SORPTION OF PU(IV) FROM NITRIC ACID BY BIFUNCTIONAL ANION-EXCHANGE RESINS

R. A. Bartsch, Z. Y. Zhang, S. Elshani, and W. Zhao
Department of Chemsitry and Biochemistry
Texas Tech University, Lubbock TX 79409

G. D. Jarvinen, M. E. Barr, S. F. Marsh, and R. M. Chamberlin
Nuclear Materials Technology Division
Los Alamos National Laboratory, Los Alamos, NM 87545

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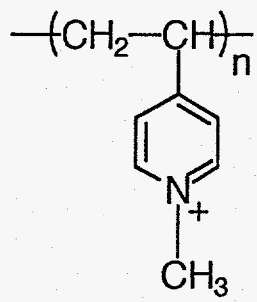
- Anion exchange in nitric acid is the process most frequently used to recover plutonium(IV) from a wide range of impure nuclear materials.

- Plutonium(IV), the most stable oxidation state of plutonium in nitric acid, readily forms an anionic hexnitrato complex that is strongly retained by anion-exchange resins.

$$Pu(NO_3)_6^{2-}$$

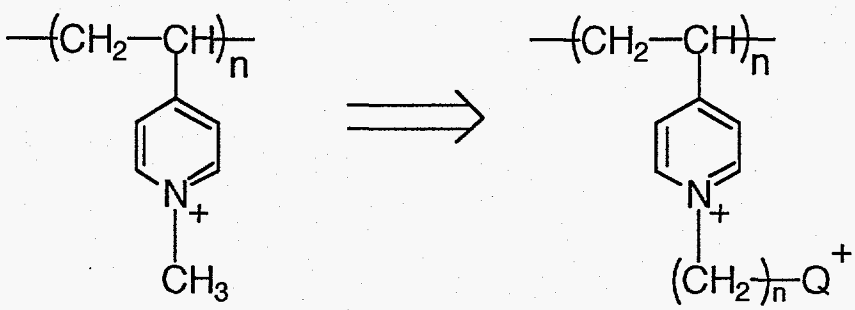
- Anion exchange is attractive for separating plutonium because the Pu(IV) nitrate complex is very strongly sorbed and few other metal ions form competing anionic nitrato complexes.

- The major disadvantage of this process has been the unusually slow rate at which the Pu(IV) nitrate complex is sorbed by the resin.



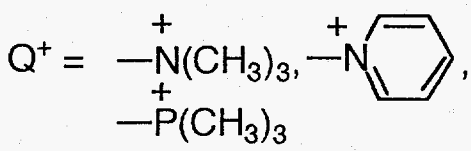
Reillex™ HPQ anion-exchange resin has been used for the past ten years in the Los Alamos full-scale plutonium recovery facility. This resin was developed jointly by Reilly Industries, Inc. and Los Alamos National Laboratory.

<u>Concept of Bifunctional Anion-Exchange Resins</u>



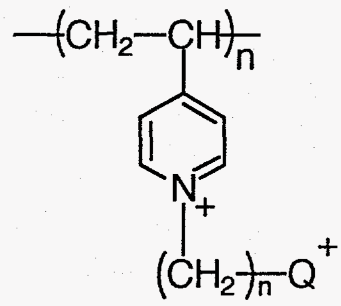
monofunctional anion-exchange resin

bifunctional anion-exchange resin



- Resin synthesis at Texas Tech

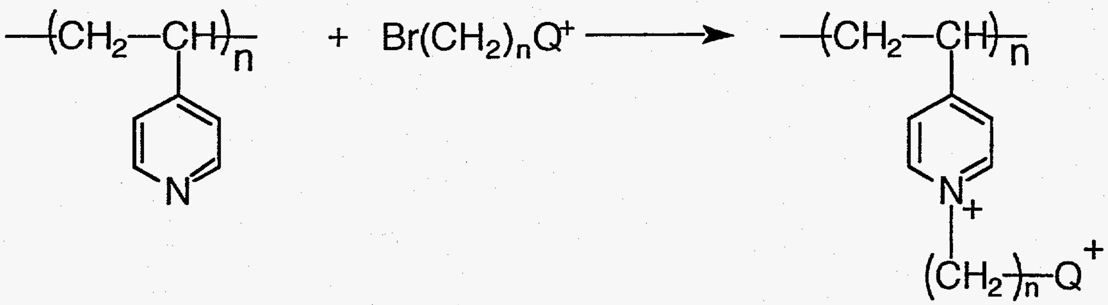
- Resin evaluation in Pu(IV) sorption at Los Alamos



- Will the second positively charged site in the repeat unit enhance the efficiency of $Pu(NO_3)_6^{2-}$ sorption?

- Is there an optimal number of methylene groups "n" in the spacer?

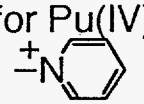
- What is the influence of varying the identity of Q^+?



Reillex™ 402
poly(4-vinylpyridine)

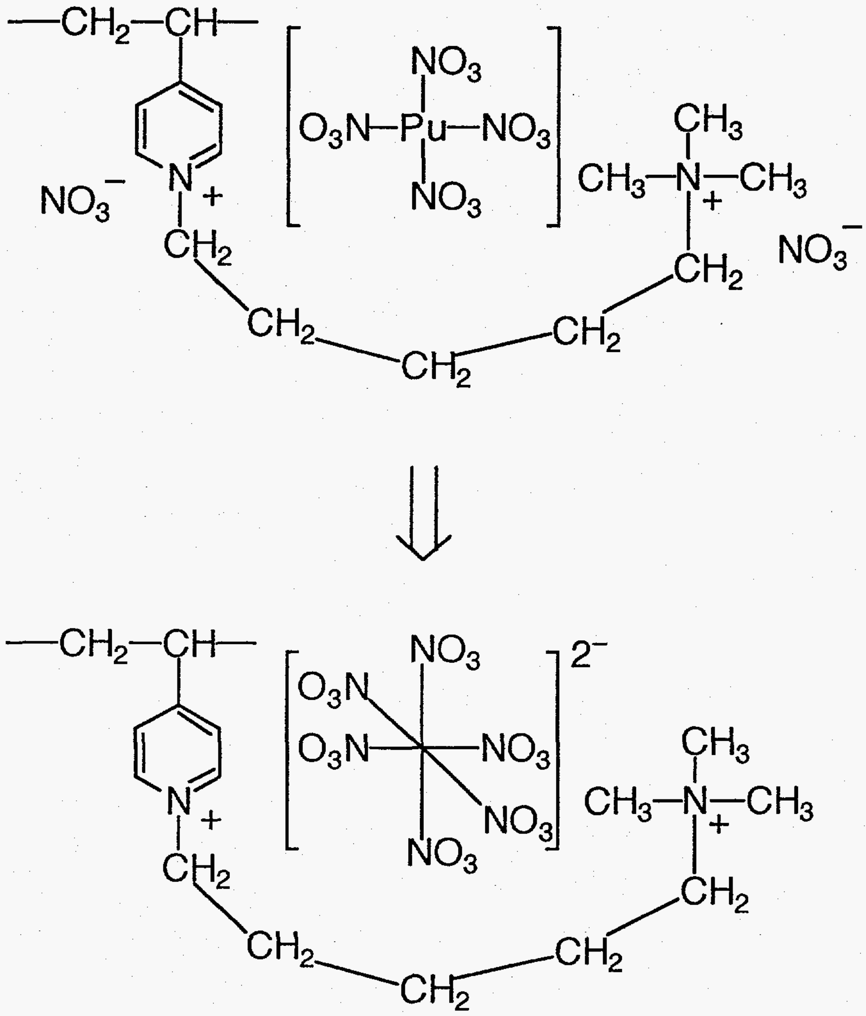
- Compared with Reillex™ HPQ, the bifunctional anion-exchange resins gave more rapid and complete sorption of Pu(IV) from 5-9 M nitric acid, but poorer sorption from 1M nitric acid.

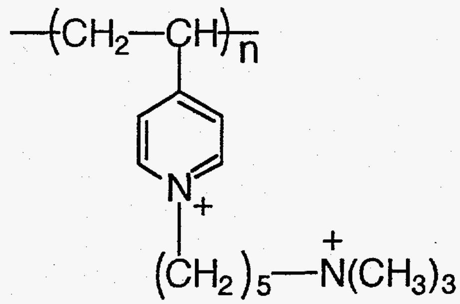
- Sorption of Pu(IV) was most efficient when $n = 5$.

- Sorption efficiency for Pu(IV) decreased in in the order $-Q^+ =$  $> -\overset{+}{P}(CH_3)_3 > -\overset{+}{N}(CH_3)_3$. However, the synthesis of $Br(CH_2)_nQ^+$ is easiest when $-Q^+ = -\overset{+}{N}(CH_3)_3$.

Reference: S. F. Marsh, G. D. Jarvinen, J. S. Kim, J. Nam, and R. A. Bartsch, Reactive & Functional Polymers, 1997, 35, 75-80.

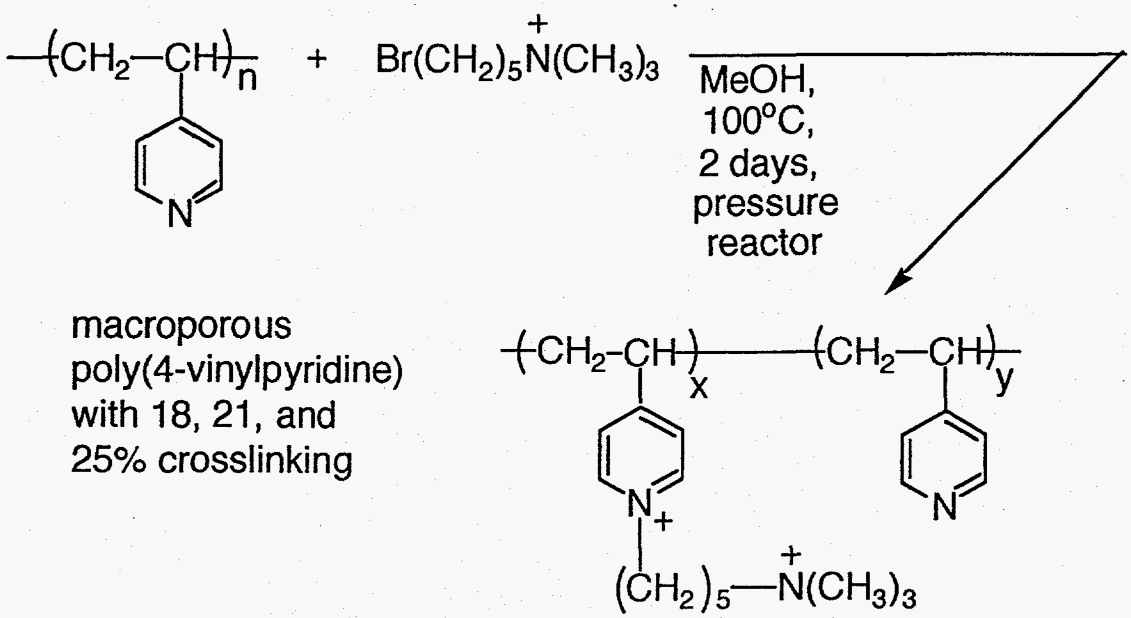
Proposed Mechanism for Pu(IV) Sorption





- Although resins derived from Reillex™ 402 resin were suitable for screening studies which involved single-stage Pu(IV) sorption experiments, the base resin suffers from compacting and would be unsuitable for use in the chromatography columns which are employed in Los Alamos full-scale plutonium recovery facility.

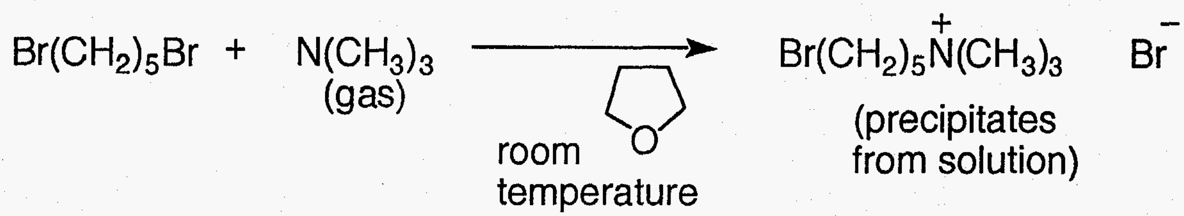
- Macroporous resins would provide the requisite physical strength.



macroporous poly(4-vinylpyridine) with 18, 21, and 25% crosslinking

- What level of crosslinking of the base resin is preferred?
- What level of alkylation of the base resin is preferred?

Synthesis of the Alkylating Agent



In the customary solvents of benzene and ethanol, a mixture of mono- and di- substituted products was obtained.

Reference: R. A. Bartsch, W. Zhao, and Z.-Y. Zhang, Synthetic Communications, in press.

Calculation of K_d Values (in mL/g) from Pu(IV) Sorption Results

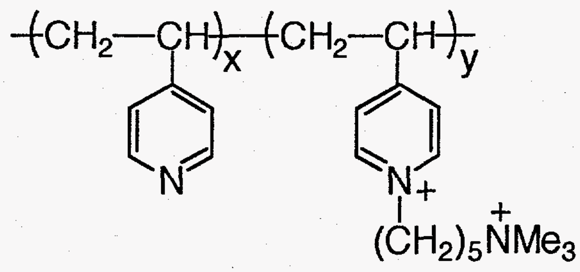
$$K_d = \frac{(P_r - P_o)S}{P_o A}$$

P_r = measured precontact activity

P_o = measured postcontact activity

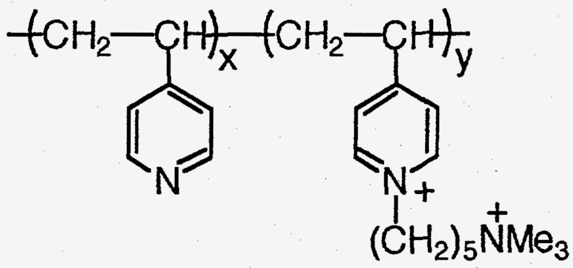
S = milliliters of solution contacted

A = grams (dry) of resin contacted

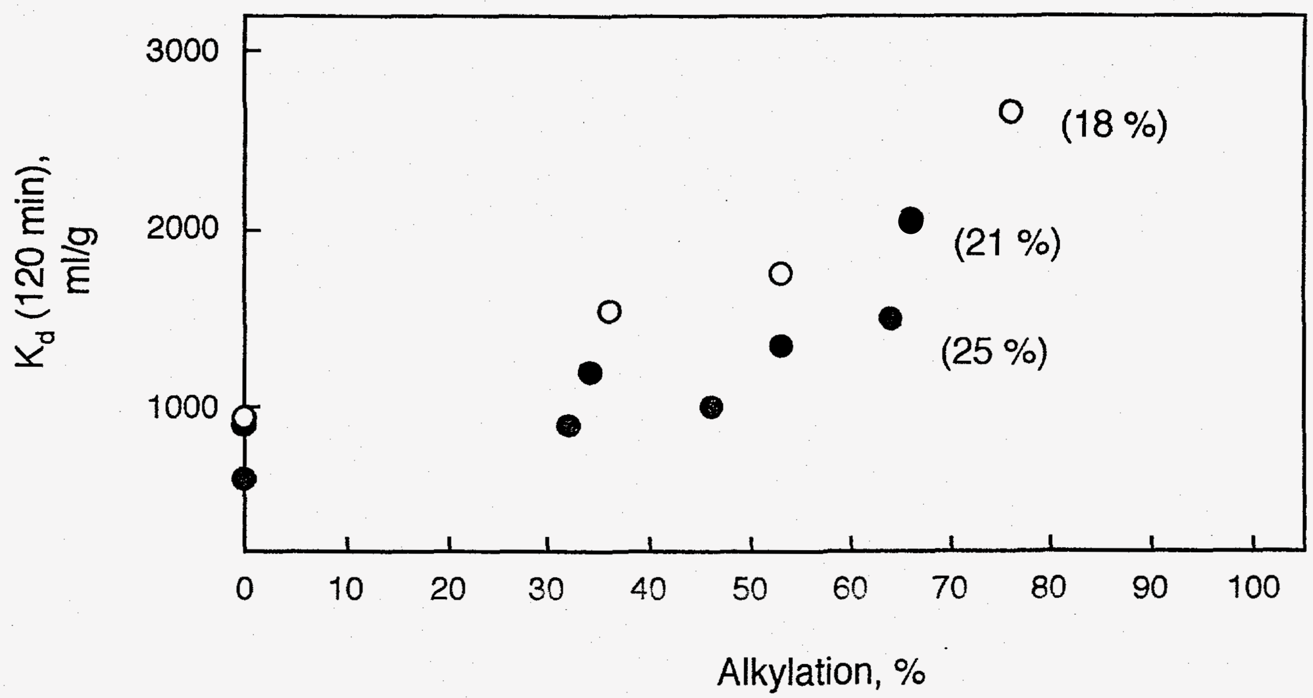


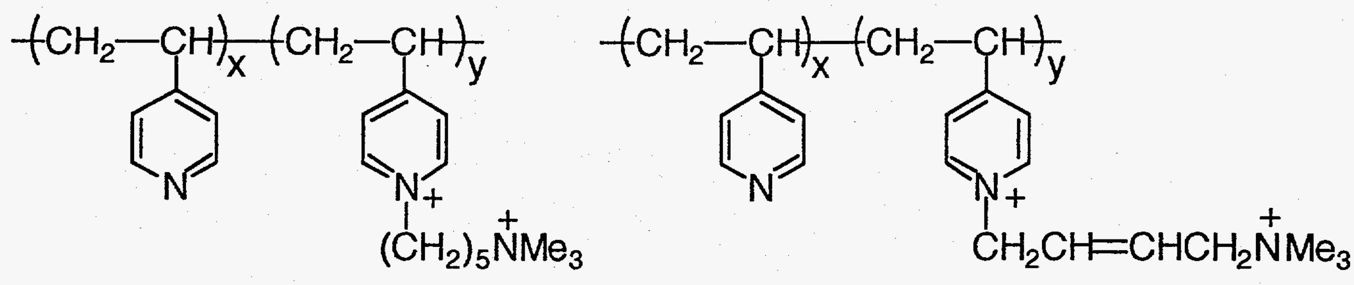
Measured K_d Values for Pu(IV) Sorption from 7 M Nitric Acid by the Bifunctional Anion-Exchange Resin as a Function of the Percent Crosslinking and Percent Alkylation

Crosslinking, %	Alkylation, %	K_d (120 minutes), ml/g
18	0	950
18	36	1550
18	53	1750
18	76	2650
21	0	900
21	34	1200
21	53	1350
21	66	2050
25	0	600
25	32	900
25	46	1000
25	64	1500



Influence of Percent Crosslinking in the Base Resin and Percent Alkylation of the Bifunctional Anion-Exchange Resin upon Pu(IV) Sorption from 7 M Nitric Acid



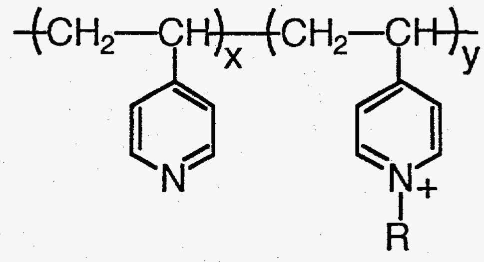


(cis and trans)

(21 % crosslinked)

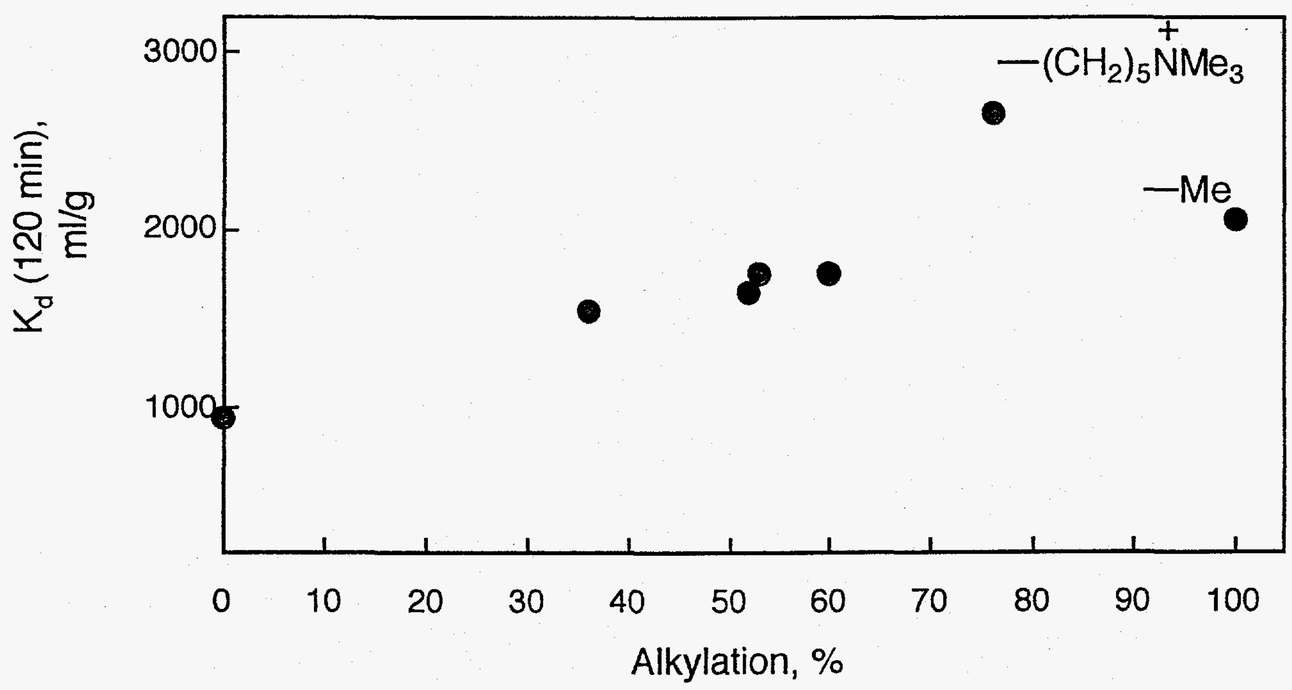
Measured K_d Values for Pu(IV) Sorption from 7 M Nitrice Acid by the Bifunctional Anion-Exchange Resin as a Function of the Spacer Length between the Two Anion-Exchange Sites

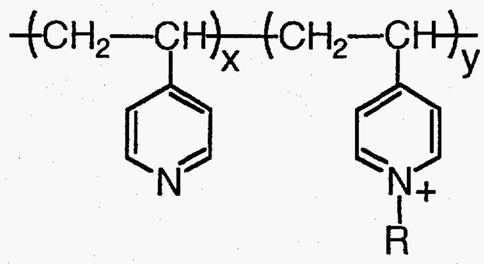
n	Alkylation, %	K_d (120 minutes), ml/g
3	66	1600
4	72	1650
5	77	2250
6	73	1800
4	76	1650
4 (cis)	78	1850
4 (trans)	73	1550



(18 % Crosslinked)

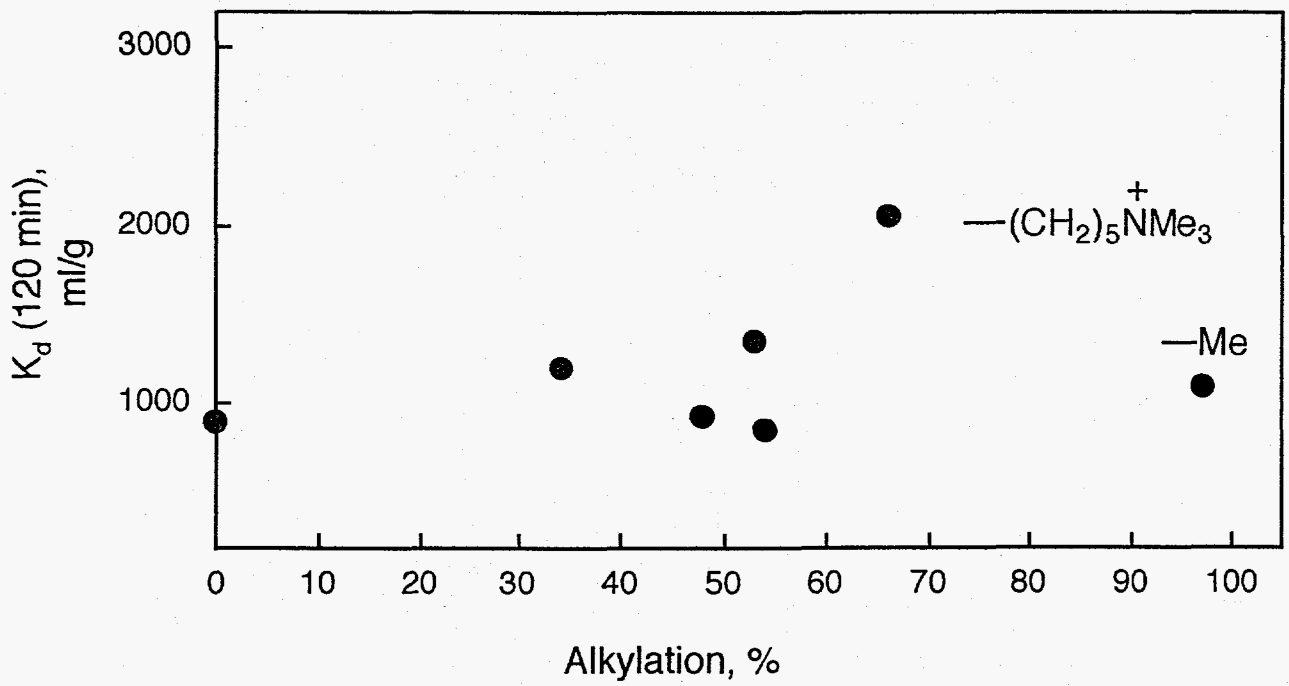
Comparison of Mono- and Bifunctional Anion-Exchange Resins for Sorption of Pu(IV) from 7 M Nitirc Acid as a Function of the Percent Alkylation



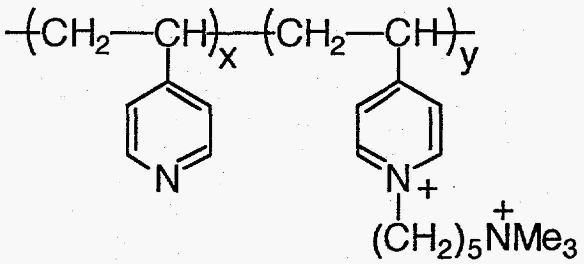


(21 % crosslinked)

Comparison of Mono- and Bifunctional Anion-Exchange Resins for Sorption of Pu(IV) from 7 M Nitric Acid as a Function of the Percent Alkylation.



Conclusions from the Study of Pu(IV) Sorption from 7 M Nitric Acid by Macroporous Anion-Exchange Resins

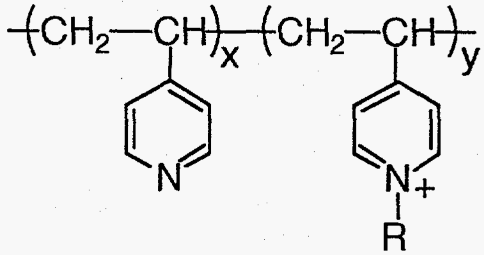


Level of Crosslinking

For these bifunctional anion-exchange resins, Pu(IV) sorption increases as the crosslinking level in the base resin decreases: 25 % < 21 % < 18 %. However the difference between the 18 % and 21 % crosslinked resins is offset by the greater physical strength of the latter. A 21 % crosslinking level is selected as optimal.

Level of Alkylation

For these bifunctional anion-exchange resins, Pu(IV) sorption is enhanced for higher alkylation levels of the 18 %, 21 %, and 25 % crossslinked base resins. The highest possible alkylation level is selected as optimal.



R

$-(CH_2)_n\overset{+}{N}Me_3$
(bifunctional)

$-Me$
(monofunctional)

Length of Spacer

For the bifunctional anion-exchange resins, Pu(IV) sorption is influenced by the number of methylene groups in the spacer. A five-carbon spacer ($n = 5$) is optimal.

Bifunctional vs. Monofunctional Anion-Exchange Resins

Bifunctional anion-exchange resins with $n = 5$ and high alkylation levels are significantly more efficient in Pu(IV) sorption than monofunctional anion-exchange resins with the same crosslinking level in the base resin. This difference is accentuated for 21 % crosslinked resins compared with 18 % crosslinked resins.

Acklnowledgement

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