table I indicates typical concentrations of the major constituents.

Table I

APPROXIMATE COMPOSITION OF PUREX CONCENTRATED 1WW

FISSION PRODUCT WASTE

Constituent	Molar Concentration
$NaNO_3$	0.6 M
$Fe(NO_3)_3$	0.5 M
$Al(NO_3)_3$	0.1 M
$Cr(NO_3)_3$	0.01 M
$Ni(NO_3)_2$	0.01 M
$UO_2(NO_3)_2$	0.01 M
H_2SO_4	1.0 M
HNO_3	2.0 M
H_3PO_4	0.01 M

In addition to the change in the composition of Purex waste, there has been a change of emphasis as to which fission products are desired. Current interest centers on the heat-generating isotopes: cerium-144, promethium-147, and strontium-90, all potentially valuable for thermoelectric or thermoionic isotopic power packages[4], rather than in the gamma emitters, cesium-137 and zirconium-niobium-95. Regardless of the change in the Purex waste composition and in the desired product or products, there has been no change in our guiding philosophy regarding the type of unit operations and recovery efficiencies. Because of the availability of the idle Bismuth Phosphate canyons for potential large-scale (megacurie) production and of the Purex head-end centrifuges for pilot plant and interim production use, we have continued to favor precipitation processes where these are applicable. We are more interested in economy of operation and in purity of product than in high yields and feel that fission product recovery will be of only marginal value to waste disposal.

Other process limitations are: 1) that reagents cannot be used which will corrode stainless steel equipment or oxidize and volatilize radioactive ruthenium and 2) dilution of the waste and increase in its solids content must be held to a minimum. The process must not be unduly sensitive to changes in feed composition or require highly precise control.

II. OBJECTIVE

The objective of the work described in this report was to determine flowsheet conditions by which cerium, lanthanum, praseodymium, neodymium, promethium, samarium and yttrium could be removed from the purex waste with a minimum of contamination from corrosion products or from other fission products. The process must be sufficiently insensitive to process variables that it can be carried out in the existing Purex plant head-end equipment and there must be no danger of ruthenium volatilization and no excessive corrosion of the stainless steel equipment.

III. SUMMARY AND CONCLUSIONS

Cerium-144 and promethium-147, accompanied by the other rare earths resulting from fission or decay can be removed from Purex 1WW in >90% yield as an insoluble, crystaline sodium-rare earth double sulfate. Precipitation is initiated by a one-to-three hour equilibration at 90 C and centrifugation at 90 C to take advantage of the lower solubility of the double sulfate salt at a higher temperature. The sulfate concentration should be one molar and the solution pH at the time of precipitation should be 0.5 to 1.5. The addition of tartrate ion to complex the iron allows the use of a higher pH and sulfate concentration, gives a more complete separation from iron, and a quantitative recovery of the rare earths. The double sulfate precipitate can be dissolved in dilute nitric acid or converted to the carbonate and then dissolved to yield a solution for further processing.

The double sulfate precipitation of the rare earths, with tartarate added, gives a good separation from impurities. One-cycle decontamination

factors of 150 for Zr-Nb and 1100 for Ru-Rh have been achieved in laboratory tests. Tests in the Purex head-end equipment with up to two-megacurie batches of cerium have corroborated the laboratory results. Decontamination factors of 70 for iron, 10 for zirconium, 20 for niobium and 25 for ruthenium have been obtained. It was found wise to limit the batch size because of heat generated by the cerium-144. Otherwise the intense decay heat leads to partial calcination in the centrifuge and to difficulty in redissolution.

IV. DISCUSSION

The high iron concentrations in current Purex waste rule out the controlled pH approach. The voluminous iron precipitate would clog the tanks and centrifuges and the high sulfate, in the presence of iron, has been found to cause most of the cerium and trivalent rare earths to co-precipitate with the iron. "Acid side" processes which would enable the rare earths to be precipitated at low pH - without formation of bulky iron precipitate - were accordingly sought. It was found[5] that the high sulfate concentration in the waste could actually be used to advantage to precipitate the rare earths, carrier free, as a sodium-rare earth double sulfate $RE_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$.

Laboratory Investigations

A series of experiments were conducted to define the optimum conditions for the precipitation of a sodium-rare earth double sulfate from the Purex concentrated fission product waste. A synthetic waste solution of the same composition as that shown in Table I was prepared. Samarium was used as a stand-in for all of the rare earth fission products. A quantity of samarium equivelent to the total amount of rare earths in a similar volume of the Purex waste was added to 250 ml of the synthetic waste solution. Fifty percent sodium hydroxide solution was added dropwise with strong continuous stirring until the pH increased to near 1.0. The solution was diluted with water to 500 ml and a final pH adjustment to 1.0 was made. During the neutralization and dilution the solution temperature was kept below 60 C. At this point, no

precipitate had formed. The solution was then heated to 90 C and held at that temperature for one hour. At the end of one hour, while the solution was still 90 C, the precipitate which had formed on heating was removed by filtration. The precipitate was nearly white, quite crystaline, and very easy to filter. Iron contamination appeared to be only slight. The precipitate was dissolved in hot nitric acid and the samarium was recovered by an oxalate precipitation followed by ignition to the oxide. The samarium recovery in the run is indicated as run number 1 in Table II.

The experiment described above was repeated and the results are shown as run 2 of Table II.

In an attempt to increase the samarium recovery, the sulfate concentration was increased to 1 molar. As in runs 1 and 2, samarium was added to 250 ml of synthetic waste solution and the solution was neutralized to pH 1.0 at a volume of 500 ml with 50% NaOH. Then 35 grams of sodium sulfate was added and the solution heated to 90 C to induce precipitation. The addition of the sodium sulfate increased the solution pH to approximately 1.5. Following a one hour equilibration at 90 C, the samarium was recovered as previously described. The results of these two experiments, given as 3 and 4 in Table II, indicate good recovery at pH 1.5 when the total sulfate concentration is at least one molar. Once again the iron contamination of the precipitate seemed to be negligible, but no analysis for iron was made. The samarium precipitate was crystaline and very easy to filter.

In the fifth experiment, lanthanum, neodynium, praseodynium, samarium, yttrium, and cerium were added to 250 ml of synthetic Purex waste in the same amounts as they are present in Purex concentrated waste. A spike of Pm-147 was added for analtyical purposes and the double sulfate precipitation was carried out in a manner identical to runs 3 and 4. The results, based on beta counting, are given as run 5 Table II. Completeness of recovery is seen to be virtually identical to the samarium-only runs.

Several precipitation experiments were carried out to define other factors which are useful from the standpoint of a plant process. Since the composition of the Purex waste is subject to change, the concentration of rare earths in the waste could, at times, be lower than the concentration used as a basis for runs 1 through 5. The possible effect of such a decrease on the recovery was determined in run 6. This run was an exact duplicate of runs 3 and 4 except that the samarium content in the feed solution was cut in half. The experiment was normal in every respect and the recovery is given as run 6 of Table II. The percent recovery is a little lower, but is still satisfactory.

Table II

PRECIPITATION OF SODIUM-RARE EARTH DOUBLE SULFATE

Run Number	Precipitation and Filtration Temp. (°C)	Precipitation pH	Sulfate Concentration at Precipitation	Percent of Samarium Recovered
1	90	1.0	0.5 $\underline{M}$	73
2	90	1.0	0.5 $\underline{M}$	69
3	90	1.5	1.0 $\underline{M}$	97
4	90	1.5	1.0 $\underline{M}$	97
5	90	1.5	1.0 $\underline{M}$	96
6	90	1.5	1.0 $\underline{M}$	92
8	90	1.5	1.0 $\underline{M}$	91
10	90	0.8	1.0 $\underline{M}$	97
11	90	0.4	1.0 $\underline{M}$	96

Experiment number 5 was repeated (run 7 - not tabulated), except this time the Pm-147 spike was omitted, and the volume of the precipitate was measured. It was found to be 2.8 ml. Thus, the sodium-rare earth double sulfate precipitated from Purex waste would be only approximately 11 ml of precipitate from each liter of waste solution.

In the seven experiments described, no attempt was made to wash the precipitate after it had been collected on a filter. Possible precipitate losses during a washing cycle were determined in experiment number 8. This experiment was an exact duplicate of experiment number 4 up to and including the filtration step. The precipitate was collected on a "M" porosity sintered glass funnel and vacuum dried. A one molar sodium sulfate wash solution - adjusted to pH 1.4 with HNO_3 - was heated to 90 C and the precipitate was slurried for 5 minutes each time in two separate 100 ml portions of the hot wash solution. The washed precipitate was then dissolved in hot HNO_3 and the samarium recovered as the oxide. The 91 percent recovery shown in Table II indicates some loss of precipitate during the washing cycle, but the loss is relatively small.

The decontamination of the rare earths from zirconium, niobium, ruthenium, and cesium was determined in run number 9. A 2 ml spike of a 1-to-100 dilution of Purex concentrated waste was added to 250 ml of synthetic Purex waste solution. Lanthanum, neodymium, praseodymiun, samarium, yttrium, and cerium were added in the same amounts as they were present in Purex concentrated waste. The double sulfate precipitation was then carried out in a manner identical to run 8. The washed precipitate was dissolved in hot concentrated nitric acid, diluted to volume, and analyzed. The rare earth feed-to-product decontamination factors were as follows:

Ru-Rh	1100
Cs-Ba	75
Zr-Nb	150

Several scouting experiments indicated that when the precipitation pH is much above 2.0 and/or the sulfate concentration much above one molar, iron contamination of the precipitate becomes quite serious unless the iron is complexed. At higher acid concentrations and lower sulfate concentrations,

iron contamination is not significant but rare earth solubility losses do become significant. Two experiments were conducted under slightly more acid conditions to evaluate the solubility losses.

In experiment number 10, a quantity of samarium equivalent to the total amount of rare earths in a similar volume of Purex waste was added to 250 ml of the synthetic waste shown in Table I. The solution was neutralized to pH 0.5 at a volume of 500 ml with 50% NaOH. Then 36 grams of Na_2SO_4 was added and the solution heated to 90 C for one hour. The sulfate addition caused the pH to rise to 0.80. Following the equilibration, the precipitate was filtered, then dissolved in nitric acid, precipitated as oxalate and ignited to the oxide. The samarium recovery of 97% was equally as good as that at a higher pH.

Run number 11 was similar to 10 except the neutralization pH was 0.12 and the precipitation pH was 0.40. A recovery of 96% of the samarium indicates a fairly broad precipitation pH range, at least from pH 0.4 to 1.5.

The rare earth double sulfate precipitated under the conditions described in this report is compact, crystalline, and easily filtered or centrifuged. On heating to 300 C, the double sulfate can be dehydrated and is then in a convenient and stable form for solid shipment. A Hanford designed shielded filter cask is being constructed to utilize these physical properties. The precipitated double sulfate will be slurried into the cask. The precipitate will be collected on a filter element within the cask and then dried in situ.

Plant-Scale Tests

The validity of the double sulfate precipitation process for removing cerium-144, promethium-147, and the other rare earths from Purex 1WW waste was demonstrated by four tests (conducted expressly for this purpose) in the Purex head-end equipment. In the first run[6], 1000 gal. of 1WW were centrifuged to remove existing solids. The resulting centrifugate - 0.3 $\underline{M}$ Fe, 1.56 $\underline{M}$ $SO_4^=$ - was neutralized to pH 0.7 - 1.1 and digested at 90 C for 30

minutes. The slurry was then cooled, centrifuged, and the precipitate cake washed with 1 $\underline{M}$ Na_2SO_4 at pH 1.0. The cake was slurried out of the centrifuge and dissolved in nitric acid. The product yield across the precipitation step for cerium-144 was 45%. The low yield may be due, in part at least, to the short elevated temperature equilibration and the ambient temperature centrifugation.

In the first plant test, a high percentage of the cerium-144 contained in the Purex 1WW waste was associated with the residual solids and was therefore disgarded prior to the sulfate precipitation. In plant test number 2, 2000 gal. of 1WW was centrifuged and the solids contained in the centrifuge were leached with nitric acid.[7] The centrifugate was discarded since 80% of the cerium-144 contained in the initial Purex 1WW was carried over on the centrifuged solids and recovered when the solids were leached. The leachate was neutralized to a pH in excess of 1.5, heated to 90 C for one hour and then centrifuged hot. The precipitation pH was inadvertantly too high and as a result iron contamination of the product was fairly serious and the fission product decontamination factor was low: Zr-Nb = 1 and Ru-Rh = 33. A total of 860,000 curies of cerium-144 was recovered in the product.

Plant test number 3 was initiated by centrifuging 2100 gal. of Purex 1WW solution.[8] The separated solids in the centrifuge were leached with 6 $\underline{M}$ HNO_3. The sulfate concentration in the leach liquor was increased to one molar by the addition of sodium sulfate and the solution was neutralized to pH 2.0. After a one hour equilibration at 90 C, the slurry was centrifuged and the separated precipitate dissolved in nitric acid. No decontamination factors could be determined because the product was incorrectly sampled. However, a material balance of solutions involved indicated a recovery of 75% of the cerium-144.

As a result of successful experimental work by L. A. Bray[9], tartrate was used in plant test number 4 to complex iron.[10] A 1213 gal. volume of Purex 1WW was neutralized, the sulfate content increased to a value slightly in excess of 1.5 $\underline{M}$, the solution made 0.17 $\underline{M}$ in tartrate, and the pH then adjusted to 1.0. This solution was then equilibrated at 90 C for one hour and centrifuged. The precipitate contained in the centrifuge was leached with nitric acid to remove the rare earths. The rare earth recovery, based on cerium-144 analysis, was 99%. Decontamination factors were: iron = 70, Zr = 10, Nb = 20, and Ru = 35.

The validity of the double sulfate precipitation process for the recovery of the fission product rare earths has been fully substantiated by a several month production effort aimed at the recovery of fission-product strontium.[9] The strontium recovery process is essentially the same as the process described above for plant test number 4. The only difference is the inclusion of lead salts to function as a strontium carrier during the double sulfate precipitation. In the strontium recovery runs, the rare earth recovery was >90%.

When a double sulfate precipitation and subsequent centrifugation are carried out using Purex fission product waste on a plant scale of operation, a very significant amount of radioactive decay heat is evolved. This heat can cause partial dehydration and calcination of the double sulfate precipitate in the centrifuge if the batch size is too large compared to the rate of dissipation of the heat. In general, plant experience has indicated 2000 gal. of Purex 1WW waste to be the maximum batch size.

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