Atomic Energy of Canada Limited

CONCENTRATION AND PURIFICATION OF PLUTONIUM SOLUTIONS BY MEANS OF ION-EXCHANGE COLUMNS

CEI-55

by

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Chalk River, Ontario

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ATOMIC ENERGY OF CANADA LIMITED

RESEARCH AND DEVELOPMENT DIVISION

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ABSTRACT

Equilibrium experiments using Dowex 50 ion-exchange resin and nitric acid solutions of Pu^{3+}, UO_2^{2+}, Fe^{2+} cations have yielded values for the absorption affinities for these ions. Trivalent plutonium was found to be far more strongly absorbed than UO_2^{2+} and Fe^{2+}.

Column studies have shown that uranium can be completely separated from plutonium even when the initial concentration of uranium is very much greater than that of the plutonium. A plutonium concentration increase of about fifty-fold can be obtained from solutions about 10^{-3} M in plutonium and 1.0M in nitric acid.

The equation

$$K_{Pu^{3+}} = \frac{X_R (1 - X_S)^3 C_S^2}{X_S (1 - X_R)^3 C_R^2}$$

for estimating the maximum amount of plutonium taken up by a column of resin of unit volume from a solution of total equivalent concentration, C_S, has been shown to hold for values of C_S up to 3 equivalents per litre. X_R, the equivalent fraction of plutonium on the resin, is the number of equivalents of plutonium absorbed by the resin divided by the total capacity of the column. X_S, the equivalent fraction of plutonium in solution, is the equivalent concentration of plutonium divided by the total equivalent concentration of cations in solution. C_R is the total capacity of the resin in milli-equivalents per gram of dry resin.

Recommendations have been made for the application and operation of ion-exchange columns in the Plutonium-Extraction Plant.

Introduction

One of the important operations necessary in a plutonium-extraction plant is that of concentrating very dilute solutions of plutonium. Uranium, ferrous and fission-product ions are the usual contaminants present in plutonium solutions obtained by backwashing the organic phase of a solvent-extraction cycle. A process giving a separation from these ions simultaneously with the concentration of the plutonium would be an advantageous step.

Evaporation and precipitation are the usual unit operations employed in concentrating these solutions, but both have serious disadvantages. During evaporation, dissolved organic material decomposes producing compounds which complex plutonium, hence making re-extraction difficult. Carry-over of activity with the distillate is also troublesome. Co-precipitation of foreign ions with the plutonium and the difficulty of transferring solid plutonium compounds are problems which arise when precipitation methods are used.

Ion-exchange processes using resin columns have been used with success in both concentration and ionic-separation operations; this has mainly been due to the development of new high-capacity resins such as the Amberlite and Dowex resins(1, 2). The present investigation was made to determine the suitability of such processes in plutonium-extraction operations, and plant operating conditions have been worked out from the laboratory data.

Theoretical Considerations

Present-day high-capacity resins are nuclear-substituted hydrocarbon polymers; cation exchangers contain phenolic, carboxylic or sulphonic acid groups, and anion exchangers have amino residues. Dowex 50, which is a very high capacity cation exchanger (about 5 meq. per gm. dry resin), has sulphonic acid groups as the sole active species and can be considered as a highly ionised solid salt. In column operation a dilute solution containing one or more cations is passed through a bed of resin where the cations are absorbed and held more or less strongly depending on the absorption affinity of each cation. The flow rate of solution through the column defines the kinetics of the operation; slow flow rates allow equilibrium to be reached between resin particles and solution, whereas faster flow gives nonequilibrium operation. Elution is carried out at slow flow rates with a small volume of solution containing a high concentration of one cation, usually hydrogen ion, or with a solution of a complexing agent which effectively reduces the ionic concentration of the element complexed. The less strongly absorbed cation is then eluted first followed by the more strongly held cations.

Two fundamental approaches have been made towards formulating the thermodynamics of ion-exchange processes. Boyd, Schubert and Adamson(3) considered ion exchange to be either a straight-forward absorption of the Langmuir type or a normal metathesis reaction to which the Law of Mass Action applied. It is practically impossible to differentiate between the two processes experimentally but the latter mechanism has been selected by several authors(3, 4, 5) to describe the process, and several kinetic equations have been evolved which fit individual cases of exchange fairly satisfactorily. These equations have been very well reviewed by Duncan and Lister(6) who tested thoroughly the mass-action concept over the complete range of concentrations of cation on the resin.

If we consider the exchange

$$Pu^{3+} + 3H_R = Pu_R + 3H^+$$

where H_R represents the hydrogen form of the resin, the thermodynamic equilibrium constant K is given by

$$K_{Pu^{3+}} = \frac{a_{Pu_R} \cdot a^3_{H_S}}{a_{Pu_S} \cdot a^3_{H_R}} \qquad (i)$$

where a represents the thermodynamic activity of the various ionic species. Owing to the obvious difficulty in estimating activities of ions in the solid phase, it has been assumed that they form ideal solutions although Gregor(7) and Glueckauf and Duncan(8) have shown that swelling of the resin during exchange affects this ideality. When equation (i) is expressed in terms of equivalent fraction in place of concentration it is seen more clearly which variables affect the amount of absorption. Making this substitution we have

$$K_{Pu^{3+}} = \frac{X_{Pu_R} \cdot X^3_{H_S} \cdot \gamma^3_{H_S} \cdot C^2_S}{X_{Pu_S} \cdot X^3_{H_R} \cdot \gamma_{Pu_S} \cdot C^2_R} \qquad (ii)$$

where X_{Pu_R} is the equivalent fraction of plutonium on the resin and X_{Pu_S} is that in solution; similarly, X_{H_R} is the equivalent fraction of hydrogen ion on the resin, and X_{H_S} that in solution. C_S is the total concentration of cations in solution in equivalents per litre, and C_R is the exchange capacity of the resin in milli-equivalents per gram of oven-dry resin. Gamma is the activity coefficient of the ion under consideration. Further simplification leads to the form -

$$K_{Pu^{3+}} = \frac{X_{Pu_R}\,(1 - X_{Pu_S})^3\;\gamma^3_{H_S}\cdot C_S^2}{X_{Pu_S}\,(1 - X_{Pu_R})^3\;\gamma_{Pu_S}\cdot C_R^2} \qquad \text{(iii)}$$

The general equation for exchange of a multivalent ion, M^{Z+}, with the hydrogen form of the exchanger is

$$K_M^{Z+} = \frac{X_{M_R}\,(1 - X_{M_S})^Z\;\gamma^Z_{H_S}\cdot C_S^{Z-1}}{X_{M_S}\,(1 - X_{M_R})^Z\;\gamma_{M_S}\cdot C_R^{Z-1}} \qquad \text{(iv)}$$

Equation (iii) is most important as far as the plutonium extraction is concerned as it predicts the amount of plutonium taken up by a given volume of resin.

The ratio $\frac{\gamma^3_{H_S}}{\gamma_{Pu_S}}$ is in principle evaluable when the mean activity coefficients for HNO_3 and $Pu(NO_3)_3$ in mixtures of both are known, but as yet no data have been published. Assuming this ratio to be unity does not appear to affect the constancy of $K_{Pu^{3+}}$ over a reasonable range of ionic strengths.

Absorption affinities have been found to be dependent on ionic charge and the Debye-Huckel parameter a^0 which is a measure of the hydrated radius of an ion(3). A cation in a high valence state will be more strongly absorbed than one in a lower i.e. $M^{4+} > M^{3+} > M^{2+} > M^+$. A decrease in a^0 for cations of the same valency causes an increase in absorption affinity; this effect is well illustrated by the absorption of the alkali metals(9) Cs > Rb > K > Na. Qualitatively, therefore, we would expect Pu^{3+} to be readily separable from UO_2^{2+} and Fe^{2+} and the following experimental work substantiates this and provides quantitative operating data.

Experimental

The equilibrium constants for the cations Pu^{3+}, Fe^{2+} and UO_2^{2+} have been derived by shaking a known weight of Dowex 50 resin with a solution containing known concentrations of the required cation and of nitric acid until equilibrium was reached, and then analysing the final solution. In this way the concentration of cation in the resin in equilibrium with a solution having a known concentration of the same cation was obtained and the values substituted in equation (iv) to determine K. A second method of determining K is to run a solution of known composition through a resin column of known weight until the effluent concentration reaches that of the feed, and then estimate the amount of plutonium on the column. A value for K_{Pu} has been obtained in this way from Run 4.

The Dowex 50 resin used in these experiments was 50 - 100 mesh conditioned by alternate exhaustion with 10% sodium nitrate solution and 6N nitric acid, the final wash being acid. It was then washed with distilled water and air dried by drawing air through the resin contained in a Buchner funnel. The resin was stored in an air-tight container, and a sample dried in an oven at 120°C to determine the moisture content. The value obtained, 45.9%, was used to estimate the amount of dry resin in a weighed quantity of the moist resin. Although exchange capacity is always based on unit weight of oven-dry resin, columns should invariably be made up from moist resin as drying tends to decrease the exchange capacity. The exchange capacity of the resin used in these experiments was obtained by saturating a resin column of known dimensions with 10% $NaNO_3$ solution and titrating the liberated hydrogen ion with sodium hydroxide. A value of 5.5 meq/gm oven-dry resin was obtained.

Tables I, II and III give the results obtained from the equilibrium experiments using $Pu(NO_3)_3$, $UO_2(NO_3)_2$ and $Fe(NH_2SO_3)_2$ with varying concentrations of nitric acid. Plutonium was obtained in the tri-positive state by reduction of Pu^{4+} with 0.1M hydroxylamine solution.

The values for the equilibrium constants are seen to be reasonably constant over a relatively wide range of total ionic concentrations. Plant solutions fed to exchange columns will invariably be less than 3M in nitric acid, the point at which $K_{Pu^{3+}}$ begins to deviate from constancy; therefore, it should be possible to predict the take-up of plutonium by a column using the average value for K_{Pu} up to that concentration. The equilibrium constants for $UO_2{}^{2+}$ and Fe^{2+} are far lower than that for Pu^{3+}, so that these cations would probably pass through the column during absorption of the Pu^{3+} and any absorbed would be eluted before the plutonium, enabling a good separation to be made.

Column Experiments

Column runs were carried out on the basis of the above results using a 10 cm long bed of resin 1 cm^2 in cross section. The column consisted of a 1 cm^2 glass tube with a stopcock at the bottom and the resin was supported by a coarse sintered disc. A constant head of about two feet of solution gave a reasonable flow rate, and critical adjustments

TABLE I

Absorption Equilibria of Pu^{3+} on Dowex 50 from Pu^{3+} - HNO_3 Solutions

Equilibrium Pu conc'n in sol'n mgm/l	HNO_3 conc'n Equivalents/l	Equivalent fraction Pu on Resin	K_{Pu} **
* 157.0	0.54	0.49	10
52.8	0.54	0.342	9.4
64.1	0.54	0.363	9.6
147.8	1.31	0.139	8.7
46.0	1.32	0.0562	8.9
54.6	1.30	0.0638	8.4
105.3	2.81	0.0147	8.6
112.1	2.78	0.0167	8.9
116.0	5.89	0.00416	19.6
112.0	5.78	0.00408	18.8

TABLE II

Absorption Equilibria of UO_2^{2+} on Dowex 50 from UO_2^{2+} - HNO_3 Solutions

Equilibrium U conc'n in sol'n mgm/ml	HNO_3 conc'n Equivalents/l	Equivalent fraction U on Resin	K_U **
1.96	0.57	0.274	1.9
1.49	0.59	0.257	2.3
1.72	1.16	0.097	2.0
1.88	1.16	0.130	2.7
1.53	1.66	0.061	2.7
1.24	2.91	0.034	5.4

* calculated from column Run 4

** as defined by equation (iv)

TABLE III

Absorption Equilibria of Fe^{2+} on Dowex 50 from Fe^{2+} - HNO_3 Solutions

Equilibrium Fe conc'n in sol'n Equivalent/l	HNO_3 conc'n Equivalents/l	Equivalent fraction Fe on Resin	K_{Fe}**
0.0799	0.48	0.308	0.34
0.0754	0.48	0.321	0.37
0.0664	1.20	0.0809	0.38
0.0647	1.20	0.0692	0.33
0.0422	3.00	0.0262	1.04
0.0405	3.00	0.0249	1.03

** as defined by equation (iv)

were made by means of the stopcock at the bottom of the column. Sieving the resin through an 80-mesh sieve removed fines that tended to plug the sinter and reduce the flow rate. Flow rates during absorption were 10 ml/min/cm^2 and 0.15 to 0.25 ml/min/cm^2 during elution. The elutriant was 6N HNO_3 which was made 0.3M in sulphamic acid in order to destroy any nitrous acid present which would oxidize Pu^{3+} to Pu^{4+}.

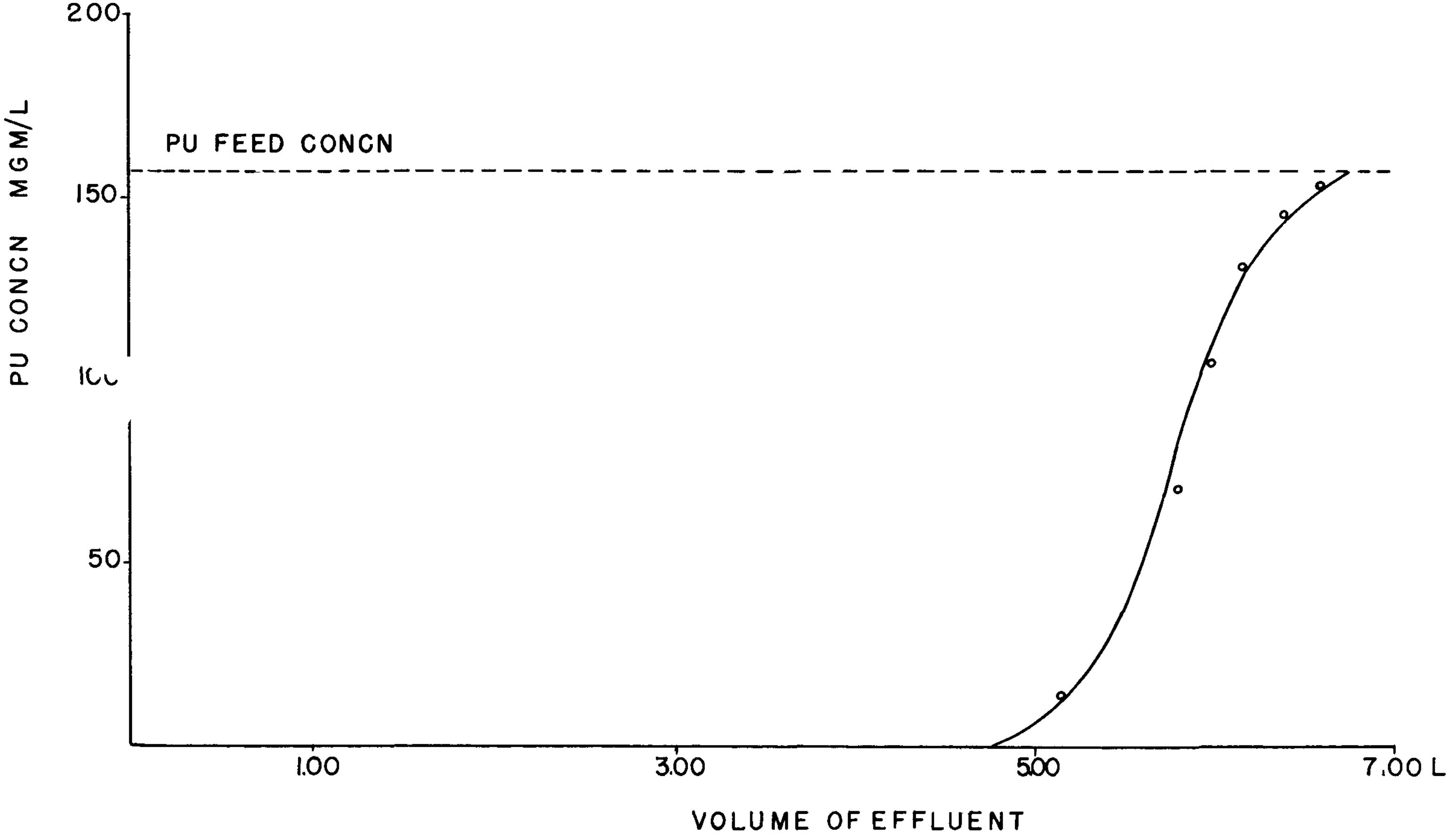
During absorption about 0.05% of the plutonium in the feed appeared in the effluent.

Graph A depicts a typical absorption curve for Pu^{3+}, (Run 4) the sigmoid curve representing the 'exchange band' which moves down the column as the resin reaches equilibrium with incoming solution. The point at which the effluent from the column acquires a concentration of the absorbed cation of about 5% of the feed solution is denoted as 'break-through'. This means in effect that the exchange band has reached the bottom of the column and when the effluent concentration is equal to that of the feed the exchange band has moved right out of the column and the column has reached equilibrium saturation.

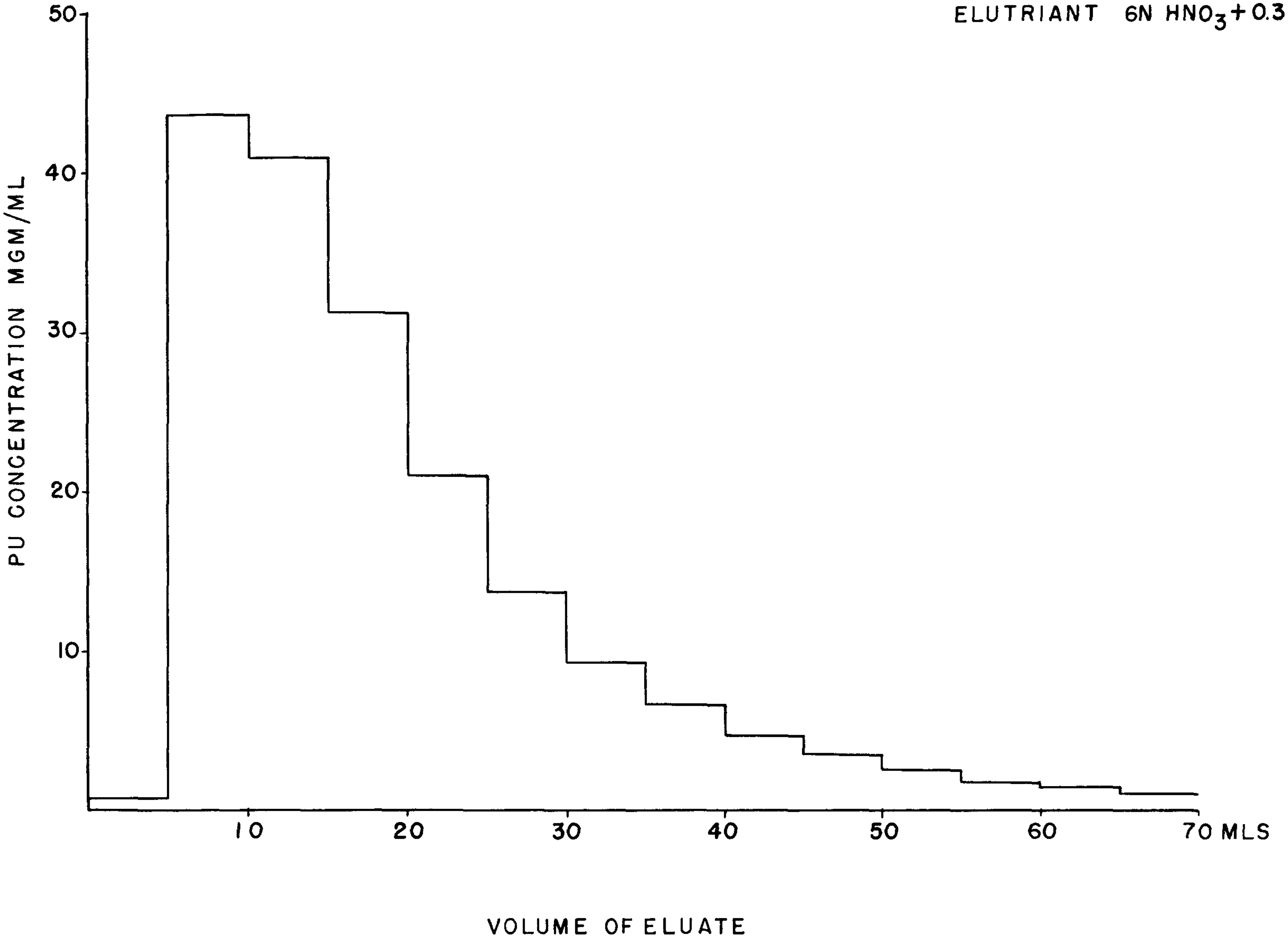
Five grams of completely dehydrated resin when slurried with water into a graduated cylinder produced a column occupying 10 cc and as the dry resin was found to have a dry density of one gram per cc the volume of water in this column is 5 cc. The 'void volume' of a column, or volume not occupied by resin, is therefore 50% of the total column volume. Graph B is an elution curve for Run 4 in which the eluate was collected in 5 ml aliquots equivalent to unit void volumes for the column.

GRAPH A

ABSORPTION OF PU^{3+} RUN 4
FEED 157 MGM/L PU, 1.2 MGM/ML U, 0.54 N HNO_3



GRAPH B



RUN 4 ELUTION CURVE

ELUTRIANT 6N $HNO_3 + 0.3\,M\ NH_2SO_2OH$

The uranium absorbed on the column in Runs 3 and 4 which was not replaced by plutonium was removed by washing with 0.25M sulphuric acid. This reduced the cationic concentration of uranium due to the formation of a stable sulphuric/uranium complex which was eluted leaving the Pu^{3+} absorbed. The results obtained from the column experiments are tabulated in Table IV.

During elution the resin bed was broken up presumably due to liberation of absorbed gas from the resin when it began to shrink on coming into contact with the strong acid. In order to get the resin bed homogeneous again for absorption it was necessary to expand the bed by countercurrent washing with 0.5N HNO_3 to remove the gas bubbles. This problem could be overcome with plant-size columns by down-flow elution followed by upflow absorption with the bed expansion controlled by loading the column with sand.

TABLE IV

Data Obtained from the Absorption and Elution of Pu^{3+} Solutions on a Dowex 50 Column

Run No.	Feed Composition Pu (mgm/l)	 HNO_3 N	 U (mgm/ml)	% of feed Pu conc'n reached by effluent	* Total Pu absorbed (gm)	% of initial Pu remaining on column after 50 ml eluate
1	274	1.09	nil	90%	0.763	13%
2	279	1.10	nil	41%	0.727	28%
3	273	0.80	4.5	10%	0.867	26%
4	157	0.54	1.2	97%	1.010	13%

Run No.	Peak conc'n of Pu in eluate (mgm/ml)	Conc'n Increase	Volume Reduction	Decontamination factor for β γ
1	32.0	49	72	-
2	24.3	37	50	-
3	28.0	47	53	5.2
4	43.8	112	132	5.1

* Total exchange capacity of column for Pu^{3+}: 2.08 gm

Runs 1 and 2 were carried out to determine the magnitude of the volume reduction to be expected on absorption and elution of nitric acid solutions of Pu^{3+} similar in concentration to those obtained in the pilot plant. It is clear from Table IV that a higher volume reduction with a much lower amount of plutonium remaining on the column is obtained by operating the column to equilibrium saturation. It should be noticed here though that 'volume reduction' is a misleading term. The volume of solution containing the plutonium in the 'exchange band' (i.e. the volume of effluent between break-through and saturation), has to be recycled or absorbed onto a series column. The more useful term is 'concentration increase', the two terms only being equivalent when the whole of the exchange band remains inside the column during absorption. This occurs when absorption is stopped before break-through is reached.

Concentration increases were calculated for a given volume of elutriant through the column owing to the difficulty of removing all the plutonium absorbed from the column. The arbitrary value of 50 ml equivalent to 10 void volumes was chosen because at this point the elution curve begins to level out so that further elution would decrease the volume-reduction factor without materially lowering the amount of plutonium left on the column. Feed solutions for Runs 3 and 4 were obtained by backwashing with hydroxylamine in dilute nitric acid a TBP extract containing plutonium, uranium and some fission products during the normal operation of the pilot plant. The acidity in Run 4 was adjusted to about 0.5N to determine whether dilution of plant solutions, which are usually about 1.0N in nitric acid, would be justified by an added concentration increase through the higher plutonium absorption at this acidity. A comparison of Run 1 with Run 4 shows that there is nothing gained by diluting the feed from 1.09N to 0.54N so far as concentration increase is concerned because the final eluates have similar average plutonium concentrations. The increase in Run 4 is slightly higher than in Run 1 due to the equivalent fraction of plutonium in the feed to Run 4 being rather greater than Run 1. One advantage of working at lower feed acidity, however, is the taking up of more of the available exchange capacity of the column and the corresponding increase in height of the elution peak. This is useful when highly concentrated plutonium solutions are required and a relatively large 'heel' can be left on the column. Inspection of Graph B shows that the first void volume of eluate should be discarded and recycled due to its low plutonium concentration.

The $\beta\gamma$ decontamination factor is the number of counts per minute per mg of plutonium in the feed divided by that in the eluate. The value of about 5 obtained for this factor will be dependent on the actual fission products present in the feed; the isotope remaining in this case appears to be Ru^{106} which is probably present in the feed in a valence state which gives it a similar absorption affinity to Pu^{3+}.

Spectrographic analysis of the eluate from Run 3 gave a figure for uranium of 0.6% of the plutonium concentration giving a uranium decontamination factor of 2.8×10^3. Iron was present in an amount greater than 1% but the exact amount of iron was not determinable. This iron must have been present as Fe^{3+} and picked up in the plant process, as any Fe^{2+} would have gone right through the column or been replaced by uranium or plutonium. Fe^{3+} would be expected to have a similar absorption affinity to Pu^{3+} and, therefore, would only be separable by chromatographic elution which is not feasible when a column is operated to obtain maximum concentration increase. Separation of plutonium from contaminating cations with similar absorption affinities is possible by absorption of all cations at the top of a relatively long column followed by elution with a solution of a complexing agent to enhance the separation. The plutonium fraction would then be acidified to break up the plutonium complex and reabsorbed on a smaller column to obtain the volume reduction. Whether this method is an advantage over chemical separation is a matter for further experimentation and plant economics.

Plant Application

The previous experiments show that Dowex 50 resin columns would be suitable to give an approximately fifty-fold concentration increase and a practically complete separation of plutonium from uranium in solutions obtained by backwashing TBP extracts with hydroxylamine solution. The amount of resin required would depend on the weight of plutonium to be handled, one litre of resin in column form having a total exchange capacity for tripositive plutonium of about 200 gm . The fraction of this capacity taken up at equilibrium can be estimated using equation (iii) with $K_{Pu} = 9.0$ when the feed analysis is known.

Operational procedure is as follows. During absorption the flow rate should be from 10 to 15 $ml/min/cm^2$. When breakthrough is reached, i.e. when plutonium appears in the effluent, the effluent is run onto a second column of similar dimensions and, when the effluent from the first column reaches about 95% of the feed-plutonium concentration, the flow is stopped. The first column is then washed with 0.5N sulphuric acid, about 40 void volumes, until all the absorbed uranium is removed; meanwhile absorption can be carried on in the second column. Elution with 6N nitric acid made 0.3M in sulphamic is carried out at about 0.2 $ml/min/cm^2$; the first void volume eluted should be recycled as it contains only a small amount of plutonium together with any less strongly absorbed cation still present on the column. The total volume of eluate collected will depend on whether a high concentration of plutonium is required or whether the maximum amount of plutonium is to be removed from the column concomittant with a reasonable concentration increase. After elution the column should be washed with 0.5N nitric acid to recondition the resin bed for the next absorption cycle. The roles of the two columns are now reversed and the exchange band of the second column is absorbed onto the first.

When maximum volume reduction is not required the above procedure can be simplified. A single column should be used in this case to absorb an amount of plutonium less than that calculated to cause breakthrough of plutonium in the effluent. If this column is then eluted countercurrently the absorption band remains reasonably well defined and does not diffuse throughout the remainder of the column thus maintaining good volume-reduction characteristics.

The same conditions can be used to concentrate the plutonium stream from the new TBP primary-extraction process. It is feasible that the whole of the plutonium purification section of this process can be replaced by using the aqueous effluent from extraction column II as feed to an ion-exchange column. As long as the Fe^{2+}/Fe^{3+} ratio remains high in this solution no interference by iron will occur.

An estimation of the size of a column necessary to replace the plutonium evaporator at present used has been made; the complete design will appear in a separate report.

Suggestions for Further Work

The present TBP secondary-extraction process might also be replaced by one using ion-exchange methods. The difficulty here is the very large ratio of uranium to plutonium coupled with a high acidity which is obtained when the Trigly is backwashed. A full investigation of this problem, including a study of the absorption characteristics of Pu^{4+}, is presently under way, using both anion and cation exchangers.

Conclusions

(1) By absorbing solutions containing about 200 mg/litre of trivalent plutonium in 1N nitric acid onto a Dowex 50 resin column, a fifty-fold concentration increase can be obtained on eluting with 6N nitric acid; about 20% of the plutonium originally absorbed is left on the column.

(2) A decontamination factor of 2.8×10^3 for uranium and 5 for $\beta\gamma$ was obtained using a plutonium solution from a standard run.

(3) The amount of plutonium taken up by a given column can be estimated once the feed analysis is known by using the equilibrium constant measured in equilibrium experiments.

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References

(1) W.E. Cohn, G.W. Parker and E.R. Tompkins. Clinton Laboratories Report MDDC-1447.

(2) F.H. Spedding, Disc. Faraday Soc., Chromatographic Analysis, (1949) 214.

(3) G.E. Boyd, J. Schubert and A.W. Adamson, J.A.C.S. 69, 2818 (1947).

(4) W.C. Bauman and J. Eichorn, J.A.C.S. 69, 2830 (1947).

(5) T.R.E. Kressman and J.A. Kitchener. J.C.S. (1949) 1201.

(6) J.F. Duncan and B.A.J. Lister, Faraday Soc. Disc., Chromatographic Analysis, (1949) 104.

(7) H.P. Gregor, J.A.C.S. 70. 1293 (1948).

(8) E. Glueckauf and J.F. Duncan, UKAEA Report AERE C/R 808.

(9) W.E. Cohn and H.W. Kohn, J.A.C.S. 70, 1986 (1948).