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RADIOACTIVE WASTE SOLUTIONS

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FROM: R. E. Blanco and J. T. Roberts

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ABSTRACT

Ion exchange, electrolysis, solvent extraction, scavenging and precipitation have been studied as methods for removing radioactive isotopes from high level wastes. Process development has been limited to laboratory research and small scale engineering tests so that the efficiency of these methods in large scale operations is unknown. Emphasis has been placed on removal of strontium⁹⁰ and cesium¹³⁷ which are the most biologically hazardous of the long lived radioisotopes.

Continuous processing of the supernate from neutralized, sodium nitrate or aluminum bearing wastes by ion exchange appears particularly promising. Cesium and strontium have been removed by factors greater than 10^5 and 10^3 , respectively. Since about 99% of the strontium remains in the neutralized waste sludge, the over-all removal for strontium was greater than 10^5 . These demonstrated purifications would reduce present Oak Ridge National Laboratory wastes to a factor of 100 above drinking water tolerance for strontium and a factor of 10 lower than tolerance for cesium. In these tests, the wastes were reduced to background levels of radioactivity and consequently, higher decontamination factors are expected when higher levels of waste are processed. Similar results are expected to be achieved for the other limiting long lived isotopes, plutonium^{239,240}, curium²⁴², and americium²⁴¹ based on their known solubilities in alkaline solutions and ion exchange characteristics. Removal factors of greater than 10^4 for strontium and cesium are predicted in the treatment of acidic aluminum wastes by the Diban-Ion Exchange process following a scavenging-precipitation step. This process is considered less efficient than the neutralized treatment method since it presents more difficult engineering problems.

Ruthenium¹⁰⁶ is not removed by ion exchange but can be removed by electrodeposition by factors greater than 200 which is sufficient to reduce the ruthenium concentration to below drinking water tolerance for neutralized high level wastes. Nitrate is eliminated by decomposition in the same cell.

Research studies on a number of organophosphorus acids has shown that di-2-ethylhexylphosphoric acid (D2EHP) may be particularly effective for the selective extraction of strontium from neutralized wastes. A strontium distribution coefficient, $E_a^O(\text{Sr})$, of 200 and a separation factor of strontium from sodium of 2000 was determined between 0.1 M Na(D2EHP) in Amsco modified with 5% tributyl phosphate and 0.5 M sodium nitrate solution at pH 5. Tributyl phosphate is of only limited interest since it can be used to extract the rare earths, ruthenium, zirconium, and niobium but does not extract cesium or strontium.

INTRODUCTION

Removal of the long lived fission products from high level radioactive wastes will permit disposal of the remaining highly salted waste by conventional industrial methods. In many cases the decontaminated wastes can be disposed directly to the ground, streams or to the ocean without further treatment. The recovered isotopes will be safely isolated in small stainless steel containers for storage or for use by industry as radiation sources. Since many fission products have short half-lives, it is practical to allow them to disappear by decay before processing is undertaken. Calculations¹ have shown that after 5 years of decay, the most hazardous isotopes remaining are strontium⁹⁰, cesium¹³⁷, americium²⁴¹, plutonium^{239,240}, and curium²⁴². In water, strontium⁹⁰ and cesium¹³⁷ are about 3000 times and 10 times more hazardous, respectively, than the third most hazardous isotope, americium²⁴¹. Decontamination factors of 10^7 and 10^9 (99.9999999% removal) are required to reduce the strontium⁹⁰ content of Oak Ridge National Laboratory (ORNL) intermediate and high level wastes to the maximum permissible concentration (MPC_w) permitted for drinking water.

Some of the treatment methods under development are designed to remove all of the hazardous long lived isotopes by a single technique to achieve a cheap bulk treatment process, whereas other methods selectively remove a single isotope. But in general, development work has concentrated on methods for the removal of cesium¹³⁷ and strontium⁹⁰ because of their more hazardous nature. The mixture of isotopes produced from the bulk treatment methods could be used for irradiation work, stored, or processed further to produce pure isotopes for specific uses. Methods studied at ORNL include ion exchange, precipitation, scavenging, and solvent extraction. In most cases, these methods are in the development stage and have not been evaluated in pilot plants on actual waste streams involving large amounts of radioactivity. Consequently, their true efficiency is unknown. The single exception is the Multicurie Fission Product Pilot Plant^{2,3} which produces isotopes from highly radioactive waste streams. The principal processing methods used in this plant are scavenging and crystallization although all of the other methods are employed to some extent for specific applications.

CONCEPT OF A MULTIPURPOSE WASTE PROCESSING FACILITY

In presenting methods for isotope recovery and waste treatment, it is important to emphasize the source of the wastes since in many cases their previous history governs the choice of a treatment method. Figures 1a and 1b show the possible routes that wastes may take considering both actual practice and proposed treatment methods. The heavy lines indicate the preferred paths, based on presently available information and on work under development.

The first step is evaporation to recover the excess acid present in the wastes from the nuclear fuel reprocessing plants. The wastes from the Hanford, Savannah River and Oak Ridge National Laboratory installations, which cummulatively represent over 90% by volume of the wastes, are then neutralized with excess caustic and stored in mild steel or concrete tanks. The single exception is the Idaho Chemical Processing Plant which stores acid wastes in stainless steel tanks. On neutralization, iron and other hydrous oxides precipitate and carry down the colloidal fission products ruthenium, zirconium and niobium. In addition, most of the other fission products such as the rare earths, strontium, zirconium, niobium, ruthenium, and plutonium are insoluble in alkaline, carbonate and sulfate-bearing solutions and are precipitated in the sludge. Most of the non-radioactive bulk chemicals remain dissolved in the alkaline supernatant solution as sodium salts of nitrate, aluminate, sulfate, fluoride and hydroxide. The supernatant solutions also contain approximately 100% of the cesium, 10% of the ruthenium, and 0.1-1% of the strontium, rare earths and transuranics although these percentages can probably be reduced by adding precipitating or scavenging agents such as alum, ferrocyanide, sulfide or phosphate in connection with the neutralization step. This is the extent of large scale waste processing at the present time.

The decontamination factors required to reduce present neutralized ORNL waste supernates to drinking water tolerance are shown in Table 1. It may be seen that factors of 10^5 , 10^4 , and 5.7 are required for strontium, cesium and ruthenium, respectively. Decontamination factors about 100 times

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Fig. 1a. Waste Treatment System-Bulk Disposal of Fission Products and Solids. Heavy Lines Indicate the Preferred Paths.

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ALTERNATE I - PRECIPITATION OR SCAVENGING OF FP AND PACKAGE DISPOSAL

ALTERNATE II - SOLVENT EXTRACTION OF FP AND PACKAGE DISPOSAL

Fig. 1b. Alternate Methods of Fission Product Separation and Package Disposal.

higher will be required for power reactor wastes. Decontamination methods under development are described in the following sections. They propose, 1) removal of the fission products from the supernate from neutralized wastes by continuous ion exchange and electrolysis (Figure 1a), or 2) from acid wastes by solvent extraction as shown by alternate II-Figure 1b. Alternate I-Figure 1b, precipitation and scavenging, is representative of methods employed in the Multicurie Fission Product Plant and is described elsewhere.^{2,3} The removal, processing, packaging and disposal of the sludge from the neutralized waste is also described elsewhere.⁴

ION EXCHANGE

Ion exchange has been studied for many years as a waste treatment method but its use has generally been confined to treating low salt bearing streams such as reactor cooling water and dilute laboratory wastes. In these cases, ion exchange is very efficient since there is little inert salt present to compete with the fission products for sites on the ion exchange resin. Conversely, the high level wastes contain high concentrations of sodium, aluminum, or nitric acid.

Ion exchange has shown increasing promise, however, as a method for treating high level wastes for two reasons; 1) the successful development of a truly countercurrent continuous contactor^{5,6} which greatly increases the engineering efficiency of the method; and 2) the remarkable affinity of essentially all the fission products of interest for phenolic cation exchange resins in alkaline solutions. This is particularly significant in the case of strontium and cesium which are difficult to extract by other methods. Thus ion exchange can potentially be used as a bulk treatment method to remove all biologically hazardous elements. As outlined in the succeeding sections, the treatment of neutralized waste supernates by ion exchange represents a promising approach which has been demonstrated in small scale engineering equipment. Since approximately 99% of the strontium remains in the waste tanks in the sludge formed on neutralization, a decontamination factor of greater than 10^3 in the ion exchange step would produce an over-all decontamination factor of greater than 10^5 for strontium.

These decontamination factors would reduce the strontium content of the solution to approximately drinking water tolerance in many applications and to 100 times this tolerance for present ORNL wastes. Decontamination factors greater than 10^5 have been demonstrated for cesium which would reduce the activity of present ORNL wastes to a factor of 10 lower than drinking water tolerance.

Of the major radioactivities, only the relatively short lived ruthenium, half life 1.0 yr, is not removed (see Electrolysis in next section). Further large scale tests are required to define the ultimate efficiency of the method for removal of all the major biological hazardous isotopes. Larger decontamination factors are expected when higher level wastes are tested.

The Diban-Ion Exchange method for treating acidic aluminum-bearing wastes, is less highly developed so that its efficiency is difficult to estimate. Based on the limited data available, the process shows some promise for treating aluminum wastes but little promise for treating wastes with high sodium concentrations.

Alkaline Wastes. Ion exchange removal of long lived isotopes from alkaline wastes is attractive in that phenolic cation exchange resins have high distribution coefficients (i.e., one volume of resin can treat many volumes of solution) for cesium, strontium, rare earths and transuranics in such solutions, and the isotopes can be removed from the resin easily with acid. Thus such a treatment is a potential means of decontaminating the bulk alkaline chemical wastes (except for ruthenium) so that they can be discharged to the environment.

Miller and Kline⁷ found that cesium is selectively sorbed by phenolic cation exchange groups in the presence of high concentrations of sodium salts in alkaline solutions. Watson and Evans⁸ and Heal and Crouch⁹ developed a method for cesium recovery from alkaline solutions containing two to four molar sodium using Duolite C-3, a commercially available resin containing both phenolic and methylene-sulfonic groups. Barney¹⁰ also found a high degree of cesium removal from alkaline waste solutions by Duolite C-3, i.e., volumetric distribution coefficients for tracer levels of cesium greater than 100 in a sodium nitrate-aluminate-hydroxide solution containing 4.2 M sodium. Goodall¹¹ found that phenolic methylene-sulfonic resins

removed cesium from synthetic aluminum bearing Hanford Redox neutralized wastes with a distribution coefficient greater than 50.

Higgins and Messing¹² found cesium distribution coefficients of greater than 100 on Duolite C-3 from a variety of synthetic alkaline waste solutions for trace levels of cesium, with the distribution coefficient dropping to about 50 for cesium concentrations of one gram per liter. Sodium distribution coefficients were approximately unity, so that the cesium-sodium separation factors were approximately equal to the distribution coefficient, i.e., 50 to greater than 100. Trace amounts of strontium and rare earths had distribution coefficients as high or higher than cesium. Distribution coefficients for transuranics were not measured but, judging from their chemistry, should behave like the rare earths. In 3 M HCl regenerant solution, the distribution coefficients are approximately 0.8 for sodium, 2 for strontium and rare earths, and 5.5 for cesium. Thus the resin is readily regenerated and further separation of cesium from strontium and rare earths and of all of these isotopes from sodium is obtained. Sulfuric acid can also be used for regeneration, but not nitric acid since it reacts with the resin.

Higgins and Messing further demonstrated, on a small engineering scale, a continuous ion exchange process for removing the cesium, strontium, and other fission products from alkaline wastes and recovering the cesium for use as a radiation source. They presented a flowsheet, conceptual plant design, and approximate cost estimate for doing this on a large scale using 22,000 curies per day from waste containing one curie of cesium per gallon as a design basis. Using this work as a basis, a flowsheet has been proposed for processing ORNL wastes (Fig. 2).

Higgins and Messing demonstrated waste decontamination factors of greater than 10^4 for cesium and greater than 10^3 for strontium and rare earths. These wastes were reduced to background counting levels, hence the true decontamination factors may have been much higher. From what is known about distribution coefficients and theoretical stage heights there is no reason to believe that any desired decontamination factor cannot be achieved. The cesium to sodium ratio in the cesium product was approximately

Fig. 2. Proposed Flowsheet for Removal of Isotopes from ORNL Neutralized Waste Supernatant.

2000 times that in the waste feed. This degree of separation is adequate for waste treatment. Better separation could be achieved by using a larger ion exchange contactor with more separation stages.

Further work on ion exchange treatment is being done at Savannah River by Tober, et al., who are working with Duolite C-10, a more porous, faster reacting form of Duolite C-3, as applied to Savannah River wastes. Continuing work at ORNL is being done on Duolite S-30, which contains phenolic groups but no methylene-sulfonic groups, as applied to ORNL wastes. Work is concentrated on demonstrating the ion exchange step on actual ORNL wastes using a one-inch diameter continuous ion exchange contactor. Batch ion exchange studies with Duolite S-30, have demonstrated cesium and barium decontamination factors of greater than 10^5 . The advantages of Duolite S-30 are ; 1) a lower capacity for sodium and consequently a better separation of cesium from sodium; and 2) it requires less acid for regeneration, thus giving higher concentration factors and lower chemical costs. Both of these advantages are due to the absence of the sulfonic groups. A possible disadvantage is that the S-30 resin may not have distribution coefficients for strontium, rare earths and transuranics as large as the C-3 resin at high sodium concentrations. This is not a problem with ORNL wastes as they are relatively dilute and contain less than 1 M sodium.

It is estimated that a six-inch diameter, twenty-foot high continuous ion exchange contactor could process all of the approximately 7000 gallons per day of ORNL wastes that are being discharged to the seepage pits (Fig. 2). It is expected that the cationic fission product would be reduced to MPC levels and would be concentrated in volume by a factor of 100. The product solution containing the fission products could be further reduced in volume by evaporation to dryness or processed further to produce pure isotopes. This step would leave ruthenium as the only fission product discharged at greater than MPC levels. The ruthenium can be removed by electrolysis if desired (see section on Electrolysis). A capital cost of approximately \$750,000 has been estimated by Blomeke and Stockdale¹³ for a plant to accomplish decontamination of ORNL wastes by this flowsheet. Most of this cost is in the building, designed for much higher levels of radioactivity than present ORNL wastes would justify on the assumption that it would be

desirable to be able to process higher level wastes in the future.

Acid Wastes. In early work Blanco, Higgins and Kibbey¹⁴ showed that fission products could be successfully removed from acidic wastes containing a large amount of inert salt, i.e., $1.0 \text{ M Al(NO}_3)_3$, using cation exchange. The colloidal ruthenium, zirconium and niobium fission products were removed by a scavenging precipitation with hydrous iron and manganese oxides. The aluminum and fission products were then sorbed on Dowex 50 resin, the aluminum selectively eluted with oxalic acid, and finally the fission products eluted with nitric acid. The aluminum was decontaminated from gross fission products by a factor of 10^3 , from plutonium by 5×10^5 , and from cesium, strontium and rare earths by 10^3 - 10^4 (Fig. 3). This process was uneconomical, however, since it involved a stoichiometric relationship between aluminum and the resin and hence required large amounts of resin in addition to large amounts of oxalic and nitric acids.

More recently, Higgins and Wymer¹⁵ proposed an alternate scheme, the Diban-Ion Exchange process, for removing strontium, cesium and rare earths from aluminum wastes (Fig. 4). In this process, the colloidal fission products are removed by scavenging, as above, and the aluminum solution subsequently evaporated to a temperature of 160°C to convert the aluminum nitrate, $\text{Al(NO}_3)_3$, to dibasic aluminum nitrate, $\text{Al(OH)}_2\text{NO}_3$ (Diban). The solution is then cooled and diluted with water to 1.6 M Al and passed into the resin column where the fission products are sorbed. The majority of the aluminum is not sorbed and passes through the column. Since the monopositive Al(OH)_2^+ ion is much less strongly adsorbed than the tripositive Al^{+3} ion, the fission products can more successfully compete for the ion exchange sites in the presence of large amounts of aluminum.

An oxalic acid scrub solution is used to decrease the amount of aluminum sorbed. The aluminum waste can then be discarded or evaporated to $6 \text{ M Al(OH)}_2\text{NO}_3$ if further storage is required. Storage in this case would require 300-400% less volume than the present practice of storing at 1.5 to $2.0 \text{ M Al(NO}_3)_3$. The fission products are removed from the resin by an $3 \text{ M ammonium carbonate}$ - $0.1 \text{ M ammonium citrate}$ solution. The ammonium carbonate can be recovered for recycle by steam stripping and the remaining fission product solution evaporated for low volume storage or the individual

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Fig. 3. Removal of Isotopes from Acidic Aluminum Bearing Wastes by Ion Exchange.

TYPICAL ALUMINUM NITRATE
WASTE

1.6 M $\text{Al}(\text{NO}_3)_3$
0.5 M HNO_3
0.04 M $\text{Fe}(\text{NO}_3)_3$
0.004 M $\text{Hg}(\text{NO}_3)_3$

CONTINUOUS CATION EXCHANGE (Dowex 50)

BATCH CATION EXCHANGE (Dowex 50)

Fig. 4. Removal of Isotopes from Acidic Aluminum Bearing Wastes by the Diban-Ion Exchange Process.

fission products separated for use as isotopes. Alternatively the fission products can be eluted with mineral acids such as nitric or sulfuric, if desired.

Distribution coefficients for cesium, strontium, and rare earths, calculated as radioactivity per unit volume of resin divided by radioactivity per unit volume of solution, between 1.6 M Diban solution and "Dowex 50X8" resin were 7, 8 and 11, respectively. Decontamination of aluminum solutions from cesium and strontium therefore, should be greater than the 10^3 - 10^4 found previously.¹⁴ A disadvantage of the Diban process is the corrosive conditions present during the evaporation step to form Diban. Since some aluminum wastes contain ammonium nitrate, their evaporation could be hazardous. Consequently, the use of hydroxyl form anion exchange resins will be considered to convert the aluminum nitrate to Diban. Resin decomposition from radiation is not considered a significant factor. Using a figure of 20% degradation when 1 g of resin absorbs 1 watt-hr of radiation,¹⁶ it has been calculated that only 0.0056% of the resin will be lost per cycle when enriched 10% U-Al fuel irradiated to 4×10^{13} n/cm²/sec and cooled 5 months is processed. The Higgins ion exchange contactor would be used to achieve continuous processing.

ELECTROLYSIS

The alkaline ion exchange method described above is expected to remove essentially all of the fission products with the exception of ruthenium¹⁰⁶. Although ruthenium¹⁰⁶ is not a major biological hazard, it is desirable to reduce the amount discharged to the environment. At the same time it would be advantageous to reduce the nitrate content of the waste since nitrate in higher concentrations is a bio-chemical poison. Early workers^{17,18} had shown the feasibility of electro-deposition of ruthenium from dilute solutions and more recently Alter, Barney, et al., at Knolls Atomic Power Laboratory (KAPL) proposed an electrolytic process for treating nitrate wastes.^{19,20,21} Consequently, electrolysis was selected by Messing and Higgins²² for further study as a solution to the problem.

Messing and Higgins considered two types of cells. The first was the KAPL nitrate reduction type which uses a simple stainless steel compartment with close spaced stainless steel cathodes and anodes (Fig. 5). Ruthenium electrodeposits on the cathode and nitrate decomposes to ammonia gas at the cathode. The sodium is converted to caustic which can be reused to neutralize more waste. The second type was a cell designed by Ionics, Inc. which contains cation and anion ion exchange membranes as barriers (Fig. 6).²³ In this cell, the cationic fraction of the ruthenium migrates to and deposits on the cathode. Similarly the sodium and nitrate ions migrate to the cathodic and anodic compartments to form caustic and nitric acid. After a series of tests, the KAPL design was selected for intensive study since it was the simplest and accomplished the objectives of ruthenium and nitrate removal more directly. This type of cell was used in the cost estimate outlined in the preceding section for treating ORNL wastes.¹³

In laboratory scale studies on the nitrate reduction type cell, Messing and Higgins showed that synthetic alkaline waste containing 0.55 - 4.83 M total electrolyte as NaNO_3 and NaOH could be decontaminated from ruthenium by factors of >210 . The nitrate of 3.0 M total electrolyte waste was reduced to ammonia with current efficiencies of 100%. Power consumption was 4.7 kwh/lb of nitrate reduced. Significant factors affecting the rate of ruthenium decontamination were temperature, cathode area, cathode current density, and electrolyte concentration. Those affecting nitrate reduction current efficiencies were the cathode current density, electrolyte concentration, and stirring rate.

They estimated that a 250-gal cell containing six type-347 stainless steel anodes and five Armco iron cathodes, 48 by 12 in., would process 1,000 liters of 2.0 M NaNO_3 --0.7 M NaOH waste in 24 hr when operated at a current density of 3 amp/in.² at 100°C. Nitrate levels would be reduced below 0.1 M with decontamination factors of >200 for ruthenium. This is more than adequate to reduce the ruthenium concentration to drinking water tolerances for both ORNL intermediate and high level wastes (Table 1). The sodium hydroxide produced could be discharged to a pit or concentrated by evaporation and reused for neutralizing more waste. In the latter case, only the purified evaporator concentrate would be released to the environment (Fig. 2).

Table 1. Decontamination Factors Required to Reduce Neutralized Oak Ridge National Laboratory Waste Supernates to MPC_w Values*

	Present ORNL Neutralized Waste Supernate		ORNL Neutralized Waste Supernate Expected from Power Reactor Fuels**		MPC _w ($\mu\text{c/ml}$)
	Specific Activity ($\mu\text{c/ml}$)	Decontamination Factor	Specific Activity ($\mu\text{c/ml}$)	Decontamination Factor	
Sr ⁹⁰	0.1	1.2×10^5	76.0	9.5×10^7	8.0×10^{-7}
Cs ¹³⁷	2.0	1.3×10^4	7.60	5.1×10^6	1.5×10^{-3}
Ru ¹⁰⁶	0.47	5.7	13.0	130	0.1
TRE(Ce ¹⁴⁴)***	0.40	1.0×10^3	7.6	1.9	4.0×10^{-2}
Pu ²³⁹	-	-	0.013	8.9×10^3	1.5×10^{-6}

(Table prepared by J. O. Blomeke, ORNL.)

* MPC_w = Maximum permissible concentration in drinking water for life-time use from Report of National Committee on Radiation Protection, National Bureau of Standards Handbook No. 52, (in press).

** Calculated using following assumptions: neutralized waste from fuel enriched to 2% U²³⁵; irradiated to 10,000 Mwd/ton; volume = 1.1 gal/kg U; decayed 10 yr; alkaline supernatant will contain 1% of original Sr⁹⁰, 1% of TRE, 10% of Ru¹⁰⁶, and 100% of Cs¹³⁷; reprocessing losses for Pu^{239,240} were 1% and supernatant contains 1% of process losses.

*** Rare earth of lowest MPC_w.

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Fig. 5. Nitrate Reduction and Ruthenium Removal Cell.

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Fig. 6. Ionics Inc. Design for Acid-Base Membrane Cell.

An experiment was run to determine the maximum ruthenium decontamination obtainable. A solution containing 0.44 M NaNO_3 and 0.11 M NaOH and Ru-106 tracer, was electrolyzed at a potential of 3 volts, a current density of 0.13 amp/in.², and a temperature of 60°C. The half-life for the ruthenium deposition was 3.4 hr (Fig. 7). A sharp break occurred at 25 hr in the plot of log gross β vs time, which represented a decontamination factor of 250. Continued electrolysis for an additional 46 hr resulted in an increase in the decontamination factor to 430. Similarly, from a solution containing 3.43 M NaNO_3 and 1.40 M NaOH , at a potential of 6.2 volts, current density of 4 amp/in.², and a temperature of 89°C, the ruthenium half-life was 2.0 hr. As in the above case a break occurred in the plot, at about the same level of activity but after about 15 hr. This represented a decontamination factor of 210. Whether or not the remaining activity was due to ruthenium or to a contaminant of the Ru-106 tracer was undetermined. If the remaining activity was not ruthenium, the ultimate decontamination factor for ruthenium is much higher than 200-400. More investigation is needed.

SOLVENT EXTRACTION

Solvent extraction has proven to be a singularly efficient method for the separation of plutonium and uranium from fission products. Consequently, efforts have been made to use solvent extraction for the recovery of isotopes from waste streams. Inherently, however, the well-known low cost solvents such as tributyl phosphate (TBP) and hexone do not extract fission products easily since they were chosen because of their ability to extract plutonium and uranium in preference to the fission products. Tributyl phosphate, for example, will extract many of the fission products under the proper conditions but will not extract cesium or strontium, the isotopes of greatest interest from the biological hazard viewpoint. Other more expensive and less familiar solvents now being studied in development programs show promise for selective extraction of strontium and cesium. These studies are approaching the point where larger scale testing is warranted to determine over-all feasibility. The following sections present the status of solvent extraction for isotope recovery.

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Fig. 7. Demonstration of Maximum Decontamination Factors by Ruthenium Plating.

Organophosphorus Acids. A number of organophosphoric acids have been studied by Coleman, et al., for the selective extraction of strontium and cesium from neutralized wastes.^{24,25} Particular emphasis was placed on their separation from sodium which is the bulk ion in neutralized waste. Sodium salts of organophosphorus acids in hydrocarbon solution extracted strontium from sodium nitrate solutions over a wide pH range. The lower limit, the pH at which each extractant was hydrolyzed completely to the hydrogen form, was a function of its acid strength, and the upper limit was set by the phase stability of the organic salt solution. With di(2-ethylhexyl) phosphate (D2EHP) the useful pH range is from about 3 to above 12. The strontium extraction coefficient from 0.5 M sodium nitrate solution with 0.1 M Na-D2EHP rose sharply to a maximum of ~200 near pH 5 (Fig. 8). The separation factor for strontium from sodium, $SF_{Na}^{Sr} = E_a^O(Sr)/E_a^O(Na)$ was about 2000 at the maximum. At this pH the reagent is approximately half in the sodium form, so that the extraction coefficient for sodium, $E_a^O(Na)$ was fixed at $0.05/.5 = 0.1$. This separation factor and extraction coefficient should provide an excellent separation of strontium from sodium nitrate solutions.

An extraction isotherm at pH 5.1 leveled off at an Sr/D2EHP mole ratio of 1/4. The shapes of the extraction-vs-pH curve and of the extraction isotherm are attributed to formation of a chelate complex with two D2EHP dimers,

analogous to the complex found in uranyl extraction with D2EHPA.²⁶ Thus, the formation of the chelate complex is highest at a pH near 5 where the concentrations of both ionized and un-ionized organic acid are favorable. At lower pH the direct competition by hydrogen ion rapidly increases, while at higher pH ionization increases until only the simple salt $(D2EHP)Sr(D2EHP)$ can be formed. Above pH 7 the strontium extraction coefficient was constant at about 10 (Fig. 8). Here the extraction varied nearly linearly with reagent concentration and with the reciprocal of the aqueous sodium concentration, consistent with existence of the organic salt as a colloidal dispersion in the hydrocarbon solution. The separation factor for strontium from sodium was constant at about 50 over the pH range 7-12. In this case the distribution coefficient for sodium, $E_a^O(Na)$, was

Fig. 8. Strontium Extraction Coefficient vs Aqueous pH. Extracted from ~ 0.5 M NaNO_3 aqueous solution by 0.1 M sodium di (2-ethylhexyl) phosphate in Amsco 125-82 modified with 5% TBP.

fixed at $0.1/0.5 = .2$ by the macro concentrations.

Table 2 shows a list of other organic phosphorus acids tested. Only dicyclohexylphosphinic acid failed to extract strontium (i.e., its distribution coefficient was $E_a^O(\text{Sr}) = 0.1$ at pH 3 to 12). None gave higher separations of strontium from sodium than did D2EHP. Several extracted strontium at significantly lower pH than did D2EHP, or gave somewhat higher extraction from alkaline solution.

Table 2. Organophosphorus Acids Tested for Extraction of Strontium²⁸

Di-n-octylphosphoric Acid in Amsco 125-82
 Bis(diisobutylmethly)phosphoric Acid in Amsco 125-82 + 3% TBP
 2, 6, 8-trimethylnonyl-4-phosphoric Acid in Kerosene
 2-methyl-7-ethylundecyl-4-phosphoric Acid in Kerosene
 3, 9-diethyltridecyl-6-phosphoric Acid in Kerosene
 Di-(2-ethylhexyl)phosphinic Acid in Amsco 125-82 + 10% TBP
 Di-cyclohexylphosphinic Acid in Benzene
 Di-n-hexylphosphinic Acid in Amsco 125-82 + 5% TBP
 Phenyl(1-hydroxy-2-ethylhexyl)phosphinic Acid in Benzene

The organophosphorus acids were less successful in extracting cesium than was the case with strontium. Although monoalkylphosphoric acids are not significantly stronger acids than the corresponding dialkylphosphoric acids,²⁷ the monoalkyl acids in hydrocarbon solution extracted alkali metal ions from aqueous solutions that were more acidic, down to pH 1. The order of selectivity for the alkali metals from nitrate solution with 1-(3-ethylpentyl)-4-ethyloctylphosphoric acid (HDPA) and others of similar structure was $\text{Cs} > \text{K} > \text{Na} > \text{Li}$. The cesium extraction coefficient from 0.5 M sodium nitrate solution with 0.5 M HDPA in kerosene was ~ 3 in the pH range 1-1.5, with separation factors from sodium of ~ 30 . Cesium extraction by sodium di(2-ethylhexyl)-phosphate was low, with cesium extraction coefficients less than those of sodium in the pH range from 4 to 11.

Cesium was removed from nitrate solution more effectively by sorption on a precipitate of zirconium phytate (inositol hexaphosphate). Sorption was highest from slightly acidic solutions, but still considerable from 2 M nitric acid in single-stage batch equilibrations using 1 g of sorbent per 100 ml of solution (Table 3).

Table 3. Cesium Sorption from Nitrate Solutions by Solid Zirconium Phytate²⁸

Aqueous Solution	pH	Per Cent of Cs Sorbed
0.5 <u>M</u> NaNO ₃	12	6
0.5 <u>M</u> NaNO ₃	0.7 to 2.2	80
2 <u>M</u> HNO ₃	0	35
1 <u>M</u> Al(NO ₃) ₃	1	97
2 <u>M</u> Al(NO ₃) ₃	1	92

Equilibrium was reached in 5 min. The limiting loading from 0.1 M cesium nitrate solution was about 1 mmole of cesium per gram of sorbent, and the limiting loading from 0.5 M NaNO₃ containing 10 ppm cesium at pH 3 was 2 mg of cesium per gram of sorbent. A column sorbed 0.7 mg of cesium per gram of sorbent from 1 M 10 NaNO₃ solution containing 10 ppm cesium at pH 1 before breakthrough. The sorbed cesium can be eluted with ammonium nitrate or chloride.

Tributyl Phosphate (TBP). In the absence of significant quantities of TBP-extractables, such as uranium or thorium nitrates, which create TBP-saturation and/or strong back-salting effects on less extractable species, the cerium and rare earths are readily extracted by tributylphosphate. In cases where nitric acid is the only aqueous salting agent, relatively strong concentrations of acid e.g., 8-16 M are required to provide usefully high rare earth distribution coefficients because the TBP-extractable nitric acid may effectively back-salt the rare earth nitrates. However, such systems have been effectively employed in the extraction and separation of the naturally occurring rare earth elements by Weaver and Topp.²⁹ In aqueous systems containing aluminum nitrate and under either acid-deficient or

relatively low acidity conditions, fairly low salt-strengths procure usable distribution coefficients for the cerium and yttrium rare earths. Both pure TBP and 30-45% solution of TBP in inert solvents have been studied.

In tracer studies employing 1.0 volume of synthetic solution ($1.6 \text{ M Al(NO}_3)_3$, 0.16 M HNO_3 , $0.02 \text{ M SO}_4^{=}$) with 0.2 volume of 100% TBP, Krieger et al.³⁰ found that a combination of chemical treatments of the aqueous waste provided a system for extraction of the cerium, yttrium, zirconium, niobium and ruthenium fission products. Greater than 99% of the rare earths were extractable without treatment. The addition of cupferron was employed to attain about 89% extraction of zirconium-niobium; and reduction by metal addition to aqueous phase was employed to attain approximately 80% removal of the ruthenium.

In other laboratory studies, wastes from the Thorex process were treated by Gresky and Wischow.³¹ The cerium rare earths were extracted from the evaporated waste concentrated with 42% TBP in Amsco diluent. The concentrates contained $2.47 \text{ M Al(NO}_3)_3$ - $0.11 \text{ M SO}_4^{=}$ and were 0.87 M acid deficient. Employing a batch countercurrent extraction and stripping system, it was possible to completely extract and concentrate the cerium rare earths. Extraction distribution coefficients for the latter were observed to be greater than 10^4 , making it possible to employ small efficient organic volumes for the extraction process.

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