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ATOMIC ENERGY COMMISSION

STUDY OF PLUTONIUM IV ELUTION FROM MACRORETICULAR ANION EXCHANGE RESIN BY 0.5M NITRIC ACID

by

M. N. Nadkarni, P. C. Mayankutty, N. S. Pillai
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भाभा परमाणु अनुसंधान केन्द्र
BHABHA ATOMIC RESEARCH CENTRE
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ABSTRACT

Recent studies on macroreticular ionexchange resins showed that they possess better kinetics than the conventional gel-type exchangers, because of their porous structure and large surface area. Besides, they are reported to exhibit better mechanical, chemical and thermal resistances. By virtue of their sponge-like structure they also exhibit less volume changes depending on the external solutions.

Preliminary studies in these laboratories indicated that macroreticular resins possess more or less the same capacities and absorption characteristics for thorium, uranium and plutonium from nitric acid solutions as the conventional resins. It was found that Pu(IV) can be loaded on the macroreticular anionexchange resin, Amberlyst A-26 from 7,2M nitric acid in much the same way as Dowex 1x4. It was also observed that the elution of Pu(IV) from Amberlyst A-26 by 0,5M nitric acid is much more rapid and quantitative than from Dowex 1x4.

A detailed study was therefore conducted to determine the elution behaviour of Pu(IV) from Amberlyst A-26 by 0,5M nitric acid. Elution profiles were determined at 25 and 60°C and the results were compared with those obtained with Dowex 1x4. Elutions from aged columns of these two exchangers were also carried out and it was found that the macroreticular exchanger yields much superior elution characteristics than the gel-type resin. The experimental details and the results of these investigations are discussed in this report.

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1. INTRODUCTION

In the Purex for the reprocessing of irradiated uranium fuels, the final step in the purification and concentration of plutonium is done by anion exchange where plutonium is absorbed on an anion exchange resin from 7.2M HNO_3 and eluted by 0.5M HNO_3 [1]. Dowex 1x4 and Permutit SK are the exchangers usually used for this purpose. The kinetics of these exchangers with respect to loading and elution of plutonium are very low at normal temperature. Hence they are usually operated at higher temperature (50-60°C). Further, 0.5M HNO_3 is not the best eluting agent, because prolonged tailing is observed during elution, though it is less at high temperature. Other eluting agents such as hydroxylamine [2], ascorbic acid and ferrous sulfamate have also been tried but all of them were found to have several disadvantages [1]. These exchangers also have certain other defects, besides their slow kinetics: low radiation and thermal stabilities, clogging of the resin bed especially in continuous contactors [7] preventing easy flows and appearance of air pockets within the resing bed due to variations in bed volumes depending on feed conditions, etc. Several other exchangers like Amberlite IRA-401, Dowex 21K, and Duolite A42 LC were also tested for this purpose, but all of them were found to be either similar or inferior to the two previously mentioned exchangers in their behaviour.

Recent studies [3,4] on macroreticular (MR) ion exchangers showed that they possess better kinetics than their microreticular counter parts because of

their porous structure and large surface area. They are also reported to have better thermal and radiation resistances. Another advantage of these resins are that since they possess rigid, porous structures their volumes do not change depending on the external solutions. These qualities of the MR resins make them ideal for column operations.

Preliminary investigations in these laboratories[5] indicated that MR resins possess more or less the same capacities and absorption characteristics for Th, U and Pu like conventional ion exchangers. It was observed that Pu(IV) can be loaded on the MR anion exchanger from 7.2M HNO_3 in much the same way as Dowex 1x4. Further studies on the elution behaviour showed that the elution of the sorbed Pu(IV) by 0.5M HNO_3 is much more rapid and quantitative from MR resin than from its microreticular counter part at normal temperature. The results of the elution experiments are summarised in this report.

2. EXPERIMENTAL

2.1 Apparatus and Materials

Elution tests were performed in glass columns of 0.6 cm diametre. High temperature experiments were conducted by passing hot water through jacketed columns. Loading, washing and elutions were done in the downward directions.

Macroporous ion exchanger used was Amberlyst A-26 (30-50 mesh) (A-26), a quaternary ammonium anion exchange resin, manufactured by Rohm and Haas Company. Dowex 1x4 (50-100 mesh) (D1) was used as its microreticular counter part for comparisons.

All the reagents and chemicals used were of Analar grade.

2.2 Procedure

The ion exchange resins were converted to NO_3^- form by passing

sufficient amount of 1M HNO_3. The resin bed was preconditioned in 10 bed volumes (BV) of 7.2M HNO_3 before loading. After loading Pu(IV) on the column from 7.2 M HNO_3 the column was always washed with 10 BV of the same acid before elution. In all the elution experiments about 95 mg Pu (about 6% breakthrough) was loaded on a 2 ml resin bed. Elutions were done in 0.5M HNO_3, collecting the eluates in fractions of 1/2 BV. Loading and washing were done at a flow rate of 1.5 ml/min/cm^2 and the elution at 0.37 ml/min/cm^2 unless otherwise mentioned.

2.3 Assay

All the estimations of Pu(IV) were done by α-counting in a 2π gas flow proportional counter.

3. RESULTS AND DISCUSSION

Fig.1 shows the results of the elutions at 25°C. It may be seen that elution of Pu(IV) by 0.5M HNO_3 from A-26 is much more rapid than from D1. Even at double the elution flow-rate the former was found to give a faster elution. At a flow-rate of 0.37 ml/min/cm^2 97.5% of the sorbed Pu(IV) was found to be eluted in 3BV from A-26 and at double the flow rate the percentage eluted was 96.7. Irrespective of the difference in flow-rates 99% of the Pu absorbed on A-26 resin was eluted in 5BV at 25°C. The corresponding elution from D1 is only 78.8% and 87.1% in 3 and 5BV respectively. In this case only 97% was found eluted even in 20 BV. Beyond 3 BV, D1 shows about 9 times more tailing than A-26.

At 60°C (Fig.2) the entire Pu sorbed on A-26 was eluted in just 3 BV, whereas from D1 the elution was only 85% in the same number of bed volumes. These results clearly indicate that though the elution efficiency improves considerably at higher temperature, at the cost of an additional

2 BV of the eluant 99% can be eluted from A-26 at the normal temperature itself. These elution results clearly show that elution of Pu by 0.5M HNO_3 from MR resin at room temperature is much faster than elution from D1 at higher temperature.

In an attempt to find a better eluting agent for Pu(IV) from D1 [6] it was reported that 98% of Pu could be eluted in 3 BV of 1M acetic acid as eluting agent at 60°C. A comparison of these results with those obtained on A-26 shows that what is possible with D1 by 1M acetic acid at 60°C is easily possible with A-26 by pure 0.5M HNO_3 at room temperature. The observations on the two exchangers are given in Table 1.

In order to check the effect of aging a Pu-loaded resin bed on the elution behaviour, the following experiment was conducted:

About 20 mg each of Pu(IV) was absorbed from 7.2 M HNO_3 on two columns, one containing A-26 and the other containing D1. After giving sufficient washing with 7.2M HNO_3, the columns were allowed to age for 70 hrs. Pu was then eluted by 0.5M HNO_3 at room temperature. The results are given in Fig.3. It may be seen that the elution from the aged A-26 column is as sharp as from a fresh column indicating the absence of any adverse effect as a result of keeping the resin in contact with Pu and concentrated nitric acid for a prolonged time. On the contrary aging of D1 has resulted in to prolonged tailing during elution. Further, several air pockets were found to appear in the D1 bed after 70 hrs. of againg, whereas A-26 was found to be intact with no apparent physical changes. This probably proves the better chemical resistance of MR resins attributed to them.

It may be noted that for obtaining the comparative elution data, the mesh sizes of the resins used were 30-50 for A-26 and 50-100 for D1. The results indicated that the coarser A-26 has undoubtedly a faster elution

kinetics than even the finer size of D1. It is well known that for certain operations the grain size of the resins used is an important factor; bigger the size better the physical characteristics of the ion exchange columns. This factor is even more important in the continuous contactor processing of Pu[7]. Here broken resin beds result in much more difficult mechanical operations because of resin pushing characteristics. Dowex 1x4 (50-100 mesh) shows very few broken beads, but because of their small sizes, they are difficult or impossible to push in plant scale continuous contactors and they also show undesirable pressure drops during feed flow[1]. But bigger bead size is accompanied by slower kinetics thus putting restrictions on the use of coarse resins. Therefore MR resins with their big, tough, spherical beads and faster kinetics have better possibilities especially in plant scale operations.

In separate experiments it was observed that A-26 has more or less the same breakthrough capacity for Pu as D1, and the decontaminations obtained from uranium and the fission product ^{95}Zr are also quite good[5].

4. CONCLUSIONS

Present studies show that the macroreticular anion exchange resin, Amberlyst A-26 (30-50 mesh) is superior to Dowex 1x4 (50-100 mesh) for the purpose of plutonium purification. The exchanger has better kinetics and hence a rapid elution of Pu(IV) can be done by 0.5M HNO_3 at normal temperature itself. Due to rigid structure and bigger grain size it has an edge over Dowex 1x4 for the purpose of column operation especially in continuous contactors.

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REFERENCES

(1) J.L. Ryan and E.J. Wheelwright, USAEC Report HW 55 893 (1959)

(2) A.M. Aiken, Chem. and Engineering Progress, 53, 82 (1957)

(3) R. Kunin, J. Amer. Chem. Soc., 84, 305 (1962)

(4) R. Kunin, et al, I&EC Prod. Res. and Develop., 1 (2) 140 (1962)

(5) M.N. Nadkarni et al., BARC-899 (1977)

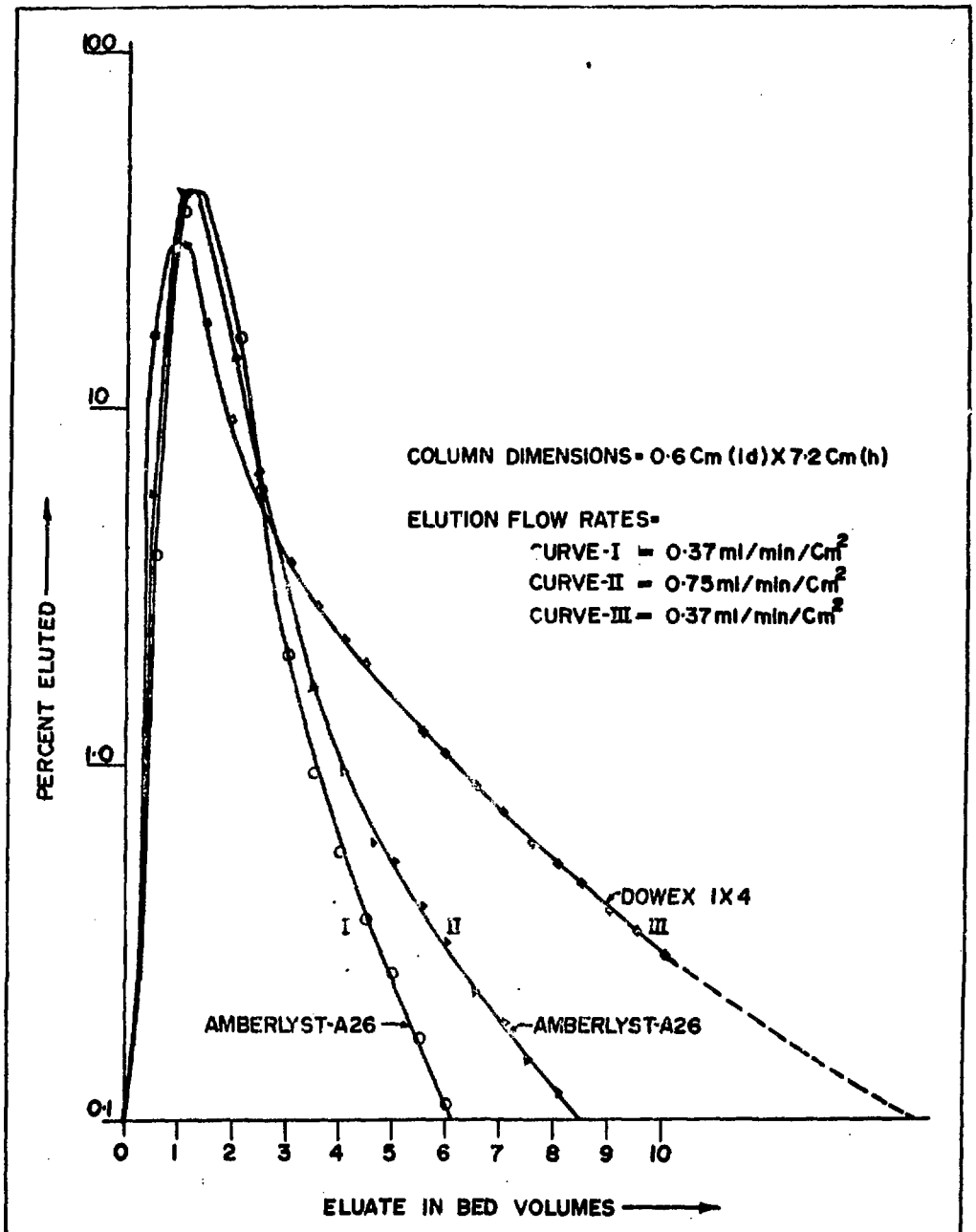
(6) T.S. Laxminarayanan et al, Proceed. Nucl. Radiat. Chem.Symp. Poona, 328 (1967)

(7) F. Helfferich and M.S. Plesset, J. Chem.Phys., 28, 418 (1958)

Table 1

ELUTION OF Pu IV FROM ANION EXCHANGE RESINS

Eluting agent	Temperature	Dowex 1 x 4		Amberlyst	
		in 3BV	in 5BV	in 3BV	in 5BV
0.5M HNO_3	25°C	78.8%	87.1%	97.5%	99.0%
0.5 HNO_3	60°C	85.0%	98.0%	100%	-
1M acetic acid (6)	60°C	98.0%	-	-	-



FIG·1 – ELUTION OF PLUTONIUM AT 25°C

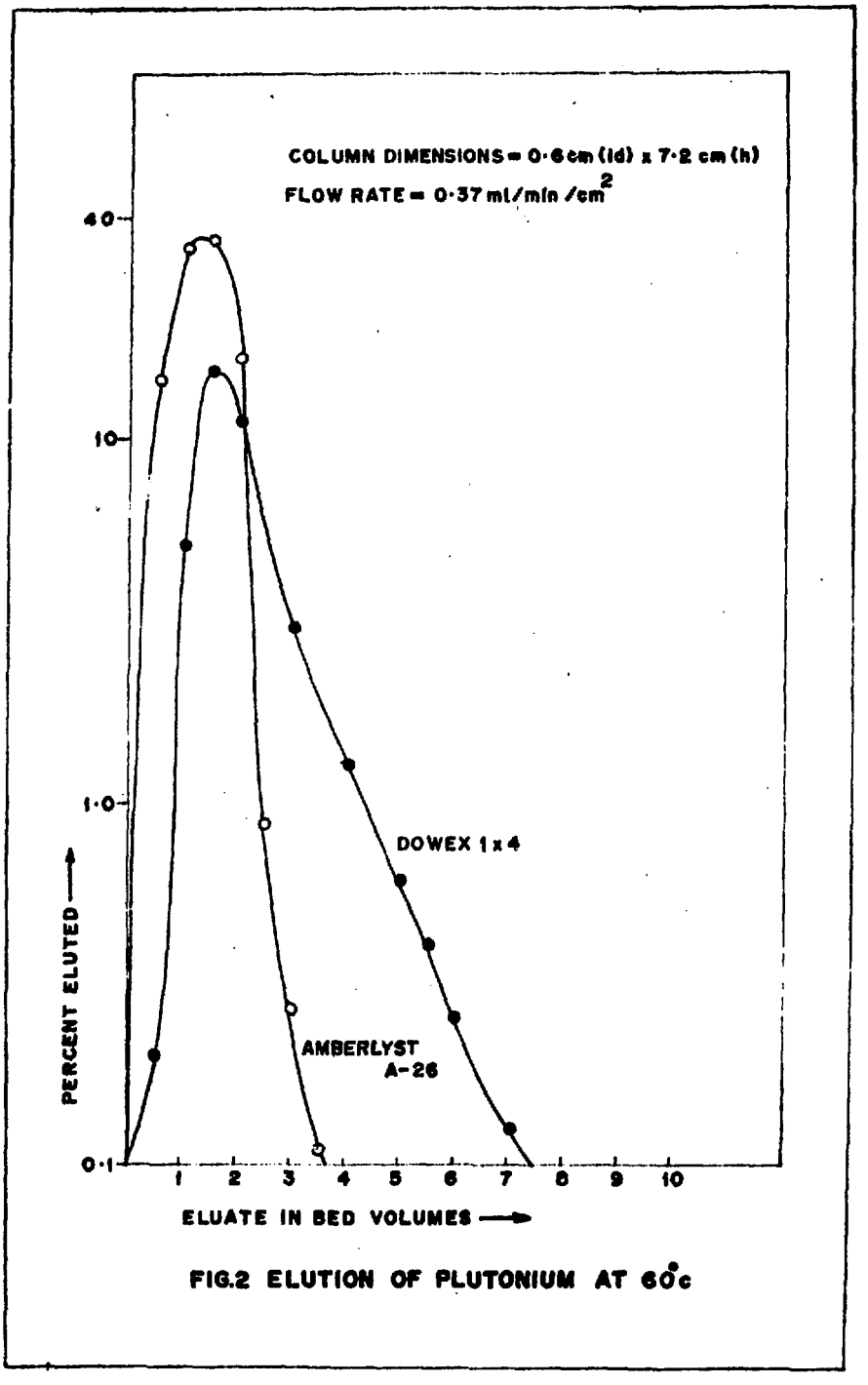


FIG.2 ELUTION OF PLUTONIUM AT 60°c

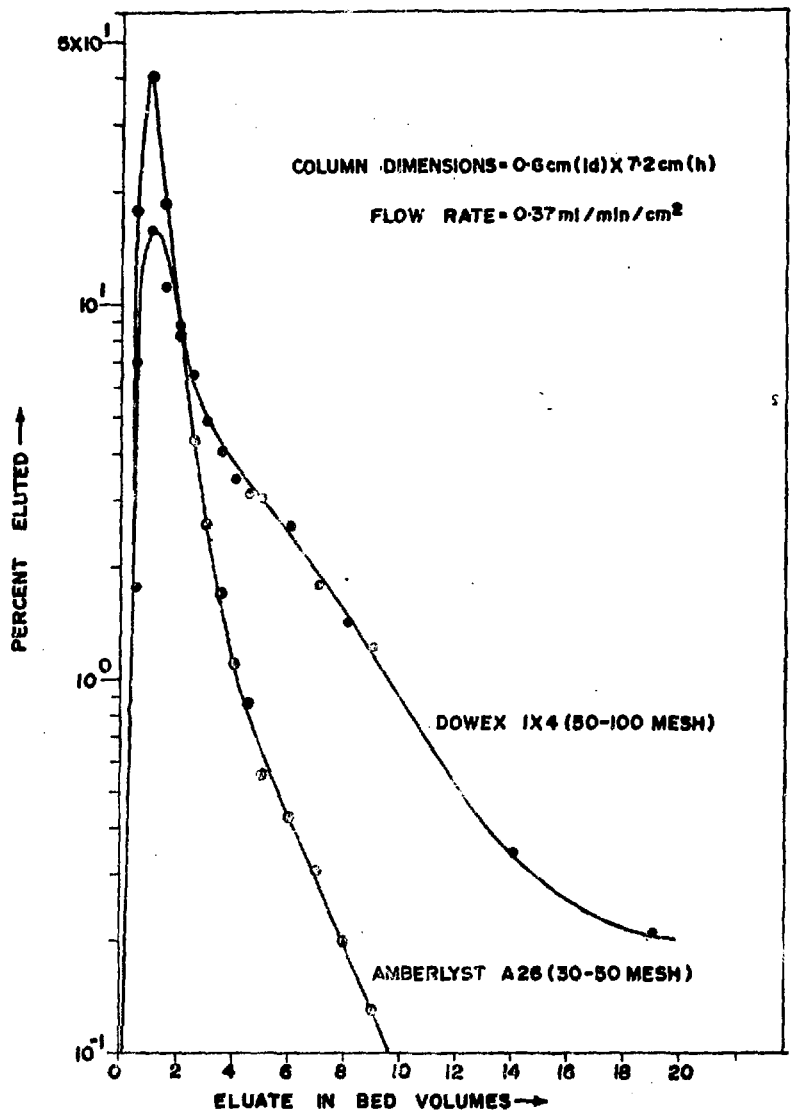


FIG. 3 ELUTION OF Pu BY 0·5M HNO_3 FROM AGED COLUMNS