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PROPOSED ION EXCHANGE APPLICATIONS IN THE
HANFORD SEPARATIONS PROCESSES

AUTHOR

Billings Brown

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PROPOSED ION EXCHANGE APPLICATIONS IN THE
HANFORD SEPARATIONS PROCESSES

by

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Billings Brown

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Process Design and Development Operation
Facilities Engineering Operation
CHEMICAL PROCESSING DEPARTMENT

November 5, 1956

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PROPOSED ION EXCHANGE APPLICATIONS IN THE
HANFORD SEPARATIONS PROCESSES

I. INTRODUCTION

A. Statement of Problem:

The use of solvent extraction techniques at HAPO for separating plutonium from uranium and fission products is rather expensive. This is in part due to solvent, chemical and process steam costs and in part to the need for complicated equipment to handle the process. It is felt that the use of ion exchange resin techniques might be economically attractive both as to lowered chemical costs and equipment simplification. Also, the decontamination achieved by solvent extraction is at times marginal. Changing to another process following partial decontamination by solvent offers the possibility of greater over-all DF's.

B. Basis for Comparison of Ion Exchange with Solvent Extraction

Ion exchange may be compared as a basic unit operation with solvent extraction. Indeed, ion exchange is solvent extraction, with the added restriction that in this special case the solvent phase is solid. This has inherent advantages:

1. The solvent cannot contaminate the product, either by solubility or by its decomposition products.
2. There can be neither emulsification nor entrainment; phase separation is simple and complete.
3. Flooding is not possible with resins.
4. No ions need be added to the solution which cannot be removed later by distillation, or destroyed by boiling.

Comparison between resin processes and Purex and Redox solvent processes can be made rather readily on the bases of decontamination, equipment required and chemical costs.

A number of possible process applications investigated for both Purex and Redox flowsheets are listed below. Those applications which appear most feasible are reported in detail in the appendices of this report.

1. Purex Tail-End Plutonium Treatment
2. Purex Final Plutonium Decontamination Cycle
3. Purex Waste Disposal
4. Purex Final Uranium Decontamination Cycle
5. Redox Tail-End Plutonium Treatment
6. Redox Final Plutonium Decontamination
7. Redox Waste Disposal
8. Redox Final Uranium Cycle

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II. SUMMARY

Ion Exchange is proposed as an alternate separations technique, to be used in Redox and Purex cycles where adequate decontamination is not now achieved or there is much loss to waste.

The technology of anion exchange resins, unknown a few years ago, has received considerable impetus from the use of these resins in uranium milling and from their use by the Canadians. Sufficient knowledge of the resins has now been aggregated to allow intelligent engineering design of anion resin cycles.

On the basis of the accumulated evidence, the following generalizations are made:

1. Cation exchange will concentrate plutonium without appreciable decontamination, unless a complicated oxalate elution schedule is used.
2. Anion exchange will decontaminate without concentrating unless a reducing agent is used for elution.

In the Purex plant, anion exchange might be used to recover plutonium but not appreciable uranium from the LW (acid waste) stream. Final concentration and decontamination of the plutonium product can be efficiently accomplished with anion exchange. It might also be found that using ion exchange as a final cycle would supplant a final solvent cycle.

In Redox operations, the plutonium product could also be concentrated by anion exchange. In this case replacing the final plutonium cycle appears to be more practicable. The waste stream from Redox is probably too concentrated in aluminum and in chromate to be readily amenable to anion exchange recovery. With reduction of the chromate concentration and considering the urgency of removing the plutonium prior to storing the waste, recovery is considered feasible if not economic.

Uranium concentrations are too great in either plant to justify the use of ion exchange techniques in final uranium decontamination cycles.

Resin life in the several radiation fields encountered in these applications is acceptably long, being commensurate with losses due to attrition.

III. PURPOSE

The objective of this study was to investigate and summarize current technology of ion exchange processes, to review potential application of these processes in HAPC separations facilities, and to develop and report on engineering parameters of the more feasible applications.

IV. DISCUSSION

A. Process Chemistry

An attempt has been made to assemble in this section that portion of the

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chemistry of plutonium and uranium which is directly applicable to the ion exchange processes, or which for various reasons limits the choice of system. The feasibility of any separations process using past or present technology, be it solvent extraction, coprecipitation or ion exchange depends upon the solubility of, and the degree to which stable complex ions are formed by the various elements which are to be separated. Particularly in the cases of uranium and plutonium, the solubility and complex ion formation are closely interrelated. Generally, these metals are most soluble, or soluble to the point of process interest, in those reagents with which the metallic ions form strong complexes. For example, the majority of the metals form insoluble carbonates. However, uranium, by reason of its exceeding ability to complex with carbonate, is very soluble in carbonate or bicarbonate solution. Also, the ability to form a negatively-charged complex is prerequisite to the ion being sorbed onto an anion resin, as for example the sorption of Pu(IV) as $\text{Pu(NO}_3)_5^-$.

Numerous of the fission products also are capable of complexing with organic or inorganic anions or with neutral molecules. This ability can assist in their separation or (as is too often the case) can cause much concern. A better understanding of the basic chemistry of the fission products by those responsible for separations process design will eventually alleviate some of the problems.

In the following sections, emphasis is placed on the solubility and complexing ability of the process materials.

1. Plutonium

a. Oxidation - Reduction

The thermodynamically stable valence state of plutonium should be Pu(VI) in aqueous solutions containing oxygen. However, in nitric acid solutions the stable form is Pu(IV) due to the presence of nitrite ion. This reduction of Pu(VI) to Pu(IV) is catalyzed by traces of ferric iron, usually present as a product of equipment corrosion. Pu(IV) is readily reduced to Pu(III) by ascorbic acid or ferrous iron, more slowly by hydroxylamine, in nitric acid solution. A search is presently being made by Hanford Laboratories for alternate reductants which preferably leave product contaminants more tolerable than the present iron or tars in solution, and which give off no undesirable gases. Plutonium may be maintained as Pu(VI) in the presence of a holding oxidant such as dichromate, provided also that reducing agents are absent (such as hexone decomposition products)(3). Strong oxidants tend to attack the ion exchange resin structure (4). Probably due to these adverse factors, no appreciable amount of work has been reported on the ion exchange behavior of Pu(VI) . This avenue may prove to be extremely favorable and should be more thoroughly explored.

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b. Plutonium (IV) Polymer

When the acidity of a Pu(IV) solution falls below 0.01 molar, a polymeric hydroxide forms in a few minutes. At 0.1 molar acidity, polymer formation is slow. Precipitation of the hydroxide (hydrated oxide) occurs at pH 2.5 to 3 (5). Some of the plugging occurring in the final concentration step at Purex has been due to polymer formation, despite the high tolerance on acid molarity of the final product (6, 7). The potential hazard of polymer formation effectively discourages the development of any separation scheme utilizing low acidity.

c. Solubility

Plutonium (IV) and (VI) nitrates are each soluble to the extent of approximately 2.1 moles per liter in the presence of 1.8 M nitric acid at 25°C (5). Plutonium (III) nitrate is also presumably very soluble. However, the solubility limit is never approached during processing. Final concentration may yield a product of 300-400 g/l. Ion exchange eluate is to date limited to approximately 100 g/l.

Plutonium (IV) not being extensively hydrolyzed, behaves like the rare earths rather than like uranium, in sulfate solution (8, 9). The temperature coefficient of solubility is negative. At room temperature, the solubility is 125 g/l, being suppressed to 90 g/l in 1M sulfuric acid and to 1.6 g/l in 9M acid (10). At temperature above 150°C, the solubility in water is less than 1 g/l, being enhanced by both uranyl sulfate and sulfuric acid (8). If the solubility is exceeded at high temperature, the plutonium precipitates as PuO₂. As is necessary with the polymer, dissolution of the oxide can be effected only with hot concentrated sulfuric or nitric acid (11). Bisulfate ion enhances the solubility, but is generally considered too corrosive toward stainless steel.

Pu(III) sulfate is soluble to the extent of 125 g/l in 0.1M H₂SO₄ (11). In more basic solutions, NaPu(SO₄)₂ tends to precipitate, with a solubility of only 1.2 g/l.

Comparing the equilibrium constant for the reaction

of 7×10^{-56} , with the stability constant for the formation of the uranyl tricarbonate complex, $K = 3 \times 10^{18}$, it is realized that the solubility of Pu(IV) in carbonate solution cannot be great. Each species is in fact soluble to the extent of only about 1 g/l even in strong (4M) carbonate solution. No data is available concerning Pu(III) carbonate. However, Pu(VI) carbonate is soluble to the extent of 8.4 g/l in 0.02 M sodium carbonate, and to 71 g/l in 0.5 M

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sodium carbonate (11), approximating the behavior of uranium (VI) in such solutions. More knowledge in this area might well lead to opportunity for new processes.

d. Complex Ion Formation

Many complex ions of plutonium are known or suspected. The hydroxide polymer is destroyed by agents such as sulfuric, nitric or hydrofluoric acids, due to the formation of stable complexes.

Between 1 M and 4M nitric acid concentration, Pu(IV) exists as the simple hydrated ion $\text{Pu}(\text{H}_2\text{O})_9^{+4}$. Between 4M and 4.6M the reaction

yields the still-positively charged complex. In 2M nitric acid, $K_{eq} = 2.9$. When the acidity rises to 8M, the further reaction

yields the negatively charged complex. Nitric acid or nitrate solutions are effective salting agents in solvent processes. Similarly, concentrated nitric acid acts as an eluant toward Pu(IV) sorbed on cation resin, complexing the plutonium. Of still more interest, Pu(IV) is sorbed strongly from 8M nitric acid by anion resins, as the negative complex. It can be water-eluted in theory, but might thus form polymer. In practice, 1M nitric acid is used, at small loss in efficiency.

Pu(IV) and Pu(VI) each form strong complexes with sulfate, with $K = 500$ for Pu(IV) at 2.3M H_2SO_4 (12). The complex is negatively charged even at sulfate concentrations below 0.5M (10), as is true also of U(VI) (13).

The order of stability of the inorganic Pu(IV) complexes is (11c):

with sulfate being stronger than nitrate.

Oxalic acid (5 per cent) has sometimes been used to elute Pu(IV). The solubility product of Pu(III) oxalate is exceedingly low (2×10^{-10}) so that complex formation is nil. Other eluants such as citrate, acetate and lactate have been used at various times with varying success.

Pu(III) forms no known negatively charged complex ions. Thus Pu(III) cannot be sorbed by anion resins, which fact suggests a partition cycle similar to that used in Redox and Purax, sorbing Pu(VI) and Pu(IV), followed by reduction to and elution of, Pu(III).

2. Uranium

a. Oxidation - Reduction

Uranium behaves in many respects in a manner similar to plutonium. However, the only species having appreciable solubility is U(VI). This highest valence state is hydrolyzed in aqueous solution to form the extremely stable, uranyl ion UO_2^{++} , which is the species uniformly present in process solutions. U(VI) can be quantitatively reduced to U(IV) using relatively strong reducing agents such as aluminum, zinc or hyposulfite, although in processing, this is not attempted.

b. Solubility

At 25°C, the solubility of uranyl nitrate is 2.6M. In 13M nitric acid, the solubility is reduced to 0.72M UN (5).

Due to the stability of the uranyl tricarbonate complex, uranium (VI) is very soluble in carbonate solutions, particularly in ammonium carbonate (9). An additional advantage gained in this system is the insolubility of nearly all metallic carbonates (14), making isolation of Pu and U relatively complete. It should also be noted that plain carbon steels are not attacked by carbonate solutions.

Uranyl sulfate is also very soluble. The entire phase diagram has been published (15).

c. Complex Ion Formation

The uranyl ion forms relatively strong complexes. The most stable is the tricarbonate (16):

This forms the basis for the basic leach process carried on in the uranium industry (17).

The nitrate complex is formed in concentrated nitrate solutions. The dissociation constant for the reaction

is 0.21, and the reaction takes place in nitrate solutions below 3M. Between 3M and 6M, undissociated uranyl nitrate predominates and provides the species which is extracted by Purex and Redox processes. At nitrate concentrations above about 6M, the anionic complex forms:

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Consequently U(VI) is sorbed from concentrated nitrate solutions by anionic resins. Elution can be accomplished using dilute nitrate solutions.

Chloride, fluoride, sulfate and phosphate each form complex ions with uranyl ion. The formation and ion exchange characteristics of these species have been exhaustively explored by those interested in the uranium milling industry. The principal complex ions formed are (18):

The extent of complexing varies with pH. The sulfate and fluoride complexes are formed in 1M acid, while the chloride, nitrate and phosphate complexes are formed only in concentrated acid.

3. Corrosion

Due to their relative instability in radiation fields, organic chemicals have not been viewed favorably for use as reagents in separations processes. Rather, inorganic systems have been extensively investigated and used. Each system has its disadvantages.

Chloride ion presents a serious corrosion problem when contained in stainless steel. Failure is very rapid. Rubber-lined equipment has been very successful in handling chloride in uranium mills, though adsorption of fission product activity might not allow its use in separations processes.

Nitrate systems are not corrosive to stainless steel when cold. Hot nitric acid becomes very corrosive, destroying steam coils of 347 stainless in a few months.

Sulfate ion does not corrode stainless steel provided oxygen or an oxidizing agent, such as nitrate ion is present. Molybdenum assists in making stainless more resistant, and type 316 is extensively used in the textiles industry where several concentrations of sulfuric acid might be handled.

Carbonate systems are non-corrosive and can be handled in even mild steel. Caustic embrittlement or stress corrosion is not a factor where vessels are not pressurized.

B. Description of Ion Exchange Resins

Solid materials capable of exchanging ions with salts in solution (aqueous or organic) are found in both organic and inorganic categories of compound. Among the latter are silica gel, zeolite materials, the various clays and alumina. All are characterized by relatively low capacity and in recent years have been

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little used as ion exchangers. The organic materials can again be divided (19, 21) into products of "natural" origin such as sulfonated coal or coconut shells, and the synthetic resins. Again, the exchange capacity obtainable with the former is limited, though generally superior to the inorganic materials.

The synthetic resinous exchangers are classified as to type into two main categories: anion exchangers and cation exchangers. These titles are somewhat misleading in the light of recent work forming the basis of uranium separations processes, wherein the uranyl ion (a cation) apparently is strongly sorbed by anion exchange resins, due of course to the formation of a negative complex. Synthetic resins in fact range in type from strong base through weak base and amphoteric materials to weak and strong acid types. Table I is an abridged list by type and trade name, together with (titrable) capacity. It is evident, and somewhat of a convenience that ion exchange materials can be thought of as being solid acids or bases, the anions or cations of which are respectively solid, while the acid cation (proton) or basic anion is free to diffuse, and can be titrated or otherwise replaced.

TABLE I (21)

Commercially Available Ion Exchange Materials

<u>Class & Name</u>	<u>Type</u>	<u>Capacity mille-equivalent/gram</u>
Strong Base		
Dowex-1 (Nalcite SBR)	Q	2.4
Dowex-2 (Nalcite SAR)	Q	2.3
Amberlite 1RA-400	Q	2.3
Permutit SK	Q	
Weak Base		
Amberlite 1R-4B	D	10.0
Deacidite	D	9.3
Amphoteric		
Alumina	--	0.01
Silica Gel	--	0.02
Aluminum Silicate (clay)	--	0.06 - 3.0
Weak Acid		
Permutit 216	C	5.30
Amberlite 1RC-50	C	10.0
Amberlite 1R-100	P	1.75
Dowex-30 (Nalcite MX)	P	4.0
Strong Acid		
Amberlite 1R-120	S	4.20
Dowex-50 (Nalcite HCR)	S	4.25
Q quaternary amine - polystyrene - divinyl benzene copolymer		
D diamine - triamine alkyl copolymer		
C carboxylic acid		
P phenolic		
S sulfonic acid		

Anion exchange resins are relatively new, having been available for only a few years. The hesitancy to use them stems in part from the belief that they would be attacked by the concentrated acid solutions used in separations processes. This is true for some resins, but certainly not for all. For example, while Dowex-2 is destroyed by 10M nitric acid, the similar Dowex-1 is unaffected by even higher molarities (22).

The composition and structure of anion exchange resins vary widely. Weak-base resins include a wide variety of polymers involving amine groups, and are characterized by a high nitrogen content and hence a high ionic capacity, as indicated in Table I. However the nitrogen, occurs as di- and triamines, hence the titrable capacity is realized only in strong acid solution. Too, exchange rates are slow due to steric effects.

Strong-base resins (Dowex-50, Permutit SK, etc) are all of the styrene-divinylbenzene copolymer type, with quaternary amine nitrogens being connected to the benzene rings by methylene carbon atom bridges. Ionic capacity is limited, but is entirely available at any pH due to the highly ionized quaternary amine groups.

Resins differ also in the nature and number of the alkyl groups in the amine, the proportion of amine groups, and the per cent of divinylbenzene (often abbrev. DVB) in the polymer.

The function of the DVB is of course to crosslink the polystyrene and render it insoluble. The per cent DVB is directly related to the pore size, hence to the ease with which ions can diffuse through the resin particle. A higher percentage DVB yields a resin which is chemically more inert, but one which reaches equilibrium with the external solution very slowly (23, 24, 25), thus causing early breakthrough during column loading and severe "tailing" during elution. This difficulty can be in some measure overcome by reducing the diameter of the resin particle at least until the increased pressure drop of fluid through the resin bed becomes prohibitive.

A compromise for most purposes is reached at about 8 per cent DVB and 80-100 mesh particles, or at a lesser per cent DVB if 20-50 mesh particles are required.

The per cent DVB also controls the swelling and shrinking which takes place when the resin is immersed in solutions of varying ionic strength.

The organic resins swell by absorbing water from aqueous solutions. They swell most in dilute solution, where the difference in osmotic pressure is the greatest (18).

Resin density changes somewhat due to this swelling and shrinking. Typical data are as are found for Amberlite LR-1, a cation exchange resin (26):

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<u>Resin form and environment</u>	<u>Depth of Resin bed, in.</u>
NatH resin/H ₂ O	24
UO ₂ resin/0.22M UNH	21.5
NatH resin/1.25M NaHSO ₄	20.5

During this particular cycle (once proposed for plutonium extraction) the resin density has been altered by 15 per cent. This change can lead to serious mechanical problems when handling resin in fixed columns.

An anion resin used extensively in uranium processing is Nalcite SBR (Dowex-1). Its swelling characteristics in nitric acid as a function of acid concentration and crosslinkage have been investigated (29) and are presented here for reference:

Expansion Characteristics of Nalcite SBR (Dowex-1) Resin

<u>Nitric Acid Normality</u>	<u>Relative volume at crosslinkage of:</u>			
	<u>1%</u>	<u>2%</u>	<u>4%</u>	<u>8%</u>
8	1.0	1.0	1.0	1.0
1	1.0	1.0	1.0	1.0
0.5	1.0	1.0	1.0	1.0
0.1	1.4	1.2	1.0	1.0
H ₂ O	2.05	1.35	1.05	1.0

One recent solution to the problem is to spring-load the resin bed to prevent channeling and fluidization (27).

Superimposed on the swelling is a change in resin density without volume change during a uranium or plutonium cycle due to the weight of the sorbed heavy-metal ions. Typical data are presented for Amberlite IRA-400 (28):

<u>Resin form</u>	<u>SP. GR.</u>
Chloride	1.14
UO ₂ SO ₄	1.23

r presenting a change of 8 per cent.

It is possible to devise a type of countercurrent contactor (30) which utilizes this density difference to obtain enhanced enrichment when operating on a uranium-hydrogen or other similar cycle.

C. Stability of Ion Exchange Resins in Radiation Fields

When ion exchange was first proposed as a possible method for decontamination, there was considerable speculation as to whether radiation damage to the resin might be economically prohibitive. Subsequent investigation has shown that most synthetic ion exchange materials are remarkably resistant to damage.

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The Rohm and Haas Company has exposed all their important resins to dosages up to 2×10^8 r, using Ta-182 and Co-60, at rates of 5×10^5 r/hr (31). At 2×10^7 r, IRA-400 retained 99 per cent of its exchange capacity; LR-120 retained 93 per cent. At 2×10^8 r, IRA-400 and LR-4B still had 80 per cent of their initial capacities. Similar experience is found at Chalk River (22), where Dowex-1 retained "most" of its initial capacity after two months, sorbing plutonium from dissolver solution. In other experiments, Dowex-1 (1% DVB) was saturated with plutonium for one month (33); no adverse effect on either capacity or elution characteristics was found. Only after 8 months exposure was there significant loss in capacity. Similarly, Savannah River predicts only a 20 per cent capacity loss per year in their plutonium tail-end resin unit (34).

Oak Ridge has obtained similar results (8, 35, 36). It was found that phenolic cation exchangers (Dowex-30) are three times more stable toward radiation than are the nuclear sulfonic types (Dowex-50) (37). Dowex-50 has approximately the same stability as the strong base anion exchange resins (Dowex-1). Evidently deamination occurs somewhat more readily than desulfonation, with quaternary amines being initially converted to the less desirable tri- and dialkyl amines.

Styrene and other polymers similar in structure to ion exchange resins have also been irradiated (38) to 10^8 rads without being unduly damaged.

The effect of Co-60 on the permselectivity of ion exchange membranes has been shown (39) to cause a selectivity loss of 4.5 per cent after 2×10^7 r, and 12 percent after 1.5×10^8 r. These membranes are in essence ion exchange resins in sheet form.

Beta radiation is one hundred times more damaging than gamma (40) when the source material is sorbed on the resin. Alphas seem to cause little damage. Neutrons are also less damaging than beta or gamma sources (8).

Finally, resins may be compared for stability with Teflon and Kel-F. These structural and gasket materials lose appreciable strength at exposures of 10^6 rads (5, 39). Kel-F perforated plates have been tested at 4×10^7 rads, equivalent to 25 years service life in the HC column, where anticipated exposure is estimated at 200 rads/hr.

Teflon degradation is negligible except in the dissolver, the HAF feed system, and the No. 1 acid concentrator.

The mechanism leading to radiation damage is as yet unresolved. Higgins (37) believes that the loss in capacity is due to hydrolysis, the active sulfonate or quaternary amine groups being lost from the organic framework. Both increase and decrease in resin porosity have been noted (31). Hydrogen is probably lost, resulting in the formation of olefinic bonds (41) and also carbonyl groups. Fisher and co-workers (31) note that steam was generated during some exposures of wet resin. Thus, all or part of the damage reported under these exposure conditions may be of thermal origin. It is also known that hydrogen peroxide is formed by irradiation of water or aqueous solutions. The peroxide would cause chemical deterioration of the resins.

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If an exchange capacity loss of 20 per cent is allowable, this level would be reached in the HC column in 100 years, or in the HAF system in 1000 hours of exposure. Thus ion exchange resins might be used in head end processes as well as elsewhere in the separations plant, without excessive radiation damage.

It has also been reported recently (42) that Savannah River losses are of the order of 30 per cent per year, which should be compared with Purex solvent losses of 300 to 400 per cent per year (6).

This loss also compares with the loss from all causes (presumably mechanical) of 26-42 per cent per year in the uranium mills (43, 44).

D. Decontamination

1. General

In Table II is compiled the existing data on the logarithmic dF's being realized in solvent and in ion exchange processes.

Table II

Single Cycle dF's for Ion Exchange and Solvent Extraction Processes

	<u>Purex (39)</u>			<u>Redox (45)</u>			<u>Aslon (33)</u>	<u>Cation (42)</u>
	HA/HC	1A/1C	2A/2B	HA/HC	1A/1C	2A/2B		
gamma dF	3.2	2.0	3.3	3.6	1.4	1.0	3.4	0.7
Uranium dF	0	3-4	?	0	6.4	?	3.5	2.3

It is apparent that both cation and anion exchange processes give decontamination from uranium approaching that of the Purex partition cycle. However, the gamma decontamination afforded by cation resins is not high. Where this is important, an anion cycle is superior.

The major difference then between anionic and cationic resin cycles lies in their relative decontamination performance. This difference is due to the manner in which cations are sorbed by each resin. On the cation resins fission products, being mainly cationic, compete directly with the Pu (III) for the resin sites and are each sorbed in an amount proportional to concentration and distribution coefficient. Anion resins will sorb only anions. Plutonium and uranium can be complexed to exhibit anionic behavior in acid solutions, and are thus sorbed on the resins. The majority of fission products cannot be thus complexed and are not retained by anion resins.

The resultant decontamination factors thus obtainable are compiled in Table III. It is apparent that much better contamination factors from both fission products and metallic impurities are to be realized using anion resins. Although no data are available for UX, and the rare earths, neither species is readily oxidized above the +3 valence state, hence anionic sorption is thought not possible.

DECLASSIFIEDHW-45119
Page 17Table IIIIndividual Decontamination Factors Realized with Resin Cycles

<u>F.P.</u>	<u>Cation</u>	<u>Anion</u>	<u>References</u>
Sr		55-100	PR-CM-3; PDB-133
Y		100	PR-CM-3; PDB-133
Ce		100	PR-CM-3; PDB-133
Ru	2.4-50	14-100	KAPL-794; ORNL 1519
Zr	5-300	10-100	HW 42471; HW 39578
Nb	5-60	10-100	PR-CM-3
I		100	PR-CM-3
Cs		50	PDB-133
UX ₁	0.7-13		ORNL-1449, 1519, 1520
RE	1-5-4		ORNL-1449

Metallic Impurities

Fe	1-195	166	ORNL-1357, PDB-133
Cr	1-9		ORNL-1357, PDB-133
Ni	1-10	100	ORNL-1357, 1519, 1520
V	15	412	ORNL 1519, PR-CM-3
As	3-47	100	ORNL 1520, PDB-133

2. Cation Resin Cycle Experience

The bulk of the work in ion exchange separations process research has been done with cation resins. Prior to the adoption of the bismuth phosphate process, Boyd (26, 46, 47) had worked out a cationic process to recover plutonium and uranium from fission products, sorbing from a UNH solution and eluting with oxalic and sulfuric acids. In spite of a 5-foot depth of resin, DF's were only 2-3. Revised elution schedules raised DF's to 80-100 per cycle (48), still too low to justify the process.

The cation process was revived as a plutonium tail end process for Purex, Savannah River and Chalk River TBP-type separations plants (27). SRP reports (42) uranium DF's of 10^2 - 10^3 , though gamma DF's are 2-3 in practice, much lower than anticipated (49). Iron contamination remains approximately 2000 ppm in the product. The elution of uranium with dilute sulfuric acid evidently causes rapid corrosion of the columns and associated stainless steel piping.

The Canadians have evidently abandoned the cation resin (Scrub) cycle in favor of an all-anionic recovery unit described in the next section.

A continuous cation exchange tail end unit is currently being designed and tested for Purex. In the light of the SRP results, it is doubtful that appreciable decontamination will be realized.

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3. Anion Resin Cycle Experience

Anion exchange resins do not sorb cations except as they form negatively charged complex ions with solution anions (see section on chemistry). Kraus (50) has determined that of groups I, II and IIIa of the periodic table, only cerium is sorbed from hydrochloric acid solutions of any concentration. Since in general the chloride complex is more stable than the nitrate, no sorption of the alkali, alkaline earth or rare earth ions (except cerium) is to be anticipated from nitrate solution.

Aluminum forms no complex species with nitrate, hence is not sorbed. This offers an approach to salvaging metal from Redox waste streams.

Chalk River experience (32, 33, 42, 51, 52) is that beta-gamma DF's of 10^3 are consistently obtained using fixed resin columns. Also, when sorbing plutonium directly from dissolver solution, over 99 per cent of the inactive metallic impurities were removed, including all components of stainless steel.

Colorado Plateau uranium mills are consistently obtaining excellent separation from metallic impurities, at the same time concentrating the uranium from 1 g/l or less to 10 g/l or more (25, 28, 53). (In one case, sorption at 10^{-3} g/l is followed by elution at 4 g/l (44).) The major impurities found troublesome here are vanadium, molybdenum and phosphate (43, 54).

E. Equipment Size

1. Column Heights Required

Shielding for process equipment is mandatory, massive and expensive. Any shortening of columns might effect a large saving in space, hence in shielding requirements. The saving in equipment cost must also be considered.

Assuming that the separation to be achieved, or the number of transfer units (Ntu) in an ion exchange cycle, is to be the same as for a solvent extraction cycle, a saving in height must be achieved in the height of a transfer unit (Htu). Typical data for Purex and Redox columns indicate that the Htu in these pulsed or packed columns is always greater than 1 foot, in some cases exceeding 2 feet.

The most nearly applicable ion exchange data is that of Oak Ridge (27, 36, 49, 53, 56, 57), as developed for use at Savannah River. In this process, Pu (III) is sorbed by the hydrogen form of Dowex-50 (cation exchange). Htu values range from 0.92 to 1.16 inches.

Chalk River work has been with an anion exchange resin, Dowex-1 (32). Until last year, they were using 8 per cent DVB resin. Since theirs is essentially a partition cycle, Pu (IV) is sorbed onto essentially a

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uranium-saturated resin. Hence ionic diffusion is much slower, and their Htu values approximate 3.5 inches. Apparently trying to reduce this height, the Canadians replaced their resin with Dowex-1 (1% DVB). Their degree of success is not yet reported. However, the data of Simpson and Wheaton (23) indicate that a three-fold reduction in Htu might be thus obtained, again arriving at a value of 1 inch for the Htu.

Smith (58) reports Htu values for sorbing Pu (III) onto Dowex-50 (8% DVB) ranging from 0.75 to 1.5 inches.

Ryan (39) has recently sorbed Pu (IV) from nitric acid solutions onto Dowex-1 (8% DVB) at a very low flow rate. Calculation based on his 0.625-inch column height and an assumed 1 per cent break through indicates that the Htu for his experiment is 0.125 inch. He also observed that sorption from metal nitrate solutions (lithium, calcium, aluminum) was exceedingly slow, which fact would lead to extremely high values for the Htu. Any attempt to apply an ion exchange process to Redox waste streams will have to overcome this apparent difficulty.

When sorbing uranium from leach solution onto 1RA-400 resin, the Htu is approximately one inch (53).

Thus, until laboratory data are obtained on a particular proposed system, it can be assumed that the separation performance of a 27-foot pulsed extraction column can be obtained in a 15-inch ion exchange bed. Conversely, increasing the bed height will achieve better separation (decontamination).

2. Throughput Rates

Ion exchange columns are normally operated at lower liquid rates than are solvent columns. To obtain the requisite capacity, resin columns will probably need to be of correspondingly large diameter. Where criticality is a consideration, multiple columns might be required.

The rangeability of flow rates (sum of both phases) for Redox columns is 250-3000 gph/ft², the onset of flooding being typically 2000 gph/ft². The Purex columns have similar limits.

3. Sorption

The Savannah River Plant will sorb plutonium onto Dowex-50 at 15 ml/m/cm², (220 gph/ft²) (36). No increase in plutonium waste loss was observed at somewhat higher flow rates (27). Judging from their data, by either doubling the resin bed length or by cutting the design safety factor from 4 to 2, sorption could be performed at double the design flow rate. However, sorption at high flow rates spreads the plutonium out over more resin. The concentration is lowered, and subsequent elution produces a less concentrated product.

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The proposed Purex tail end ion exchange facility (6) proposed to move the XAW (sorption plus scrub) stream at a mass rate of flow of 175 gph/ft², approximating the SRP conditions. Hence the 2BP stream will be handled in a single column of sub-critical diameter.

The Canadians find it necessary to sorb Pu (IV) at the very low flow rate of 0.375 ml/m/cm² (5.5 gph/ft²) (52). Again, these data are taken from a partition cycle, where uranium is being displaced by plutonium. Such a low flow rate would necessitate multiple units in parallel when handling HAPD amounts of plutonium.

Ryan (39) used a flow rate of 0.5 ml/m/cm² to obtain his extremely low Htu value (see above). Since the Htu has been found (23) to be proportional to the square root of the flow rate, his Htu would reach 1 inch at a mass flow of approximately 450 gph/ft². This is a reasonable value.

Higgins (59) proposes that his contactor be run at 840 gph/ft² during the sorption step, when recovering uranium from ore. To obtain the desired separation of this high flow rate required a 66-inch resin column. However, it should be pointed out that in countercurrent (as opposed to batch) column contacting, using more resin for sorption need not lower the concentration of the eluate.

These flows might well be compared with the Purex silica gel facility (60), which will operate at 15 gph/ft², handling the uranium product stream in a 30-inch column. Thus the sorption step presents no particularly difficult design problem except perhaps that of obtaining adequate flow distribution in a short column.

4. Elution

Elution traditionally has required more time than sorption, if a concentrated product is to be obtained.

At Savannah River uranium is eluted at 2 ml/m/cm² (29.4 gph/ft²) and plutonium (III) at 0.2 ml/m/cm² (36). Increasing the flow rate to 0.4 ml/m/cm² decreased the product concentration by 4 per cent, while an increase to 0.6 ml/m/cm² resulted in a product concentration decrease of 8 per cent, indicating a considerable deviation from equilibrium in the column.

Purex tail end plutonium elution was to have been at the rate of 90 gph/ft² (6). This has been altered due to the discovery of a severe pinch in the elution section (39).

Chalk River found that to maintain equilibrium, elution at 0.14 ml/m/cm² was required (61).

Uranium mill practice is to report solution retention times (contact times) rather than flow rates. Eluting uranium from LRA-400, an 18-minute retention time gave a product concentration of 42 g/l, while doubling the flow (9-minute retention) gave a concentration of 18 g/l (28).

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Another mill reports uranium sorption with 3-minute retention and elution with 12-minute retention, corresponding to 10 and 2.5 ml/m/cm² respectively (54).

An old proposal by Boyd (26) was to have eluted uranium from 1R-1 resin at a flow rate of 100 gph/ft². It was found that 180 gph/ft² gave non-equilibrium elution and a reduced product concentration.

More porous resins can be eluted faster to give the same product concentration. Fisher (24) presents some comparable data on uranium at elution rates of "1 gpm/ft²", a different units system. Further comparison of several resins is made in a later publication (25). Batch tests on uranium elution have also been performed (53, 62).

Higgins (59) recommends uranium elution from Permutit SK at 42 gph/ft² using a 32 inch countercurrent column. This resin was developed to have excellent elution characteristics, and is far superior to 1RA-400 or Dowex-1 in this respect (i.e., less "tailing").

While these representative volumetric flow rates for elution are quite low, this need not present a design problem. In the usual case, concentration of the product is highly desirable, hence eluant flow need be only a small fraction of that required in sorption. For example, plutonium sorption at 300 gph/ft² from a feed solution containing 0.5 g/l might be followed by elution at 50 g/l, thus requiring only 3 gph/ft² of eluant (at constant cross-section).

Ryan (39) reduces Pu (IV) to Pu (III) by adding ascorbic acid to the eluant. Since Pu (III) is not sorbed by anion resins, the elution rate is limited solely by the time required for reduction. This has been reported as being 5 minutes under certain practically attainable concentrations. It is anticipated that further work will demonstrate the feasibility of this method, notwithstanding the high price of ascorbic acid (34).

Higgins (59) proposed a similar method to elute uranium from SK resin at a higher concentration by converting the sulfate complex to the chloride complex on the resin, followed by elution with water.

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APPENDIX I

PUREX PLUTONIUM PRODUCT CONCENTRATION BY ANION EXCHANGE

INTRODUCTION

That the Purex plutonium stripper and concentrator requires alteration or replacement by some other means of concentration has been mentioned. Previous suggestions have centered around the use of a cation exchanger to concentrate the plutonium tenfold while obtaining very little additional decontamination (6).

The purpose of this proposal is to suggest that an alternate process employing an anion exchange resin would give the requisite concentration while offering the possibility of substantial additional decontamination.

SUMMARY

An anion exchange process for the concentration and decontamination of plutonium product is described. The Purex 2BP stream is made 7.3M in nitric acid and the plutonium is sorbed from this solution onto Permutit SK resin. Elution is with ascorbic acid in 1M nitric acid. The necessary equipment is small in size and simple in construction. Resin life is long, with damage by attrition being more important than that due to radiation.

The anion exchange cycle will afford significantly greater decontamination from fission products than will the corresponding cation exchange process.

DISCUSSION

Equipment Size

Savannah River sorbs plutonium onto cation resin at a mass flow rate of 220 gph/ft² (36). At this rate the Htu is less than one inch, and is probably about 0.3 inch (27). Ryan's data indicates a corresponding Htu value of 0.4 inch for anion resin (39).

Operating at a capacity factor of 1.44 and at HM #4 conditions, an acidified 2BP flow of 43 gph is required. With the column limited to 5-inch diameter by criticality, the mass flow rate becomes 316 gph/ft². This is still a reasonable flow rate. However, increasing the plant capacity factor to 4.0 will require the mass flow rate to be increased to 880 gph/ft², or will require multiple parallel columns. Higgins (59) finds this flow rate to be operable, requiring however 5.5 ft. of column height when sorbing uranium. The pressure loss through such a column would be 6 psi when using +20 mesh resin, but 150 psi with 50-100 mesh resin particles. Use of a 7-inch column, if deemed subcritical, will enable a more realistic design.

At a capacity factor of 1.44, each cubic foot of resin will sorb 4 hours' production (29, 54). A 5-inch column containing 1 cu.ft. of resin is 7.3 ft. in length. To increase this length further, or to decrease the cycle time to less than 4 hours, appears unfavorable. Thus fixed resin columns present a less likely arrangement than the continuous but more complicated Higgins type exchanger.

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Comparison with Cation Exchange Methods

With considerable progress being made toward the installation of a cation exchange Purex tail end facility, it seems appropriate to review the points of similarity and difference between cation and anion exchange processes.

Concentration of Eluate Attainable

There seems to be a popular misconception, possibly based on Canadian work (32), that a concentrated plutonium eluate is unattainable from anion resins. It is true that the Chalk River first-cycle eluate concentration is routinely less than 1 g/l. However, their first cycle is a partition cycle, wherein the resin is saturated with an excess of uranium. Other Canadian work (29) shows that an eluate concentration of 40 g/l can be expected when uranium is absent. Ryan (39) recently confirmed this.

Decontamination from Fission Products and Ionic Impurities

Cation exchange offers beta-gamma decontamination of the order of 5 to 10 - fold under laboratory conditions (6). In practice however the gamma DF is 3-6 (42). Separation from uranium is by a factor of 10^2 to 10^3 .

Anion exchange provides a gamma DF of 10^2 to 10^3 (29), and a separation factor from uranium of 412 (33).

The experience with iron with both cation and anion exchange resins is parallel, showing that approximately 2000 ppm remains in the product from either resin cycle (29, 42). With the great majority of other metallic impurities, the decontamination achievable by using anion resins is much greater than is obtained with cation resins. Considerable data is available in Chalk River reports (32).

Solution Flow Rates and Concentrations

The most obvious way in which the techniques required for anion and cation resins differ is in the acid concentrations required in the feed and eluant solutions. Cation resins sorb from weakly acid solution and are eluted with concentrated acids or salts. Anion resins sorb from highly acid solutions or solutions of high ionic strength and are eluted with dilute acid or salt solutions.

The acidity of the 2BP stream is nearly correct for cationic sorption. To effect optimum anionic sorption, however, the 2BP must be made 7.3 molar in nitric acid, which requires increasing the flow from 5 to 11.2 relative to the HAF. This dilution is detrimental in that it doubles the mass flow rate, which in turn both increases the Htu and decreases the equilibrium sorption.

Conversely, plutonium is usually eluted from the cation resin with 6M nitric acid thus obtaining a product marginally acid with regard to specification without further adjustment by dilution and evaporation. The anion resin is eluted with 1M acid which presents no comparable problem. The eluate may be further acidified as necessary to prevent polymer formation.

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Effect of Product Stream Components on Adsorption

Resins are readily damaged or rendered inactive by numerous types of maltreatment. Some possible causes of activity loss are pointed out in this section.

Solvent

Dissolved TBP or its decomposition compounds are without effect on the resin. However, should the organic phase be admitted to the resin column, the pores of the resin particles would become filled with organic liquid which would prevent access by the plutonium nitrate complex. This loss in activity is reversible, in that the organic phase may with some difficulty be rinsed from the resin with a third solvent. Assuming however that prevention is the surest cure, the 2 BP stream should be provided with a coalescer-decanter to prevent solvent entrance to the ion exchange columns.

Radiation Stability

There is no evidence that alpha radiation has any effect on the life of Dowex-1 type resin (22). Beta and gamma emitters should be removed prior to this step in the process. A charge of resin should last for over one year, with loss by attrition being controlling.

It should also be mentioned that anion resins with alkyl groups other than methyl on the quaternary nitrogen are readily destroyed by radiation. Dowex-2, having an ethanol group, remains active for only a few days in the presence of plutonium.

Effect of Acid Concentration on Adsorption

Investigators at Chalk River (63) found that anionic plutonium sorption is a function of solution acidity. Optimum sorption occurs from 7.3M acid, with loading declining sharply at higher or lower acidities.

Some anionic resins are attacked and oxidized by concentrated nitric acid. However, the resins containing trimethyl quaternary amine groups are stable in 10M nitric acid. These same resins are the most suitable in other respects for plutonium sorption.

Acid Concentration and Resin Swelling

If a resin is not adequately cross-linked with divinylbenzene, swelling will occur in dilute solutions. The behavior of Dowex-1 is described in the section describing ion exchange resins. It is apparent that within the working range of acidities contemplated for sorption and elution, swelling is not a problem at any crosslinkage. However, rinsing a low cross-linked material with water would cause expansion which, if the resin was confined, would lead to damage through breakage.

Ion Exchange Flowsheet

Figure I presents a preliminary flowsheet employing anion exchange as a final product purification and concentration step. As illustrated, the sorption step is coupled to the Purex 2BP stream without alteration of 2A-2B column operation. The process could apply equally well to Redox 2B or 3B streams.

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Following acidification to 7.3M, the plutonium is sorbed as the nitrate anionic complex. The exact Pu(IV) concentration is not important. On the portion of the equilibrium curve involved, doubling the Pu(IV) concentration in the feed solution can result in only a 10 to 15 percent increase in resin loading. When operating at the described conditions, the capacity of the resin is approximately 3.7 lbs. plutonium per cubic foot. This represents a kinetic "equilibrium" rather than the ultimate resin capacity under static conditions (29).

A scrub stream of 7-8M nitric acid will selectively elute uranium and will serve also to rinse any adherent fission products from the resin column.

In a fixed bed application, the plutonium is next eluted using 1M nitric acid. Elution can be hastened (and the eluate concentrated tenfold) by reducing Pu (IV) to Pu (III) by means of ascorbic and sulfamic acids. However, it has not yet been clarified as to whether the oxidation products of such reductants are detrimental to the final product solution. Using a Higgins or other similar countercurrent contactor, reduction of Pu(IV) to Pu(III) might be found unnecessary due to the longer contact time available in such units. Extremely porous resins (1 percent DVB) can be eluted at fair concentrations using dilute nitric acid alone (29).

Inasmuch as the resin has been "regenerated" using nitric acid, it is now ready to be put directly into the sorption cycle again, after filling the column with 8M acid to displace the dilute acid.

The Pu(IV) product is sufficiently low in acid to meet specification. In fact, acid may have to be added to prevent polymer formation. If Pu(III) is obtained as a consequence of reduction during elution, it will require oxidation prior to storage or shipment.

Slip water, as used in the Higgins unit, may contain some plutonium at times, as when an interface is lost between slip water and solution. Therefore slip water should be recycled to some point of water addition to the process such as the 2AS makeup.

Suggested Laboratory Investigations

- (a) The equilibrium and kinetic study currently being undertaken by Ryan (39) should be enlarged to provide breakthrough, saturation and decontamination data.
- (b) The effect of the presence of residual ascorbic and sulfamic acids or their oxidation products during final product processing (peroxide precipitation) should be investigated.
- (c) The best resin from the considerations of radiation stability, chemical stability, capacity and kinetics needs to be chosen.

FIGURE I

FINAL PLUTONIUM PRODUCT CONCENTRATION BY ANION EXCHANGE

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APPENDIX II

PUREX FINAL PLUTONIUM PURIFICATION BY ION EXCHANGE

INTRODUCTION

The final decontamination cycle for plutonium has occasionally been exceeding design specification (39). A gamma dF of 4.0 has been achieved. More usually however the plutonium product fails to meet specification. Also, in raising the plant capacity factor to 4.0, it may be feasible to use ion exchange methods in the final plutonium cycle, rather than to install annular solvent extraction columns.

DISCUSSION

This proposal is similar to the previous one (of Purex tail-end treatment) with the exception of different flow rates, impurities and generally higher activity levels.

The LBP stream is too dilute to introduce to an anion exchange column, having a flow relative to the HAF of 64 after oxidation and acidification. This would require a mass flow of 1800 gph/ft², thus necessitating at least 3 units in parallel even at the present capacity factor of 1.44.

One alternate suggestion is to reduce the LBP in volume by evaporation following the cross-over oxidation step. Another proposal is to reduce the LBX flow, which is probably impractical.

If it can be assumed that the LBP and LWF streams behave similarly on evaporation, then reducing the LBP to a flow of 3.0 relative to the HAF would concentrate the remaining solution to 10 g/l in plutonium and to 6-7 M in nitric acid. The plutonium concentration and boildown are both less than in the present final plutonium evaporator. Conditions would be more nearly parallel to the No. 1 acid stripper and concentrator, which combination has given reliable service thus far. Alternately, the concentration could be carried to a boildown of say 5 to 1, with the remaining acid concentration being supplied by 13 M acid butt.

The material balance flowsheet following evaporation would be similar to that shown for application to the 2BP. Plutonium loading and final eluate concentration would be increased slightly due to the increased plutonium concentration in the feed.

Solvent decomposition products generated in the concentrator are generally without effect on the ion exchange equilibrium of Pu(IV), differing in this respect from their detrimental effect on solvent extraction. Red oil, if generated, would be harmful.

The ferrous sulfamate and nitrite ion will be destroyed in the concentrator. No interference from these ions is expected. No other ions are reported as being present in the LBP, aside from the nitric acid.

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CONCLUSION

If preceded by a stripper-concentrator, an anion exchange cycle could be applied to the oxidized LBP stream, replacing the present 2A-2B solvent cycle. Gamma decontamination and plutonium losses would likely be similar to those now obtained.

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APPENDIX III

ION EXCHANGE METAL RECLAMATION FROM PUREX WASTE

INTRODUCTION

According to Purex Chemical Flowsheet HW #4 (5), the LWW stream contains 0.2 per cent of the uranium and 0.2 per cent of the plutonium. Small as these values are, they represent a loss of about \$1000 per day in metals value most of which might be salvaged.

A recent proposal (2) suggests that the LWW stream be processed to recover cesium, cerium and strontium, using B-plant equipment and facilities. It is proposed herein that this waste stream be processed also for the recovery of plutonium.

SUMMARY

Plutonium together with some uranium can be sorbed by anion exchange resins from solutions 7-8M in nitric acid. This is essentially the concentration found in the Chalk River separations process.

Two 1 ft³ resin beds can easily handle the present flow rate. Space is probably available in the vicinity of the No. 1 acid concentrator. If B-plant is converted to fission-product recovery, space is readily available therein.

Radiation damage is slight, necessitating changing the resin approximately once a year.

Judging from uranium mill performance, a plutonium recovery of from 90 to 98 per cent might be expected.

DISCUSSION

Equipment Design

Operating at HW No. 4 conditions as currently modified (HAF concentration = 746 gal/ton) and at a capacity factor of 1.44, the LWW flow is 75 gph. The uranium concentration is approximately 3 g/l and the plutonium about 1.6 mg/l. During flushes the plutonium concentration may be many times higher. The fission product activity is identical to that of the HAF, or 2300 gamma curies/gal.

Sorption

With the column diameter limited to 5 inches by criticality, the required flow becomes 550 gph/ft². This compares with Savannah River sorption at 220 gph/ft² (36) and with the maximum rate used by Higgins (sorbing Uranium) of 840 gph/ft² (4). In current experiments, Ryan (39) is sorbing Pu(IV) from synthetic LWW at 160 gph/ft², the 40 cm column indicating no leakage of plutonium in 24 hours. Extrapolating his results to 550 gph/ft² indicates that 40 cm of exchange band height should be sufficient.

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Above the exchange band, the Pu(IV) concentration on the resin is 60 g/l. Each cubic foot of resin (depth = 7 ft.) should sorb for 1000 hours prior to plutonium breakthrough. It may be found expedient to elute prior to plutonium saturation in order to recover also a portion of the uranium. There is sufficient capacity (1.7 Kg) in a one cubic foot exchanger to recover all the plutonium from any ordinary equipment flush.

The waste stream at a capacity factor of 4.0 cannot be handled in a single unit. Three or 4 exchangers operating in parallel will be required.

Elution

Savannah River elutes plutonium at 3 gph/ft². This could probably be increased somewhat due to the change in valence effected by the reducing agent. Using ferrous sulfamate in 1M nitric acid, 100 gph/ft² is estimated as being an acceptable elution rate, wherein equilibrium is maintained between resin and solution.

If fixed bed operation is used, elution should be upflow to avoid leaving a "heel" at the bottom of the column, which would be lost during the next loading cycle.

Continuous Operation

The comparatively long resin column necessary to obtain adequate capacity while avoiding criticality suggests the use of a Higgins type continuous contactor. Only the exchange band height (40 cm) of resin column need be exposed to the LWW stream, thus reducing resin inventory and prolonging resin life. However, the small amount of plutonium involved in this proposal probably would not justify the use of such an elaborate apparatus. Space limitations are also on the side of fixed resin columns.

Auxiliary Equipment

Eluant make-up and storage (ferrous sulfamate in 1M nitric acid) should provide for 500-1000 gallons. Storage should be provided also for 1000 gallons of eluate, at medium activity (100 gamma curies/gal). The eluate will be periodically recycled to the dissolvers.

Should the unit be located in B-plant, a shielded return line is required to carry the product stream from B-plant back to the dissolvers.

Resin Stability

The radiation field expected in the LWW is 2.3×10^4 r/hr. Resins have been tested at a dosage of 5×10^5 r/hr (31). A cumulative dose of 2×10^8 decreases capacity by approximately 20 per cent. Thus a service life of over one year is indicated.

Resin Disposal and Replacement

The deactivated resin will require periodic replacement. The most logical disposal method appears to be to flush it into the waste neutralization tank thence into the underground storage tanks. The resin has a specific gravity of 1.15 and would pro-

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bably float on the self-concentrated waste solution.

Addition of fresh resin might be from a hopper supported by the crane. Alternately, it could be charged as a slurry from the eluant make-up tanks, subject to the usual hazards of plugged lines.

The resin could also be contained in a perforated basket, which might be changed periodically and buried as a unit.

Choice of Resin

Among the strong-base anion exchange resins, Permutit SK has the best characteristics. Dowex-1 and Amberlite 1RA-400 have less desirable elution characteristics, although in other properties they resemble the Permutit resin.

Effect of Waste Components on Metals Recovery

General

Uranium and plutonium are present in very low concentrations relative to some other waste components. The effect of each of these chemicals on uranium absorption is discussed briefly.

Nitric Acid

The 1M nitric acid concentration is 7.5 M. Chalk River experience is that optimum resin loading for plutonium is achieved at 7.3M nitric acid (63). Uranium is only weakly held as the nitrate complex (50). The nitrate also interferes with uranium being sorbed as the sulfate complex (4).

Sodium Nitrate

The effect of the 0.65M sodium nitrate is principally due to the increased nitrate ion concentration, causing it to be in excess of the 7.3M optimum indicated above. This may decrease the resin capacity for plutonium by 25 per cent from the optimum.

Iron

Ferric iron can be sorbed by the resin as the sulfate complex. It is then slowly displaced by uranium and plutonium complex ions. At high flow rates such as are contemplated in this proposal, the effect of iron appears as a loss in resin capacity. Decontamination from iron is marginal, though certainly adequate for waste recovery.

Sulfate

There is sufficient sulfate present in the solution to complex all of the uranium and plutonium, in spite of the iron competing for the sulfate and in spite of the nitrate competing for the uranium and plutonium. The sulfate complexes of uranium

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and plutonium in solutions of such low concentration are very stable. The distribution coefficient for the uranyl sulfate complex is also significantly higher than that of the nitrate. Hence the uranium will likely be sorbed as the sulfate complex. Unfortunately the plutonyl sulfate complex is not appreciably sorbed. Thus any plutonium complexed as sulfate becomes unavailable for nitrate complexing and sorption as such.

Fission Products

The fission products do not alter the sorption equilibrium. The principal contaminants will be zirconium and cerium, these ions being the most anionic of the group (33).

Suggested Laboratory Investigations

- a) The equilibrium and kinetic data for the sorption of plutonium from synthetic "flush" solutions are currently being obtained. Similar data should be obtained using a feed solution comparable in plutonium concentration to that found in the LWV during normal operation.
- b) The most appropriate eluant needs to be selected. Ferrous sulfamate or ascorbic acid in dilute nitric acid appear to show promise. Hydroxylamine causes too much gas evolution to be practical.
- c) The best resin has yet to be determined. Mesh size, crosslinking and pore size are among the factors which control elution characteristics.
- d) The effect of elevated temperatures (90°C) on resin stability should be established. Favorable results here might obviate the need for cooling the LWV stream.

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APPENDIX IV

REDOX PLUTONIUM PRODUCT CONCENTRATION BY ION EXCHANGE

INTRODUCTION

The final plutonium stream (3BP) in the present Redox stream must be concentrated from 2.8 g/l to 100 g/l in plutonium. This concentration step could be accomplished using ion exchange, which would also afford a reserve measure of decontamination.

Extending this reasoning somewhat would allow elimination of the final plutonium cycle (3A-3B) with substitution of an ion exchange cycle to furnish the required decontamination.

Finally, it might even be possible to replace the entire final plutonium decontamination cycle, using ion exchange to do the entire task.

These possibilities are critically reviewed in this section.

DISCUSSION

Final Product Concentration

According to Redox Chemical Flowsheet HM-5 (45) the plutonium is presently concentrated from 2.8 g/l in the 233-S Building. At present capacity, a mass flow of 220 gph/ft² is indicated through a 5-inch exchange column. This is identical to Savannah River sorption rates. The solution is 0.34 M in nitric acid.

Hence the situation is analogous to the Purex final concentration step already covered in detail in a previous section. Provided that decontamination is adequate in previous cycles and that only concentration is required, cation exchange in a Higgins contactor is all that is required.

If further decontamination is desired over this step, anion exchange must be used, preceded by concentrated nitric acid butt to bring the acid concentration to 7.3 M. The acid addition would dilute the feed twofold, increasing the mass flowrate to 500 gph/ft². Increasing the column diameter to 6 inches would give a more workable design if criticality allows this.

As in the Purex tail end proposal, a continuous contactor such as the Higgins unit is applicable here. The required exchange band being approximately 1.5 ft. a comparatively short column will be adequate.

Final Decontamination Cycle Using Anion Exchange

The 2BP, being twice as concentrated in plutonium as is the 3BP, offers an even better opportunity for the application of ion exchange. The present gamma decontamination accomplished by the 3A-3B columns is not great. According to HM No. 5 Flowsheet (45)

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the DF is only 2.3. During the week of 8-9-56 the DF was 2 (64), being 5 the previous week (65). The 3A-3B cycle also causes a twofold dilution which must be overcome in the final evaporation step.

Ion exchange offers greater decontamination and also appreciable concentration. The 2AF contains uranium equivalent to 5 percent of the plutonium. At this contamination level, anion exchange should be capable of obtaining an additional DF from uranium of 100. Ion exchange when used as a third cycle (following two previous ion exchange cycles) gives a gamma DF of 10 (33). Used as a novel process following two solvent extraction cycles, a third ion exchange cycle might be expected to give better results than this.

Ion exchange used at this point also offers 99 percent cleanup of inert metallic impurities (32). Elution as Pu(III) should give an eluate concentration of 40 g/l or more.

After acidification to 7.3 M, the mass flow rate is only 250 gph/ft², if handled by a 5-inch diameter Higgins contactor (59).

Flow Sheet

The tentative flow sheet for the final purification of plutonium is shown in Figure 2. Some flow rates and acid concentration values, such as the IAS and XBI may require adjustment for optimum decontamination.

The 2BP stream is acidified to 7.3 M with 13 M nitric and fed to the resin column either countercurrently or batchwise. The resin is scrubbed with nitric acid of the same strength to elute any adsorbed uranium and to rinse away the adhering fission products. The resin flow or cycle length should be adjusted to give maximum resin loading of plutonium to obtain maximum decontamination as well as maximum concentration in the eluate.

Elution is with 1 M nitric acid containing sufficient ascorbic acid to reduce Pu(IV) to Pu(III), plus sulfamic acid added as a holding reductant. It may be necessary following elution to displace the dilute acid with 7.3 M nitric acid to prevent plutonium loss at the beginning of the next cycle. This is especially needful if a batch column process is used.

Replacement of Redox Final Plutonium Cycles with Ion Exchange

The 1BP is thought to be not amenable to ion exchange techniques. The aluminum nitrate concentration is so high that the kinetics of sorption would be too slow to be practical. The flow is too great to be handled in a single subcritical column. The presence of sulfate is also detrimental. Considering these numerous factors against the use of ion exchange at this point, its use is not recommended.

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FIGURE II

ANION EXCHANGE CONCENTRATION OF REDOX PLUTONIUM PRODUCT

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APPENDIX V

ION EXCHANGE METAL RECLAMATION FROM REDOX WASTE

INTRODUCTION

According to Redox Chemical Flowsheet HW No. 5 (45), the waste stream contains 0.3 per cent of the uranium and 0.7 per cent of the plutonium. These values appear small enough, but it should be realized that about 7,000 grams of Pu and 20,000 lbs of U were lost to waste storage during the fiscal year 1956 (66). This represents a loss in metal in the range of \$500,000 to \$1,000,000.

A process whereby all or part of this loss could be recycled to the HAF or IAF streams might not be difficult to justify.

SUMMARY

The plutonium, but not the uranium, can be sorbed from waste solution using an anion exchange cycle, provided that the chromate concentration can be greatly reduced. The presence of all other ions can probably be tolerated. It is not unreasonable that 90 to 95 per cent of the plutonium can be salvaged.

A fixed bed anion exchange unit is suggested, with 4 parallel columns of 5-inch diameter, each 4 feet deep. Space is available in D-cell between D-10 and D-9.

A decontamination factor of the order of 10^3 to 10^4 is expected based on the performance of similar processes. The pH may require adjustment to effect optimum decontamination. No other feed treatment step is anticipated.

DISCUSSION

Equipment Design

Operating at HW No. 5 conditions and at a production rate of 15 tons per day, the flow to waste storage is 330 gallons per hour. If the columns must be designed for criticality, multiple parallel columns will be required, since use of a single 5-inch column would require a superficial volumetric flow rate of 2400 gph/ft². This compares rather unfavorably with Savannah River sorption flow rates of 220 gph/ft² (36), and even with the maximum flow rate reported by Higgins (59) of 840 gph/ft². Ryan's data indicates an exchange band height of 1 foot at 160 gph/ft² (5W, 6W) which extrapolates to 5 feet at 800 gph/ft². Higgins found that 5.5 feet of height were required to sorb uranium at the above flow.

Designing for plutonium recovery from intermittent equipment flushes presents a lesser problem. A recent flush (64) contained 1405 g of plutonium in 370 gals of acid after buildown. A single column could recover this by sorbing for 3 or 4 hrs.

The resin columns are envisioned as being 5 inches in diameter by 4 feet in length, each containing 0.5 cu. ft. of resin and having a plutonium capacity of approximately

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500 g at a flow rate of 600 gph/ft². Four such columns in parallel are required. The pressure drop of Redox waste through a 4 foot bed of 10-20 mesh particles is approximately 25 psi at 25°C or 6 psi at 75°C. The pressure drop would be somewhat alleviated if 7-inch columns can be accepted. To maintain capacity a porous resin particle is required. However, 1 per cent DVB resin has been found to be compressible if the bed depth is greater than 7 inches (33). A minimum DVB content of 2 per cent is indicated. If the problems of pressure drop and flow distribution at these conditions can be solved, other problems might not be found insurmountable.

Each column thus has a sorption cycle time of several weeks during normal plant operation, but will saturate in a few hours during flush runs. It is felt that feed solution can be either bypassed or stored in D-13 and D-10 during the occasional required elution period, as an alternate to incorporating three more columns and their associated valving.

Elution at the (SPR) rate of 3 gph/ft² will require 24 hours to elute 90 per cent of the plutonium when using ascorbic acid as eluant-reductant. Inasmuch as there is no premium on either eluate concentration or quality, using ferrous sulfamate as reductant at a higher flow rate appears more attractive.

In-line monitoring of the outlet stream for alpha break-through is deemed essential due to the rapid rate at which the flushes are processed relative to the time required for manual sampling and laboratory analysis.

Because the resin may require changing twice a year, it may be convenient to contain it in a disposable perforated cartridge with lifting bail.

Sufficient space exists in D-cell for the installation. Sampling can be performed in D-9 and H-4 as is done currently.

Effect of Waste Components on Metal Recovery

General

With Pu and U present in the waste essentially as minor components, it is conceivable that those ions present in vastly greater quantity may exert a pronounced and perhaps detrimental effect on the recovery of metal. The composition of the waste in the waste collection tank is tabulated, with the calculated molarities for U and Pu (45).

<u>Component</u>	<u>Molarity</u>	<u>Ratio(M/Pu)</u>	<u>Ratio(M/U)</u>
Al (NO ₃) ₃	2.20	2x10 ⁵	390
HNO ₃	-0.52	—	—
Na ₂ Cr ₂ O ₇	0.14	1.3x10 ⁴	25
NaNO ₃	1.0	9x10 ⁴	180
Fe(SO ₄) ₃	0.006	500	1.1
(NH ₄) ₂ SO ₄	0.02	1650	3.2
Cr(NO ₃) ₃	0.004	470	0.9
Pu	0.00001(0.0024g/l)	1.0	0.002
U	0.0058(1.4g/l)	520	1.0

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Nitrate

The distribution coefficient (g U per g resin/g U per ml solution) for U(VI) is 1000 in a solution 2.5 M in aluminum nitrate and 0.5 M in HNO_3 (50). The waste solution approximates this concentration (81) in nitrate. Nitrate is reported to decrease uranium loading in sulfate solutions (4). Ryan reports complete sorption of Pu(IV) accompanied by essentially negligible uranium sorption (39). However, Chalk River is adsorbing Pu(IV) at a NO_3^-/Pu ratio = 4000 without difficulty, although without appreciable concentration (32). No data exists on the anionic behavior of Pu(VI) in nitric acid or nitrate solutions. However, being in many respects similar to U(VI) it is probably strongly sorbed as the nitrate.

Aluminum, Chromic Ion

Hydrated cations are known to slow the kinetics of adsorption (39), though they are not themselves adsorbed (4). An adsorber column several feet in length is indicated.

Dichromate

Chromate and dichromate are both strongly sorbed by anion resins. The high ratios of Cr(VI)/U and Cr(VI)/Pu may make sorption of Pu and U exceedingly unlikely, by Cr(VI) being preferentially sorbed. It may be necessary to reduce most of the Cr(VI) to Cr(III), although Cr(VI) in slight amount is necessary as a holding oxidant for Pu(VI), should this prove to be the most useful form. An effort might also be made to avoid adding such large excess of dichromate to the RA column. Chromate can be reduced to Cr(III) by adding nitrite ion to the solution. Chromate can be removed from the resin using 3 M sodium hydroxide (67).

Sulfate

The distribution coefficient for U(VI) and presumably for Pu(VI) also is very high (35,000) in 0.01 M sulfuric acid, having a maximum value at a $\text{SO}_4^{2-}/(\text{U} + \text{Pu})$ ratio of 2 to 1. At higher sulfate concentration, sulfate competes with the uranyl sulfate complex for the resin sites, and metal sorption falls off rapidly with increasing sulfate concentration. In the waste stream, with a sulfate/uranium ratio of 6 to 1, a distribution coefficient of 1000 would appear not unlikely in the absence of nitrate. However, the nitrate effectively prevents sorption of the uranyl sulfate complex. Unfortunately also, Pu(IV) sulfate is not sorbed, although Pu(VI) sulfate may well be.

Iron

With solutions containing large amounts of ferric iron, the resin initially becomes saturated with the ferric sulfate complex. The uranium and plutonium must then displace the iron, and the rate of this displacement is slow (4). If equilibrium is not attained, the iron contamination of the product metal will

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be great, and the capacity of the resin for U and Pu will appear low, resulting in losses. Iron can be easily reduced to the ferrous state in which it is not sorbed. However, this cannot be done without also reducing the plutonium. It appears that the ferric iron must be tolerated. Alternate remedies might be to reduce the excess of (ferrous) iron added earlier in the process, to sorb the iron onto a cation exchanger prior to U and Pu removal, or to complex the iron with a chelating agent. Ryan has not found appreciable interference from iron, although analysis of his resins shows a high iron residue.

Sodium and Ammonium

Sodium ion causes a decrease in the amount of uranium sorbed as sulfate complex, while ammonium causes an increase. While the sodium concentration in the waste is greater than that of the ammonium, its effect is not as great as that of ammonium ion at low concentrations. The best estimate is that the net effect of these two cations is small.

Fission Products

Chalk River experience is that log DF's of up to 4.1 have been attained in a single sorption cycle in 7 M nitric acid solution. In the 7 M nitrate waste solution, fairly good decontamination should still be expected. Cerium may be found to be the worst offender.

Hexone

Dissolved organic materials have no effect, except that solvents such as acetone tend to dissolve the resin. Undissolved hexone, if allowed to break through the waste concentrator, would coat the resin and destroy its activity. This effect is reversible and activity is restored upon thorough rinsing.

Effect of pH on Adsorption

This is difficult to evaluate. The sorption of uranium increases sharply with increasing pH up to pH = 3.5, after which there is no further increase. Plutonium probably reacts similarly. However, the sorption of ferric iron increases even faster with pH. Hence in the waste solution raising the pH may not increase uranium and plutonium loading. Precipitation of any component must be avoided to prevent the carry-down of uranium. Plutonium polymer formation should also be avoided. It is desirable to evaluate the effect of pH by experiment, adjusting it preferably by addition of ammonium hydroxide or nitric acid, inasmuch as addition of these ions to the waste solution will probably be the least detrimental.

Radiation Stability of the Resin

As indicated in the section on radiation, resin life is expected to be of the order of 1000 hours when immersed in waste solution. Since elution requires more contact time than sorption, resin life expectancy prior to discard is estimated at 5000 hours of operation using a Higgins type countercurrent contactor, or 2000 hours using fixed bed adsorbers.

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Resin Choice

So-called strong base anion exchange resins are the only type suitable for this service. Their capacity is not as great as that of the weak base resins, but the rate of elution of uranium from the strong base resins is much faster. Radiation instability further rules out the Dowex-2 type of resin. The 3 stable resins are: Dowex-1, IRA-400 and Permutit-SK. Of these, the Permutit SK has by far the best elution characteristics. No data concerning its radiation stability have been published.

Suggested Laboratory Investigations

The following are laboratory or semiworks investigations the results of which would assist in the final design.

- a) Laboratory study of the sorption of U(VI) from simulated waste solution. Equilibrium and kinetic data both desired.
- b) Repeat (a) using a solution spiked with Pu(VI), to study plutonium loading.
- c) Repeat (a) or (b) using solutions containing fission products, to evaluate decontamination.
- d) Evaluate the effect of pH on sorption.
- e) Evaluate the effect of flow rate on both sorption and elution.
- f) See what benefit is derived from adding a chelating agent to render iron innocuous.

Note: Ryan is presently engaged in items (a) and (b) and others in Chemical Processing Department will soon have installed in the Purex sample gallery a column to obtain data under item (c).

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BIBLIOGRAPHY

- (1) PDB-135 Pilot Plant for the Separation of Plutonium by Anion Exchange, Part I. Mooradian, A.J., 11-3-54.
- (2) HW-43835 The Isolation and Packaging of Fission Products at Hanford. Tomlinson, R.E., 6-27-56.
- (3) KAPL-314 A Survey of Developments in Plutonium Process Chemistry for 1948-9. Alter, H.W. and Zebroski, E.L., 3-17-50.
- (4) AOCO-68 A Summary Report on the Ion Exchange Process for the Recovery of Uranium. Kaufman, D. and Lower, G.W., 1954.
- (5) HW-31000 Purex Technical Manual. Author not stated, 3-25-55.
- (6) HW-42471 Purex Ion Exchange. Swift, W., 4-9-56.
- (7) Private Communication re Purex Operation, L. L. Zahn Jr., 7-56.
- (8) ORNL-1141 Progress Report to August 20, 1951. Elster, W.K., 3-26-52.
- (9) AECU-3645 Reactor Handbook Vol. II: Engineering. 2-55.
- (10) "The Transuranium Elements" National Nuclear Energy Series, Div. VIII, Vol. 14B. Anderson, H. H.
- (11) "The Actinide Elements" National Nuclear Energy Series, Div. VIII, Vol. 14A. Seaborg, G.T. and Katz, J.J.
- (12) CN-3819 Ionic and Molecular Species in Solution. Hindman, J.P., 5-19-47.
- (13) AOCO-61 Ion Exchange Studies, Part I: Equilibrium Constants. O'Connor, T.L., 7-28-54.
- (14) CL-697 Project Handbook. Mulliken, R.S., editor, 11-44.
- (15) Seccy, C.H., J. Am. Chem. Society 70: 3450 (1948); 72: 3343 (1950).
- (16) RMD-2614 The Chemistry of Uranium in Carbonate Solutions. Bullwinkel, E.F., 3-24-54.
- (17) RMD-2617 A Study of the Factors Affecting the Efficiency of Carbonate Leaching. Hoffman, C.J.; Watson, W.I. and Schwien, 3-31-55.

DECLASSIFIED

HW-45119
Page 42

- (18) Y-816 Topical Report on Anion Exchange Studies. Spivey, E. Virginia et al., 10-8-51.
- (19) "Ion Exchange Resins", Kunin, R. and Myers, R. J. John Wiley (1950).
- (20) Kunin, R. and McGarvey, F., Ion Exchange, Ind. and Eng. Chem. 47: 565-75 (1955).
- (21) A/Conf. 8/P823 Survey of Separations Processes, Lawroski, S., 7-7-55.
- (22) PDB-121 The Separation of Plutonium by Anion Exchange Resins in 10M Nitric Acid, Part IV: Effect of Plutonium Loading and Contact Time on Resin Performance. Korchinski, I. J.O. and Allam, I.W., 5-18-54.
- (23) Simpson, D.W. and Wheaton, R.M., Ion Exclusion, Chem. Eng. Prog. 50, 45 (1954).
- (24) RMD-2511 A Comparison of Anion Exchange Resins Used in the Recovery of Uranium. Fisher, Sallie A., 12-1-52.
- (25) RMD-2518 Recovery of Uranium by Ion Exchange. Fisher, Sallie A. and McGarvey, F., March 17, 1953.
- (26) CN-1882 Final Report Part III: The Adsorption-Desorption Behavior of Uranyl Ion in the Separation of Pu(IV) and the Fission Products from Aqueous Uranyl Nitrate Solutions. Boyd, G.E., 1-29-46.
- (27) ORNL-1357 An Ion Exchange Process for Plutonium Isolation and Purification. Overholt, D.C., Tober, F.W., and Orth, D. A., 10-1-52.
- (28) AOCO-20 Progress Report for January 16 - March 15, 1952. Author not stated.
- (29) CMI-66 The Adsorption of Plutonium by Anion Resins Part II: Column Studies. Durham, R. W., 1-54.
- (30) Selke, W. A. and Bliss, H., Continuous Countercurrent Ion Exchange, Chem. Eng. Prog. 47: 529 (1951).
- (31) RMD-2528 The Effect of Gamma Radiation on Ion Exchange Resins. Fisher, Sallie A., 2-19-54.
- (32) PDB-133 The Separation of Plutonium by Anion Exchange in 10 Molar Nitric Acid Solution Part V. Korchinski, I.J.O. and Allam, I.W., May 18, 1954.
- (33) PR-CM-3 Progress Report, Chem. & Met. Division, July 1 to September 30, 1955. Issued September 30, 1955.

DECLASSIFIED

HW-45119
Page 43

- (34) HW-43022 Trip Report. Hopkins, H. H. Jr., May 11, 1956.
- (35) ORNL-1225 Radiation Damage to Organic Ion Exchange Materials, Higgins, I.R., March 16, 1953.
- (36) ORNL-1520 Progress Report No. 11: Ion Exchange Isolation Processes for Plutonium and Uranium, Overholt, D.C. et. al., May 6, 1953.
- (37) CF-51-11-56 Ion Exchange Studies, Quarterly Report. August 10 - November 10, 1951. Higgins, I.R.
- (38) HW-29007 Stability of Fluorothene Under Exposure to Gamma Radiation. Adler, K.L., 8-11-53.
- (39) HW-43938H Separations Technology Monthly Report for June 1956. Richards, R. B., July 11, 1956.
- (40) WAPD-RM-171 Organic Material in the Effluent from Gamma-Irradiated Ion Exchange Resin. Newton, R.F. and Brown, P.E., 2-17-53.
- (41) KAPL-914 Report of the Chemistry and Chemical Engineering Section for February, March and April 1953. KAPL Staff. 7-23-53.
- (42) HW-39578 Report on Trip to Savannah River Plant and Oak Ridge National Laboratory. Irish, E.R. and Darby, D.O., 10-20-55.
- (43) ACCO-46 (Part 2) Cyclic Column Tests on IRA-400 and XE-75 Resins. Schiff, N.N. and Viklund, H.I., May 3, 1954.
- (44) ACCO-57 Pilot Plant Tests on Anaconda Ore from Grants, N. Mexico. Holis, R.F. et al. July 22, 1954.
- (45) HW-38684 Redox Chemical Flowsheet HW No. 5. Merrill, E. T. and Stevenson, R. L., 8-16-55.
- (46) CN-3346 Final Report Part VI: Semiworks Demonstration of the Adsorption-Extraction Process. Boyd, G.E., 3-6-46.
- (47) CN-1859 Ion Exchange Adsorption. Boyd, G. E., 4-19-45.
- (48) CN-3337 The Development of an Adsorption-Extraction Cycle with High Decontamination. Swartout, J. A. et al. 12-10-45.
- (49) ORNL-1397 Progress Report: Ion Exchange Isolation Process for Plutonium and U-233. Overholt, D. C. 12-20-52.
- (50) A/Conf. 8/P/837 Anion Exchange Studies of the Fission Products. Kraus, K.A. and Nelson, F. 6-23-55.

DECLASSIFIED

HM-45119
Page 44

- (51) HAN-53E88-1 Plutonium Extraction by Ion Exchange at Chalk River. Langmuir, D. B. 2-3-54.
- (52) PDB-136 Pilot Plant for the Separation of Plutonium by Anion Exchange. Part II: Anion Exchange Column Design. Morrison, I.A.W., 10-21-54.
- (53) ACCO-26 Preliminary Studies of the Adsorption of Uranium in a RIP System. Abrams, C.S. and Klufman, D. 7-27-53.
- (54) ACCO-56 Utex Ore Stock piled at Monticello. Moutton, H.D. Jr., 7-19-54.
- (55) ORNL-1449 Progress Report: Ion Exchange Isolation Processes for Plutonium and U-233. Overholt, D.C. et al, 3-4-53.
- (56) ORNL-1519 Terminal Report for the ORNL Pilot Plant Investigation of the Purex Flowsheet. Chandler, J. M. and Darby, D. O. 2-5-54.
- (57) ORNL-1585 Progress Report No. IV: Ion Exchange Isolation Processes for Plutonium and Uranium. Overholt, D. C. et al. 10-23-53.
- (58) Smith, R. C., private communication.
- (59) CF-54-12-101 Recovery of Uranium from Ore Pulp by the Higgins Continuous Ion Exchange Contactor. Part I: Synthetic Ore Pulps. Higgins, I.R. 12-9-54.
- (60) HM-28799 Silica Gel Tail-End Treatment for Redox. Sloat, R. J., 8-17-53.
- (61) PDB-103 The Separation of Plutonium by Anion Exchange in 10 Molar Nitric Acid. Part III: Laboratory Scale Investigation on Dissolver Solution. Korchinski, I.J.O., 12-1-53.
- (62) RMO-2505 Recovery and Purification of Uranium by Ion Exchange. Progress Report January 1 - April 1, 1952.
- (63) PDB-148 The Separation of Plutonium by Anion Exchange in Nitric Acid Part IV: The Effect of Variation in Nitric Acid Concentration. Allam, I.W. and Jones, R. W., 1-14-55.
- (64) HM-40456 No. 243. Summary of 202-S Building Operation to 8-9-56. Harmon, M.K., 8-13-56.
- (65) HM-40456 No. 242. Summary to 8-6-56.
- (66) Rohrmann, C. A. and Jansen, G., Current Investigation of Redox Waste Stream Salvage Potential. 8-56.
- (67) RFP-64 Sorption of Chromate by Dowex-1. Woodward, R.W. and Hampton, L., 2-55.

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