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FISSION PRODUCT RECOVERY FROM RADIOACTIVE EFFLUENTS

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INTRODUCTION

Of the many fission product isotopes formed in the fission reaction, some are of sufficiently long half-life and formed in sufficient yield to be of major importance from the standpoint of long-term waste disposal or retention or of recovery for utilization as radiation sources. The more important of these isotopes, with their daughters, are shown in Table I. Cesium-137 is promising as a gamma radiation source because of its long half-life, high fission yield, and high gamma/beta ratio. Strontium-90 is of interest for applications where a long-lived beta-only emitter is desired. The others are of lesser interest although they may find application where their short half-lives are not a serious deterrent. In the area of waste disposal or retention, interest centers on the removal of cesium-137 and strontium-90, again because of their long half-lives and because of the severe biological hazard of strontium-90.

TABLE I

RADIATION CHARACTERISTICS OF PRINCIPAL FISSION PRODUCTS

Nuclide	Thermal Fission Yield from U-235, %	Half-Life	Principal Radiation, MEV	
			β	γ
Cs-Ba-137	5.9	30 y	1.2	0.66
Sr-Y-90	5.9	28 y	2.2	None
Ru-Rh-106	0.38	1.0 y	3.53	0.51 (25 %) 2.41 (0.3 %)
Zr-Nb-95	6.4	65 d Zr, 35 d Nb	0.4	0.75
Ce-Pr-144	6.1	285 d	3.0	2.2 (1 %)

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This paper describes some processes, presently under development in the Hanford Laboratories, for the recovery of certain fission products, particularly cesium, from currently available process effluents. The proposed processes are, to some extent, similar to processes previously used successfully at Hanford for the pre-disposal treatment of aged process effluents. Hanford's experiences with this program are described briefly.

Fission product recovery, particularly the removal of long-lived isotopes from process effluents, is frequently considered an integral part of ultimate waste disposal. A common concept is that, if cesium-137 and strontium-90 are removed, the remainder can be disposed of after a relatively short storage period during which short-lived isotopes will decay to non-hazardous levels. Some discussion of the relationship of fission product recovery to ultimate waste disposal and of the limitations of this relationship is presented in the final section of this paper.

FISSION PRODUCT RECOVERY

Research at Hanford on fission product recovery has concentrated largely on cesium since it was felt that this is the fission product most likely to find a large scale market in the near future. The recovery of other fission products has been considered to be of secondary interest, and schemes for their recovery have accordingly been designed to fit into a main-line cesium recovery process. Furthermore, interest centered on the use of precipitation techniques because of the existence at Hanford of idle precipitation facilities.

It should be noted further that the selection of an optimum process for the recovery of fission products from a radioactive waste solution will be very dependent on the composition of the waste and the method of waste disposal employed. Thus Oak Ridge has successfully used the fractional crystallization of ammonium alum to recover cesium from the high aluminum nitrate ARCO chemical separations plant waste⁽¹⁾, and the British are reported to use phosphotungstate carrying to recover cesium from their waste, a nitric acid solution which is stored in stainless steel tanks without neutralization.⁽²⁾ At Hanford, uranium and plutonium are recovered from irradiated fuel elements by means of the Purex process.⁽³⁾ This is a solvent extraction process which employs tri-n-butyl phosphate as extractant and nitric acid as salting agent. The bulk of the nitric acid is recovered from the waste by distillation for reuse, and the concentrated waste is then neutralized with caustic and stored in the alkaline condition in underground mild steel tanks. The flowsheet composition of this waste is shown in Table II. In actual practice, the composition of the unneutralized waste is rather variable with the concentration of many of the inert constituents often exceeding the above values and with traces of corrosion products, uranium, and aluminum also present. This is shown by the numbers in the third column. Although large quantities of fission products are present in the Hanford storage tanks, recovery from this material would be more expensive than from the current plant waste, and the latter should be adequate to satisfy the expected demand. Therefore effort was concentrated on recovery of cesium from the fresh waste.

TABLE II
COMPOSITION OF PUREX WASTE

<u>Constituent</u>	<u>Molarity</u>	
	<u>Flowsheet</u>	<u>"Actual"</u>
HNO ₃	7.6	6
Fe	0.11	0.3
Al	-	0.1
Na	0.38	1
U, Cr, Ni	Trace	Trace
SO ₄ ⁼	0.21	0.4
Total Fission Products	~ 0.01	~ 0.01
Cesium	~ 0.001	~ 0.001

Several precipitating agents were scouted in the initial work. These included tetraphenyl boron, cobaltinitrite, silicotungstate, and various ferri- and ferrocyanides. The latter showed the most promise and were selected for intensive development. As has been found to be the case with many other scavenger reactions, coformed precipitates were found to be much more effective than preformed. The ferrocyanides of zinc, nickel, copper, iron(III), iron(II), cobalt, cadmium, uranium(VI), and manganese(II) and the ferricyanides of nickel, copper, and zinc all precipitated cesium to some degree. From the standpoint of extent of cesium recovery, volume of precipitate to be handled, and specific activity of product, zinc ferrocyanide, zinc ferricyanide, nickel ferrocyanide, and iron(III) ferrocyanide were the most efficient. Nickel ferrocyanide was effective over the widest pH range (from about 5 M nitric acid to pH 10) whereas zinc ferrocyanide gave the smallest precipitate volumes and highest specific activity. Details on the effects of variables are reported elsewhere.⁽⁴⁾

A flowsheet based on the use of zinc ferrocyanide is shown in Figure 1. Noteworthy features of the cesium zinc ferrocyanide process are the large volume reduction (ca. 1000 fold) and the high specific activity of the precipitate, which is about 45 percent cesium by weight (dry basis). The precipitated cesium is also of high radiochemical purity since most of the fission products are removed on the ferric hydroxide precipitate. This process has been tested with full level plant waste and is currently undergoing pilot plant development.

The product of the cesium zinc ferrocyanide process is a definite compound with the composition Cs₂ZnFe(CN)₆.⁽⁴⁾ It appears to have a lower solubility

than zinc ferrocyanide itself, and most complete cesium precipitation occurs when zinc and ferrocyanide are added in quantities stoichiometric to the cesium. Although cesium zinc ferrocyanide is acceptable from a specific activity standpoint since it is very nearly half cesium by weight, there is some reason to think that it may undergo slow radiation decomposition with resultant gas evolution. Therefore, methods have been developed to convert it to cesium chloride, which is known to be satisfactory for irradiation source use. This can be done in a variety of ways,⁽⁴⁾ e.g., by calcination followed by water leaching, acidification of the leach solution with hydrochloric acid, and evaporation to dryness; by dissolution in sulfuric acid followed by sulfide precipitation of iron and zinc, and anion exchange removal of sulfate; or by hydrolysis with steam⁽⁵⁾ at 250-300°C followed by leaching, acidification, and drying. The latter process has been selected for engineering prototype testing.

The most difficult step in the cesium zinc ferrocyanide process is the centrifugation (or filtration) and washing of the ferric hydroxide precipitate. The handling characteristics of this precipitate are considerably improved by slow neutralization with gaseous ammonia or by urea hydrolysis (homogenous precipitation); however, the large bulk of the precipitate is still a problem at high iron concentrations. Therefore, the removal of cesium after only partial neutralization and prior to iron precipitation has also been investigated.⁽⁶⁾ Nickel ferrocyanide, zinc ferricyanide, and zinc cobalticyanide were the most efficient cesium carriers at low pH, with the zinc ferricyanide giving the best recoveries and smallest precipitate volumes. Recoveries of 89 to 98 percent were obtained from full level plant waste solution. However, it was necessary to use a ten-fold excess of precipitant, and the precipitate was contaminated with up to ten percent of the initial zirconium and ruthenium activities. Thus, further processing would probably be required to improve the radiochemical purity and specific activity of the cesium product. Choice between the "acid side" flowsheet and the cesium zinc ferrocyanide process for a particular application would probably depend on the composition (iron, uranium, and aluminum concentration) of the waste and on the results of larger scale comparative tests.

A scheme for the recovery of other fission products, in addition to cesium, is shown in Figure 2. Control of pH is utilized to fractionate the fission products into groups, and appropriate precipitation reactions are then utilized to isolate individual elements. Final packaging of strontium, cerium, and rare earths would probably be as the fluorides or fused oxides, since these have good chemical and radiation stability. Cesium recovery would be by ferrocyanide precipitation, as before.

An engineering study of the probable cost of producing fission products in Hanford facilities has been made.⁽⁷⁾ It appears that cesium-137 (as cesium chloride) can be produced and sold at a price of about 50 cents per curie at a processing rate of the order of a megacurie per year. Production at a high rate or concurrent production of other fission products would reduce this price substantially.

HANFORD WASTE SCAVENGING EXPERIENCE

Procedures similar to those just described for the recovery of cesium and strontium have been used successfully at Hanford for the decontamination of certain process effluents prior to discharge to the ground. The solutions contained ferric, sulfate, and phosphate ions in moderate concentrations ($< 0.5 \text{ M}$) in addition to high concentrations of nitric acid and/or sodium nitrate. By simply making the solutions alkaline (pH 8-10) ferric hydroxide and phosphate were precipitated. Most of the total radioactive content present was coprecipitated with these solids. Decontamination factors for strontium ranged from 80 to 200. However, very little of the cesium present was removed. Precipitation of nickel ferrocyanide prior to or during neutralization of acidic wastes or in the supernatant liquid from already alkaline wastes removed cesium very thoroughly. Cesium decontamination factors as high as 10^4 were obtained, and factors in excess of 10^3 were routine for a single strike in large-scale processing. Ferrocyanides other than nickel (copper, iron, cobalt, zinc) are also effective carrier precipitants for cesium as noted elsewhere in this paper. Nickel ferrocyanide was chosen for this application because it is relatively inexpensive and because it functioned best in the pH range (8-10) dictated by other aspects of the process. More complete removal of strontium than that obtained by making the solutions alkaline was desired. By adding inert calcium or strontium nitrate to the solutions prior to treatment, strontium decontamination factors were increased to 500 or greater. Following settling of the solids produced in these treatments, the supernatant liquids contained strontium-90 and cesium-137 in the range of 0.02 to 0.1 $\mu\text{C}/\text{ml}$. Total fission product content ranged from one to 20 $\mu\text{C}/\text{ml}$ depending on the age of the effluent. References 8, 9, and 10 describe these procedures in much greater detail.

It should be emphasized that the procedures just described did not produce an effluent which could be discharged directly to public waters. Concentrations of many of the isotopes present were many-fold greater than the maximum permissible in drinking water. These effluents could be discharged to ground safely at Hanford only because of an unusually favorable combination of climate and geology, as well as remoteness from habitation and from public waters. The discharge area has a deep ground water table (250-350 feet) overlaid with a sandy, permeable soil having considerable adsorption capacity for many cations. Ground water under the discharge area has a low hydrologic gradient and moves toward the adjacent Columbia River slowly. At no point in the area is ground water removed for domestic or agricultural purposes. Wastes discharged into the ground near the surface percolate through a long exchange column of soil before reaching ground water. Much of the residual fission product content is absorbed by the soil. Of those radioisotopes which do reach ground water, only those with relatively long half-lives (> 3 years) are of prime concern since the short-lived isotopes will decay to sub-hazardous levels before reaching the Columbia River. Thus, if the discharge system is so operated that no long-lived isotopes reach ground water in hazardous concentrations, the operation as a whole is safe. In practice, the operating criterion adopted was that no radioactive nuclide having a half-life greater than three years should exist in the ground water at concentrations greater than 0.1 the maximum permissible in potable water. Several million gallons of separations process effluents were treated and

discharged to ground in this program. Total cost including preparation of the discharge sites was about five cents per gallon of waste treated.

Cesium-137 and strontium-90 are the only fission products having long half-life and produced in high yield in the neutron irradiation of uranium. Low concentrations of long-lived alpha emitting isotopes were also present in the scavenged waste. However, past experience has shown that these latter are much more completely adsorbed and strongly held in soil than cesium or strontium. Consequently, the quantity of waste which could be discharged to any given area of soil was limited by the adsorption of cesium-137 and strontium-90. Since maximum permissible concentrations in potable water (MPC) for cesium-137 and strontium-90 are 1.5×10^{-3} and 8×10^{-7} uc/ml, respectively,⁽¹¹⁾ it is apparent that operation of the discharge system within the established criterion required that additional decontamination factors of about 10^3 for cesium-137 and 10^6 for strontium-90 be obtained through adsorption of these isotopes by the soil.

To determine approximately how much of the scavenged waste could be discharged per unit discharge area, soil column tests were made on each batch (300,000 to 500,000 gallons). In these, the number of column volumes of waste passed through the soil column before either cesium-137 or strontium-90 in the effluent exceeded 0.1 MPC was determined. This value and an estimated effective soil column length to ground water were used to establish the volume of waste which could be discharged to any given area.

The testing program brought to light some interesting observations on the effect of various constituents on the adsorption of strontium and cesium by soil. For example, it was found that the adsorption of strontium depended on the amount of phosphate present,^(12,13) and a minimum phosphate concentration in the discharged waste had to be specified. Also, it was found that very low concentrations of aluminum (in the range of 0.001 M) had a seriously adverse affect on the adsorption of cesium and strontium. Although not a fission product, cobalt-60 was one of the more troublesome isotopes in this disposal program. It was present in low concentration, presumably due to neutron reactions with impurities in fuel or cladding materials. For some reason, as yet not completely explained, adsorption of cobalt from the scavenged wastes by soil was essentially negligible. Consequently, it was necessary that the cobalt-60 content in the discharged waste be no higher than that specified for ground water. Since cobalt-60 has an intermediate half-life (5.2 years) this specification was set at the MPC or 4×10^{-4} uc/ml for some waste batches. The cobalt-60 which does reach ground water will be used as a tracer for further determinations of ground water flow. These effects imposed very severe limitations on the allowable volume discharged per unit area for some batches of waste. They are cited here to emphasize the caution required in carrying out a waste disposal program even under exceptionally favorable conditions. Under less favorable conditions the problems would be increased many fold.

RELATION OF FISSION PRODUCT RECOVERY TO WASTE DISPOSAL

Historically the recovery of certain fission products, particularly long-lived nuclides, from separations waste has become identified as an integral

part of ultimate waste disposal. In particular, it is argued that, if the long-lived isotopes such as cesium and strontium are removed, the remainder can, after a few years storage, be relatively easily disposed. It would be well to examine this concept in terms of the objectives of a fission product recovery program. The current incentive for the recovery of significantly large amounts of fission products presages use of their radiant energy for processing of foods, destruction of parasites, and initiation of chemical reactions. Economic studies have shown that recovered fission products must be made available at very low cost to compete with conventional forms of energy where these will perform the same task. Even where the effect desired can be obtained only by high energy radiation, fission products must compete economically with machine-made radiation. Thus, the objectives of a large-scale fission product recovery program are the long-familiar ones of low cost and high volume.

Separations process effluents currently available for large-scale fission product recovery contain cesium-137 and strontium-90 in concentrations of between 10^3 and 10^4 uc/ml. To reduce these nuclides to drinking water tolerances, minimum decontamination factors of about 10^6 and 10^9 , respectively, would be required. Suggested recovery processes give decontamination factors ranging from only about ten to 100. This is due to the necessity of keeping the process simple and producing a product of high specific activity. Economically competitive processes giving decontamination factors of 10^3 may possibly be devised, but it appears highly improbable that competitive processes giving decontamination factors of 10^6 to 10^9 can be developed. Effluents from presently suggested cesium and strontium recovery processes will contain many times drinking water tolerances for cesium-137 and strontium-90. Thus, even though these effluents are stored until all short-lived nuclides have decayed to sub-hazardous levels, they still cannot be safely discharged where they might contaminate public waters. Complete confinement of the wastes, further treatment to reduce these isotopes to non-hazardous levels, or controlled disposal to ground under favorable conditions of soil retention and remoteness from public waters would be required. It is well to remember that process effluents from which fission products may be recovered also contain small amounts of plutonium, uranium, and other alpha emitting isotopes. These have generally much longer half-lives than and represent about as great a hazard as most fission products. Their presence must be considered in the disposal of any effluent where it may enter public waters.

There are however, undeniable fringe benefits to waste disposal resulting from fission product recovery. Thus, the magnitude of the hazard or catastrophe should a waste storage tank rupture would certainly be diminished if most of the cesium and strontium had been removed. Also, the energy produced by radioactive decay is adsorbed by surrounding media and converted into thermal energy. In highly radioactive solutions, the decay heat may be sufficient to produce boiling while in large masses of highly radioactive solids (as would be derived by evaporating radioactive wastes to dryness) very high temperatures may be reached if thermal conductivity is low. Long-lived isotopes account for a relatively small portion of the decay energy of short-cooled wastes from the processing of irradiated uranium. The Cs^{137} - Ba^{137} and Sr^{90} - Y^{90} parent-daughter chains together account for less than ten percent of the total decay energy in process effluents at usual processing

times (about 100 days after removal from a reactor). However, after five years ageing of the wastes, they account for more than two thirds of the total decay energy. In long-term storage or ultimate disposal techniques in which decay heat is a problem, prior removal of cesium-137 and strontium-90 will reduce the problem. It has been calculated that, under some loading conditions, underground waste storage tanks at Hanford might boil (requiring cooling or condensate return) for a century or more. Removal of most of the cesium and strontium prior to storage of the wastes would reduce this time to a few years.

In summary, recovery of specific fission products from process effluents may reduce heating problems in long term retention of radioactive wastes. It appears unlikely that the very high cesium-137 and strontium-90 decontamination factors required to permit eventual uncontrolled release of the wastes will be obtained in economically competitive recovery programs.

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CESIUM RECOVERY FROM PUREX WASTE CESIUM ZINC FERROCYANIDE PROCESS

FIGURE 1

INTEGRATED FISSION PRODUCT RECOVERY

FIGURE 2