1

This invention is concerned with the treatment of aqueous radioactive waste solutions from the recovery of jacketed fissionable radioactive elements discharged from atomic fission reactors. The invention is more particularly concerned with the treatment of these waste solutions to effect the separation of certain radioactive components to a degree whereby such waste solutions may be discarded or further processed in normal patterns with considerably modified and simplified techniques.

Radioactive slugs, bars or the like employed in atomic fission reactions are commonly jacketed with a relatively noninterfering metal such as aluminum, hafnium-free zirconium or stainless steel. Recovery of the valuable major radioactive components in such slugs or bars is obtained through a treatment involving solution of the entire material in nitric acid and the separation and recovery therefrom of the major radioactive elements, such as uranium. The solution remaining after the extraction of the chief radioactive elements constitutes a waste liquor which contains fission product nitrates. These waste liquors constitute a serious disposal problem. The problem-causing radioactive components are mainly cesium and strontium which, because of their fairly long half-life and their tendency to enter biological processes in place of sodium or calcium, must be segregated. Radioactive ruthenium, also present, has a shorter half-life and has a greater biological effectiveness per unit mass. Other radioactive components in the effluent waste system constitute a much smaller problem for various reasons, such as short half-life, inherent volatility, or other reasons.

Many schemes for disposal of these waste liquors have been studied and even more have been suggested. At the present time practice requires long term tank storage permitting decay of radioactivity to safe limits. Inasmuch as long term tank storage has sizable economic drawbacks in the extremely high cost of tank construction, and the added uncertainty of useful tank life, the advent of a practical method of coping with the problem of the radioactive components and their removal from relatively large volumes of associated liquid, which includes respectable amounts of non-radioactive components, is of appreciable importance.

One approach to this problem has been the concentration of radioactive fission products by fixation in inert solids. In general, this process included treatment of the waste-nitrate containing solution by evaporation and calcination to the oxides, with subsequent acid leaching of the radioactive oxides and adsorption of these radioactive oxides from the leach liquor on montmorillonite clay. The capacity of cation exchange of such clay is in the order of about 1–1.5 milli-equivalents per gram, and the fission products adsorbed on the clay are fixed in a relatively non-leachable form by subsequent calcination to about 1000° C. While this provided a measurable reduction in the amount of material to be segregated for normal decay aging, processing and equipment require-

2

ments are relatively costly and complex. In addition, the separation of the radioactive components is, at best, incomplete such that residual salts, such as those of aluminum, zirconium, or the like, are still contaminated and relatively radioactive. Thus this system, while approaching an answer to the general problem, fails to provide either a complete or a satisfactory answer.

It has been found that the more objectionable radioactive fission products, particularly cesium and strontium, can be removed directly from waste liquors by a special treatment and adsorption. The radioactive cesium and strontium, and where desired, ruthenium are substantially completely concentrated by adsorption and disposed of for ultimate radioactivity decay in dry storage requiring relatively little space and practically no specialized equipment.

In accordance with this invention, radioactive cesium and strontium, and, if desired, ruthenium ion components of nitrate waste liquor solutions containing the same and substantially greater bulk amounts of normally adsorbable nonradioactive ions from fission reaction systems are separated and recovered by a process comprising, treating such as solution to form the normally adsorbable bulk ions other than cesium, strontium and ruthenium radioactive ions into a composition substantially inert to ion exchange, subjecting such treated solution to ion exchange with a siliceous acid-form ion exchange material, adsorbing radioactive ions on said siliceous exchange material, and separating and recovering the siliceous adsorbent containing adsorbed radioactive fission products.

Typical waste liquors resulting from the recovery of uranium as the spent fissionable material in fission reaction systems in which the uranium is commonly jacketed with a suitable metal, such as aluminum or zirconium which is essentially hafnium-free, comprise jacket-metal and other metal nitrates and ammonium ion materials in up to appreciable concentrations. For example, a typical solution after separation of the uranium has high hydrogen ion concentrations and may comprise about 1.6 molar concentration of aluminum nitrate, about 0.07 molar concentration of ammonium ion, about 0.004 Fe^{+3}, about 0.01 molar concentration mercury and 0.02 molar concentration SO_4^{-2}, as well as the problem trace amounts of remaining radioactive components. These components include cesium, strontium, ruthenium, the rare earths and others. Of the radioactive components, cesium-137 and strontium-90 are the most troublesome because of their moderately long half-life, specific biological fixation and high specific activity; ruthenium has a relatively short half-life and the disposal problem in connection therewith is somewhat less serious. The rare earths have even shorter half-lives and, even if retained in the bulk ion composition, constitute a relatively minor problem in ultimate disposal of the various components of the waste liquors.
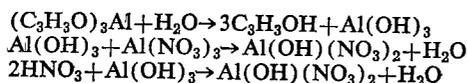
Ordinary adsorptive treatments fail completely to effect the desired degree of separation. In general, the reason for this failure is that the bulk ions such as aluminum or zirconium compete so strongly for the active exchange sites on the ion exchange material that there is little if any possibility of the trace ions such as cesium and strontium successfully competing for an active exchange site and thus being selectively removed by adsorption from waster solutions. In order to permit a successful adsorption of cesium and strontium ions, it is necessary to con-

vert or inactivate the bulk competing ions to a form having substantially no affinity for adsorption sites on ion exchange materials.

Inactivation of the bulk ions is now made possible by a special treatment of the waste solutions. Such treatment effects conversion of the bulk ions, for example, aluminum or zirconium to a sol with a pH in the range of about 2 to 6, having no appreciable affinity for adsorption sites on ion exchange materials. Cesium, strontium and certain other radioactive ions are substantially unaffected by such special treatment and their selective adsorption on a suitable siliceous hydrogel is thus made possible.

Conversion of the bulk ions, normally aluminum, zirconium and/or iron in the acidic aqueous waste solutions to sol form is effected by the addition of compounds of tri- and higher valent metals which form such sols; such additives are basic or adjusted in basicity to help neutralize the acidity of the waste solution, but such additives are substantially free of ions which would compete with the problem radioactive ions during the adsorption step. Thus, such additives are substantially free of the alkaline elements. Suitable additives for the formation of the mono- or polybasic metal nitrate sols are one or more of the type of the oxides or hydrous oxides of aluminum, titanium, iron, thorium or zirconium; metal organic compounds of the same metals, such as aluminum isopropylate; or oxycarbonates, such as $ZrOCO_3$; and the like.

For example, conversion of the bulk ions in the waste solutions to sol form as the monobasic metal nitrate may be effected, when the chief bulk ion is aluminum, by the addition of aluminum isopropylate in about a stoichiometric amount with an increase in pH of the solution approximately 3–4. It is, likewise, possible to form the monobasic aluminum nitrate sol by digestion of the waste liquor with pure hydrous aluminum oxide. This in situ reaction may be typified as follows:

$$(C_3H_3O)_3Al+H_2O \rightarrow 3C_3H_3OH+Al(OH)_3$$
$$Al(OH)_3+Al(NO_3)_3 \rightarrow Al(OH)(NO_3)_2+H_2O$$
$$2HNO_3+Al(OH)_3 \rightarrow Al(OH)(NO_3)_2+H_2O$$

It is to be understood that in zirconium-containing systems zirconium may substitute for aluminum; also mixed component sols are possible or even preferable.

Decomposition or removal of the nitrate ion also may be used in the preparation of these sols. For example, a sol is prepared by reduction of part of the nitrate ion to nitrogen and nitrogen oxides by hydrogen, using a catalyst of the group VIII metals of the periodic table, to give a ratio of polyvalent cation to residual nitrate ion between 1:1 and 1:2. Reduction may also be accomplished by chemical reducing agents, such as sulfides which will give the desired reduction of anion concentration without increasing the cation concentration. Other methods whereby suitable sol formation can be obtained include the partial removal or destruction of nitrate ion to a ratio to the polyvalent ion in the range of 1:1 to 2:1. This may be effected under controlled heating conditions or controlled radiation. In all cases similar reactions may be performed with Zr, Fe, Cr and other cationic species present as major components of the waste liquors.

In some waste liquors, fluorine may be present as fluorides in quantities of up to about 10%. This appears to have no adverse effect on the operation of this invention.

The inorganic adsorptive materials suitable for use in this invention include the hydrogels comprising silica-alumina, silica-zirconia, silica-magnesia and to a lesser effective degree such natural clays and earths which may naturally or by suitable modification have a relatively high ion adsorptive capacity. One such material capable of adjustment by treatment to have an outstandingly high adsorptive capacity is the zeolytic material described in U.S. 2,617,712, which is described as a potassium zeolite, acid, treated to a hydrogen state. A possible modifica-

tion of the adsorptive materials includes those having chemisorbed thereon alumina, zirconia or magnesia.

The ion exchange material particularly suited to this operation comprises silica-alumina hydrogel in which the alumina comprises up to 25% by weight of the combined weight of the silica and alumina. In a preferred form this hydrogel, containing in the order of about 200–300% by weight of water, is treated in a base exchange operation with aluminum salt solution to deposit on the surface thereof in the base exchange active sites exchangeable aluminium ions. In subsequent base exchange reaction with the treated waste liquor the sols having no appreciable affinity for the adsorption sites pass through the system while the problem radioactive components, not comprising an integral part of the sol, exchange with the surface hydrogen ions adsorbed on the siliceous hydrogel and are retained there to the limit of capacity of the hydrogel. By discontinuing the adsorptive reaction prior to the breakthrough point of the adsorbable components, i.e., the point at which the radioactive components would show in the effluent liquor, substantially complete adsorptive removal of the radioactive ions from the waste liquors is effected. Removal of the adsorbing material containing the adsorbed fission products, with ultimate drying and calcination as to about 1000° C., gives a relatively small bulk material having the included radioactive components in a relatively insoluble form which may be subsequently stored in pits or other generally inaccessible places for the decay of radioactivity.

A definitely favorable aspect in connection with the treatment herein proposed is that the bulk ions in the waste liquors, substantially freed of dangerous radioactivity, may be separated and recovered for reuse. This is of particular importance, for instance, in connection with systems employing zirconium as the uranium jacketing material in that such zirconium is highly purified to be substantially free of its sister metal hafnium. Such purified zirconium is quite expensive and the recovery of this material for reprocessing constitutes a substantial saving.

The other radioactive component of possible troublesome nature is ruthenium. Removal of the ruthenium by adsorption on silica-alumina hydrogel is not practical without modification of the hydrogel to specifically take care of such ruthenium. This is easily effected by inclusion in the siliceous hydrogel of specific reactants for ruthenium such as lead oxide, bismuth oxide, calcium acid phosphates, or other including the highly effective and preferred metallic iron in finely divided state and relatively small amount. The quantity of iron to be included is only slightly in excess of the amount required to adsorb substantially all of the ruthenium in the solution being exchanged.

A particularly effective and preferred form of this invention involves the use of a continuously moving bed of the adsorptive material in which countercurrent flow of the waste liquor with the adsorptive material gives a continuous controllable process in which the liquid effluent is free of the problem radioactive ions and the solid effluent comprises the particulate solids of the adsorptive material containing the adsorbable radioactive components.

It is to be noted that in order to prevent or minimize precipitation of solid material in the bulk ion inactivated sol, treatment of the waste liquor to form the basic metal nitrate sol should be effected just prior to contact with the siliceous hydrogel adsorptive material.

EXAMPLE I

The particular effectiveness of aluminum base exchanged silica-alumina hydrogel as opposed to the common potassium base exchanged silica-alumina hydrogel is observed as follows:

Similar batches of speroidal form silica-alumina (85% and 15% by weight, respectively) homogeneous hydrogel were prepared by well-known procedure and dried to approximately 235% water content (dry basis). The sev-

eral batches were base exchanged, as noted below, to remove sodium ion. Cesium ion containing solutions having 0.001 normal Cs_2SO_4 and 0.01 normal Cs_2SO_4 were prepared. Approximately 60 cc. of the hydrogel spheres, having a diameter of about 2.0 mm., in a 50 cc. burette were treated by upflow of the cesium containing solutions with the results shown in Table I.

Table I

CESIUM ION SORPTION ON SILICA-ALUMINA
HYDROGEL BEADS
Charge solution; .001 N Cs_2SO_4 (130 p.p.m.); .01 N Cs_2SO_4 (1300 p.p.m.)]

Hydrogel Base Exchange	Charge	Effluent	
	Cesium Solution	Cumulative Volume, cc.	Cesium, p.p.m.
0.5% Al(NO₃)₃	.01 N	30	0.2±.2
		50	0.2
	.001 N	10	0.3
5-15% Al(NO₃)₃	.01 N	20	0.2
		40	0.2
K₂SO₄	.01 N	30	1.7
	.001 N	50	0.7
		60	0.4

The results in the above table demonstrate the superiority of the ion exchange capacity of the aluminum treated siliceous hydrogel.

EXAMPLE II

A solution containing approximately 1.6 molar concentration aluminum nitrate, 130 p.p.m. of cesium ion as the hydroxide and 0.5 molar concentration hydrogen ion as nitric acid was prepared. In one thousand parts by weight of this solution were dissolved with heating and stirring at atmospheric pressure about one hundred and fifty five parts by weight of aluminum isopropylate. A similar solution without added aluminum isopropylate was likewise prepared.

The ion exchange material was spheroidal form silica-alumina (85%–15%, respectively) homogeneous hydrogel, base exchanged to low sodium level with 0.5 molar aluminum nitrate solution. Two equal samples of the ion exchange material were employed in a manner similar to that of Example I for the ion exchange treatment of the solution containing the aluminum isopropylate and the other solution similar in all respects except that it contained no aluminum isopropylate.

The effectiveness of the conversion of the aluminum ions to aluminum nitrate sol and neutralization of excess nitric acid is observed by reference to Table II below.

Table II

REMOVAL OF CESIUM IONS FROM 1.6 M ACID-ALUMINUM
NITRATE SOLUTION
[Adsorbent: 55 cc. 1/16″ silica-alumina hydrogel beads base exchanged
with 0.5 M Al(NO₃)₃]

Solution	Cumulative Volume of Effluent, cc.	Ca⁺ Anal., p.p.m.
Treated to 2 pH with (C₃H₈O)₃ Al	19	1.1
	30	1.4
Without (C₃H₈O)₃ Al	20	1.9
	35	15.8

EXAMPLE III

A waste solution from the recovery and separation of uranium and plutonium from zirconium jacketed uranium oxide pellets, irradiated to 10,000 megawatt years per ton of uranium and cooled 500 days before processing, contains as major components the nitrates of Zr^{++++} and NH_4^+ with appreciable quantities of nitric acid and hydrogen fluoride. The gross gamma activity of the waste solution is 62.7 curies per gallon. Conversion of the bulk ions to sol form as the monobasic metal nitrate is effected by the addition of aluminum isopropylate in an amount

about twice the weight of the zirconium ion present in the solution with concomitant elevation of the pH to approximately 2.5. The resulting sol is diluted to a viscosity of about 5 centistokes and passed countercurrent to a downwardly moving bed of silica alumina hydrogel beads of the same type as employed in Example II. The countercurrent contacting is effected at a rate to permit adsorbtion of radioactive components from the waste solution on to the beads in an amount equivalent to about 2–2.5 milliequivalents per gram of solids in the beads.

After contacting, the beads containing the adsorbed radioactive components are dried and then calcined at a temperature in the order of about 1000–1050° C. for about 2 hours to set the material in a relatively water insoluble form. The calcined material is then transferred to a remote storage area for ultimate decay of the radioactivity.

The effluent sol is analyzed at less than 3×10^{-6} microcuries (μc.) of cesium-137 ion and less than 1×10^{-6} μc. of strontium-90 ion per milliliter. The effluent having such relatively low concentration of radioactivity, after a relatively short storage period during which reasonable radioactivity decay of residual radioactive components occurs, is then treated to recover the zirconium for reworking as zirconium metal without the elaborate special precautions required for the working and fabrication of radioactive metals.

While the foregoing description and examples have been directed to the use of a siliceous inorganic ion exchange material, it is to be understood that this material is employed when it is necessary to set the separated radioactive ions in a water insoluble form. With the inorganic ion exchanger a glass-like material is made available by high temperature calcination for storage under circumstances such that leaching of the radioactive components will not occur to any appreciable degree, and will thus prevent the introduction of a high degree of radioactivity into ground waters or the like during storage for radioactive decay. It is readily understood therefore that high-acid ion exchange material other than the siliceous inorganic type may be employed in accordance with this invention when such long-term radioactivity decay storage is not the primary aim. Thus it is possible, if desired, to recover for immediate use radioactive cesium and strontium, for example by adsorption on organic ion exchange materials of relatively high-acid strength. Thus radioactive cesium and strontium may be separated from waste liquors, treated in accordance with this invention, and subsequently recovered from the ion exchange material as by elution or calcination to the oxide form with the concomitant removal of the ion exchange material during calcination.

From the foregoing, it is evident that highly effective removal of the problem ratioactive components in fission product waste liquors is possible through the method herein described.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The process for the separation of adsorbable radioactive cesium and strontium from fission reaction nitrate waste liquors containing the same and substantially greater bulk amounts of normally adsorbable non-radioactive ions, such process comprising treating such a liquor with an additive comprising at least one of the compounds selected from the group consisting of the alkali-free isopropylates of aluminum and zirconium, and the alkali-free oxycarbonate of zirconium, thereby forming with said additive a sol including said normally adsorbable non-radioactive ions, whereby said non-radioactive ions in said sol have no appreciable affinity for adsorption sites on hy-

7

drogen ion exchange material; contacting said treated liquor with hydrogen ion exchange material and adsorbing by said contact substantially all of said radioactive cesium and strontium; and separating said contacted ion exchange material containing adsorbed radioactive cesium and strontium.

2. The process in accordance with claim 1 wherein said hydrogen ion exchange material is silica-alumina hydrogel base exchanged with aluminum ion.

3. The process for the separation of adsorbable radioactive cesium and strontium from fission reaction nitrate waste liquors containing the same and substantially greater bulk amounts of normally adsorbably non-radioactive ions, such process comprising treating such a liquor containing at least one molar concentration of aluminum ion with alkali-free aluminum isopropylate to form monobasic aluminum nitrate of pH 2–6, thereby forming a sol including said normally adsorbable non-radioactive ions, whereby said non-radioactive ions in said sol have no appreciable affinity for adsorption sites on hydrogen ion exchange material; contacting said treated liquor with hydrogen ion exchange material and adsorbing by said contact substantially all of said radioactive cesium and strontium; and separating said contacted ion exchange material containing adsorbed radioactive cesium and strontium.

4. The process for the separtion of adsorbable radioactive cesium and strontium from fission reaction nitrate waste liquors containing the same and substantially greater bulk amounts of normally adsorbable non-radioactive ions, such process comprising treating such a liquor containing at least one molar concentration of zirconium ion with alkali-free zirconium isopropylate to form monobasic zirconium nitrate of pH 3–4, thereby forming a sol including said normally adsorbable non-radioactive ions, whereby said non-radioactive ions in said said sol have no appreciable affinity for adsorption sites on hydrogen exchange material; contacting said treated liquor with

8

hydrogen ion exchange material and adsorbing by said contact substantially all of said radioactive cesium and strontium; and separating said contacted ion exchange material containing adsorbed radioactive cesium and strontium.

5. The process for the separation of adsorbable radioactive cesium and strontium from fission reaction nitrate waste liquors containing the same and substantially greater bulk amounts of normally adsorbable non-radioactive ions, such process comprising treating such a liquor containing at least one molar concentration of zirconium ion wiht alkali-free zirconium oxycarbonate forming thereby a basic sol of pH 3–4, including said normally adsorbable non-radioactive ions whereby said non-radioactive ions have no appreciable affinity for adsorption sides on hydrogen ion exchange material; contacting said treated liquor with hydrogen ion exchange material and adsorbing by said contact substantially all of said radioactive cesium and strontium; and separating said contacted ion exchange material containing adsorbed radioactive cesium and strontium.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,101,998   August 27, 1963

Thomas H. Milliken, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 11, for "Cs₂So₄", each occurrence, read -- Cs_2SO_4 --; column 7, line 35, after "hydrogen" insert -- ion --; column 8, line 12, for "wiht" read -- with --; line 15, for "sides" read -- sites --.

Signed and sealed this 28th day of April 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents