

The influence of resin functional group on the ion-exchange recovery of uranium*

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SYNOPSIS

The selectivity of ion-exchange sites varies with the matrix of the polymer, the nature of the site, and the method of application. The effect of these variables on the recovery of uranium is examined, with particular attention to vinyl pyridine and to symmetrical and asymmetrical quaternary ammonium sites. The effect, on the loading, of high concentrations of chlorides in the liquors is discussed, and other components of the liquors that may cause fouling of the resin are also considered. The discussion is supported by the results of tests conducted on various types of resins.

The economics of the process is discussed briefly.

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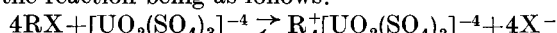
Die selektiwiteit van ionruilposisies wissel volgens die matriks van die polimeer, die aard van die posisie en die toepassingsmetode. Die uitwerking van hierdie veranderlikes op die herwinning van uraan word ondersoek met besondere aandag aan vinielpiridien en aan simmetriese en asimmetriese kwaternêre ammoniumposisies. Die uitwerking van hoë chloriedkonsentrasies in die vloeistowwe op die lading word bespreek en ander bestanddele van die vloeistowwe wat belemmering van die hars kan veroorsaak, word ook oorweeg. Die bespreking word gestaaf deur die resultate van toetse wat op verskillende soorte harse uitgevoer is.

Die ekonomie van die proses word kortliks bespreek.

Introduction

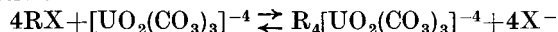
Uranium is found widely in igneous and sedimentary rocks, usually where faults and upheavals have occurred. It is extracted from these ores by leaching with an acid or an alkali, depending on the chemical demands of the minerals present with the uranium. Since the uranium content is fairly low even in rich ore (0,1 to 0,3 per cent), the uranium salts have to be concentrated and then freed from contaminants^{1, 2}.

Ion exchange received attention in the late 1940s as a valuable method for concentrating and purifying uranium. The process involved adsorption of the uranyl sulphate complex on a strongly basic anion-exchange resin, the reaction being as follows:



Uranyl sulphate can be stripped from the resin with nitrate, usually provided as an ammonium nitrate or magnesium nitrate solution. Chloride and sulphuric acid solution can also be used for the elution. When these steps are conducted properly, the concentration of uranium can be increased as much as a hundredfold by the ion-exchange step. Ionac A-580 (SK), a vinyl pyridine strong-base anion exchanger, was used in these early plants.

There are ores that cannot be processed by acid and require an alkaline leach. In these cases, the uranyl carbonate complexes are involved and follow the reaction



Elution is accomplished in the carbonate process with sodium chloride or ammonium nitrate. The exchange process concentrates the uranyl salts about fiftyfold and also accomplishes a considerable amount of purification.

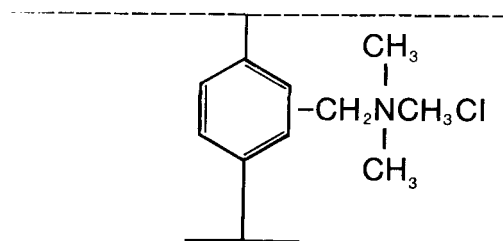
Since the stripping liquors tend to be recycled back into the process stream, there is a gradual increase in the nitrate, chloride, and sulphate contents of the pregnant loading solution. Control of these concentrations by bleeding off results in environmental problems.

Anion Exchangers

There are four types of anion exchangers available for the recovery of uranium. Three have been used commercially. Their chemical properties as related to the exchange sites are discussed below.

Strong-base Type I Resin

Strong-base Type I resin was used initially, when ion-exchange processes were developed for the recovery of uranium. The exchange properties of this resin are due to the symmetrical arrangement of side chains round the quaternary ammonium exchange site. This is illustrated as follows:



When this resin is hydrated, the resin holds about 50 per cent moisture, which depends on the degree of cross-linkage. Depending on the method of preparation, this copolymer is held together with divinyl-benzene cross-linkage or varying amounts of methylene bridging between aromatic rings. These links have a significant influence on the mechanical properties of the resin and also influence the rate of exchange, particularly for ions of large molecular mass like uranyl complexes. The availability of the site to perform exchange with certain ions of a particular geometrical shape (for example, chloride and nitrate) is particularly important. The

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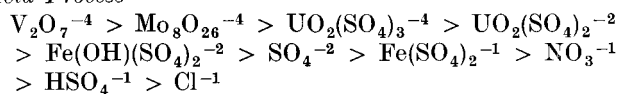
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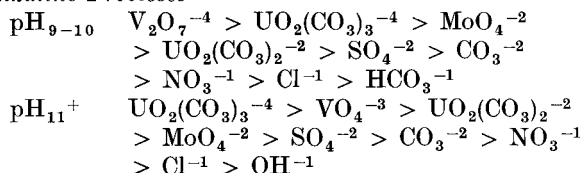
result of this interaction is an increased affinity for chlorides and nitrates, which reduces the tolerance of these resins for chloride and nitrate as compared with sulphate, bicarbonate, etc.

A typical affinity series is given below for acid and alkaline processes:

Acid Process



Alkaline Processes

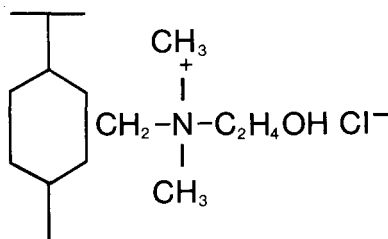


These series should be viewed as relative affinities in the sense that differences in concentration have a considerable influence. The concentration of sulphate and bisulphate in acid solutions is of direct significance, bisulphate being a major component at low pH values. The alkaline processes give different affinity series depending on pH. At high pH values, the concentration of carbonate becomes a substantial factor and the affinity becomes greatly influenced by the concentration of major components. This is also true of the concentration of uranium as compared with that of the other components.

The uranium is stripped from the exchanger by a liquor that is compatible with subsequent precipitation procedures. Usually 1M or 2M nitrate, chloride, carbonate, or sulphuric acid is used to displace the uranium complex. The shape of the stripping curve depends on particle size, resin type, degree of porosity, gel moisture, and stripping agent used. The peak concentration is a measure of the ability of uranyl complexes, which have large molecular masses, to diffuse from the resin particle.

Strong-base Type II Resins

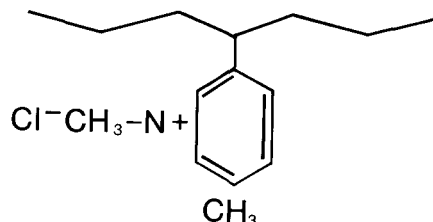
Strong-base Type II resin has received attention because of its reduced selectivity for chloride and nitrate compared with the Type I resins. The exchange site is very similar to that of Type I, except for a change in symmetry by substitution of an ethanolic group for one of the methyl groups. This is shown in the following illustration:



The affinity series for Type II strong-base resins is fairly similar to that for Type I, except that the differences between members of the series are less pronounced. The affinity for chlorides and nitrates is considerably less than for Type I. This has been recognized as a possible advantage when uranium is being removed from liquors having substantial concentrations of chlorides.

Vinyl Pyridine Strong-base Resin

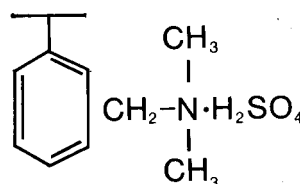
Vinyl pyridine strong-base resins are based on aromatic rings containing nitrogen, and are quaternized. The pyridine resins illustrate a distinctly different type of grouping, still of the strongly basic class but with functional groups having considerable structural availability. The structural formula for a typical pyridine strong-base resin is given as follows:



This resin has affinity series similar to those of the other strong-base resins, but the increased availability of the functional group makes the stripping particularly efficient with nitrates. Stripping agents containing chlorides show substantial efficiency as compared with the values obtained for other strong-base resins. Sulphates and carbonate strip in a manner similar to that for other strong-base resins.

Weak-base Resins

Weak-base resins (styrene-DVB macroporous, such as Ionac AFP-329) have been used in a few field installations. They are effective in operations in which sulphuric acid leaching is used. While these resins have a selectivity somewhat similar to that of the Type I and Type II strong-base resins, their functionality is not as pronounced and is less than that of Type II, except for alkaline conditions, in which the stripping is very effective. Once the resin has been converted to the free-base form, the exchanger has no capacity if the influent is not acidic. The nature of the functional group is as follows:



Typical operating results on a weakly basic anion exchanger used for the recovery of uranium are given in another section of this paper. The overall results of tests with these resins indicated somewhat slower stripping than with the highly ionized strong-base resins.

Other weak-base resins that have been used in the past with varying degrees of success in plant and pilot-plant operations include vinyl pyridine-DVB beads (e.g., Ionac P-901), condensation-type polyamines (e.g., Ionac A-305), and cross-linked acrylic polyamides (e.g., Ionac A-365).

Physical Factors

Initially ion-exchange resins were used in fixed beds. For these columns, the resins were required to have a size distribution ranging between 16 and 50 mesh. Relative density was not a critical variable, and the

resins were required only to be dense enough to permit a normal flow-rate of 2 to 4 gal/min/ft³ during backwashing. Ease of stripping became an important measure of the suitability of the resin for the recovery of uranium.

Modern contactors have been designed for the processing of unclarified liquors. This has substantially changed the requirements upon which resin specifications are based. First, the units are usually operated with upflow while the resin is held in the flowing stream by hydraulic considerations or by retention screens. In other cases, the resins are held for periods of time on plates in the columns. These various requirements have placed the emphasis on particle size, relative density, good kinetics, and efficient stripping.

Relative Density

The difference in density between the particle of resin and the flowing liquor is an important value for upflow operation. While small differences can be counteracted to some degree by the adjustment of particle sizes, very large beads are not easily available and serious rate losses can be experienced when they are used. Table I gives a summary of the relative densities of some typical resins.

TABLE I
RELATIVE DENSITIES OF VARIOUS ANION EXCHANGERS

Type of resin	Relative density			
	Cl	SO ₄	UO ₂ (CO ₃) ₃	UO ₂ (SO ₄) ₃
Type I gel	1,12	1,19	1,29	1,28
Type I macroporous	1,09	1,16	1,28	1,28
Type II gel	1,12	1,19	1,30	1,30
Type II macroporous	1,10	1,17	1,27	1,28
Vinyl pyridine gel	1,12	1,19	1,31	1,31
Weak base	1,10*	1,18	†	1,33

*Refers to the free-base form; other values for this resin represent acid forms.

†A carbonate complex is not possible in these resins.

The bed expansion for the various resins under consideration follow correlations summarized by Leva³. The flow for initial bed expansion is a function of void volume, particle size, fluid density, gravity differential, and fluid viscosity. Once this relationship has been established, the actual slope of the expansion line can be calculated by the method developed by Richardson and Zaki⁴. Fig. 1 shows typical curves for a resin with coarse particles. The breaks at about 15 gal/min/ft² show the difficulty in retaining beds when they are expanded more than 100 per cent. As the bed approaches transport, the particle distribution plays an important role in the details of the expansion curve.

Macroporous ion-exchange resins of high capacity are employed because of their higher resistance to attrition compared with gels. Anion exchangers that have a small amount of resilience during impact are particularly suitable when used in equipment that subjects the resins to stress. Fig. 2 shows the results of pumping tests on gel and macroporous resins. In these tests, the resin is pumped round at a rapid rate through a pump that has plastic impellers and housing to minimize external damage (unrelated to in-use conditions). While the

results must be compared in a relative fashion, they have been supported in field installations.

Another test commonly used employs Chatillon compressive loading with individual beads. Table II gives a summary of such tests as a function of particle size for Ionac URA-260. Again, these results show that a small amount of plasticity in the beads greatly influences the test results. With good, whole beads, the bead strength is directly proportional to the diameter, as shown in Fig. 3.

Uranium Loading

The four types of resin all have a good loading capacity for uranium. The best resins permit efficient stripping

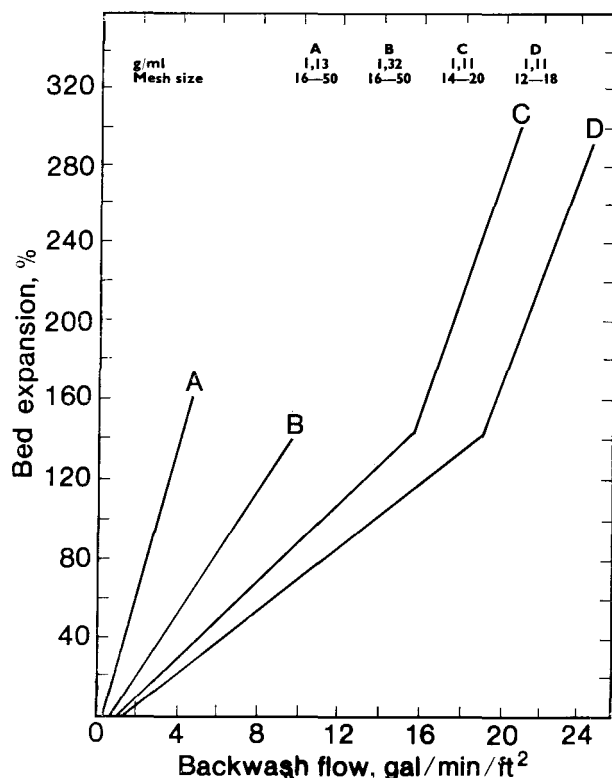


Fig. 1—Expansion of beds of Ionac ASB-I and Ionac URA-260—Cl-[UO₂(SO₄)₃]⁻⁴ form—of various particle sizes

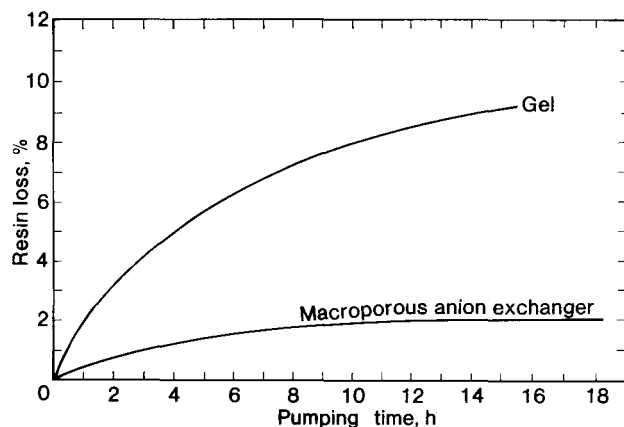


Fig. 2—Comparison of gel and macroporous anion exchangers undergoing pumping attrition

TABLE II
MECHANICAL STRENGTH TESTS ON IONAC URA-260 MACROPOROUS ANION EXCHANGER

Screen size mesh	Average diameter mm	Cross-sectional area mm ²	Mechanical strength g/bed
-10+12	1,84	2,65	921 ± 135
-12+14	1,54	1,86	825 ± 325
-14+16	1,30	1,32	614 ± 123
-16+18	1,10	0,95	506 ± 54
-18+20	0,92	0,66	461 ± 30
-20+30	0,72	0,41	238 ± 80

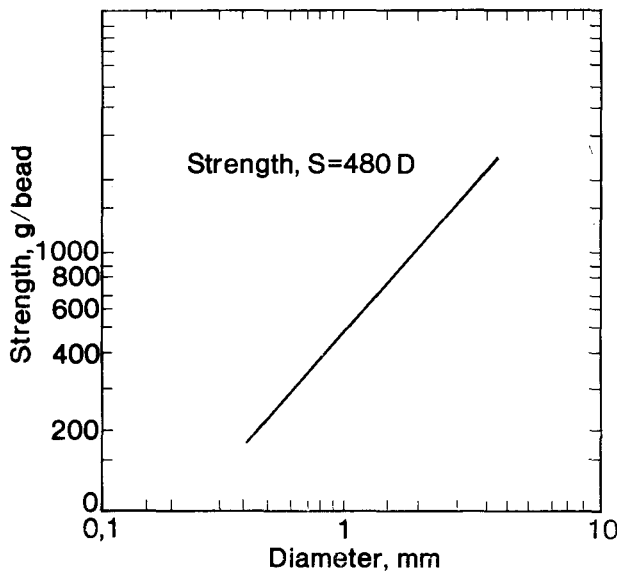


Fig. 3—Chatillon measurements on Ionac URA-260

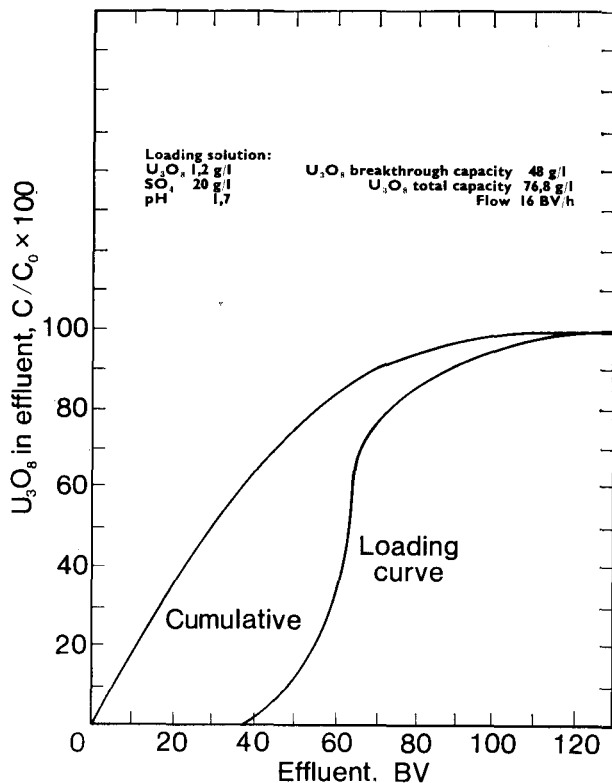


Fig. 4—Loading curve for Ionac URA-260 — uranyl sulphate complex

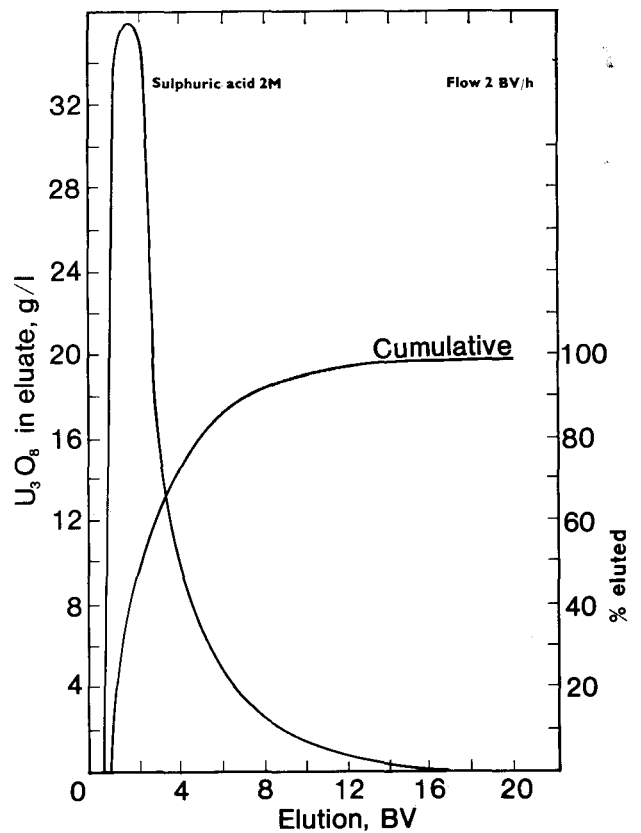


Fig. 5—Elution of Ionac URA-260 with sulphuric acid

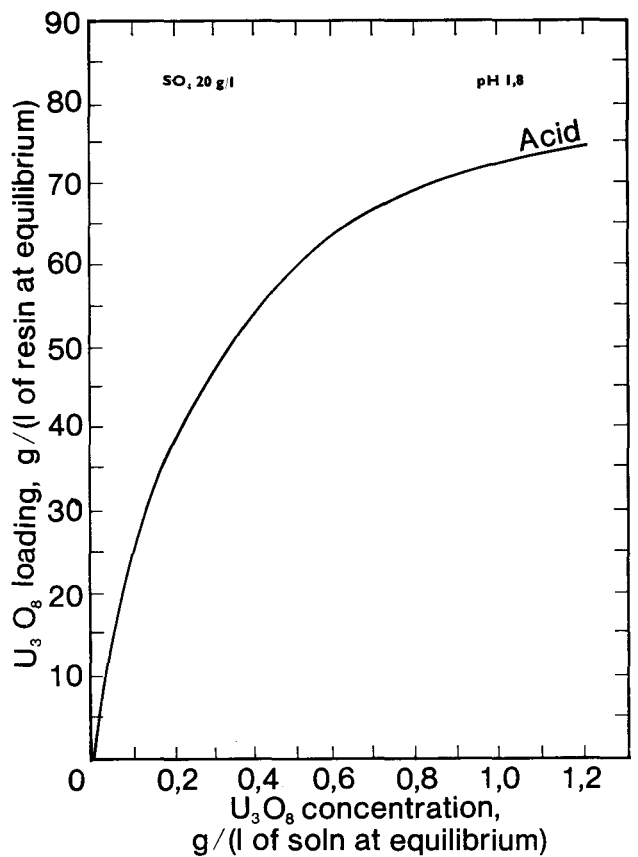


Fig. 6—Equilibrium curve for Type I resin — uranyl sulphate complex (after Hollis and McArthur⁶)

under the proper operating conditions. This section illustrates the results of tests on carbonate and sulphuric acid liquors, and liquors with high chloride contents. The liquors used were both synthetic laboratory preparations and typical mine liquors. The analysis for uranium was done by the bromo-PADAP method⁵. On the graphs, U_3O_8 in the effluent is expressed as a percentage of the initial U_3O_8 concentration, i.e., $C/C_0 \times 100$.

Acid Leach Liquor

These studies were conducted on a typical acid mine liquor with a high uranium grade. The results are shown in Figs. 4 and 5 for a macroporous Type I strong-base resin, Ionac URA-260. As shown, a typical gel resin loaded about 10 per cent higher but stripped less efficiently. The loading is not far from the equilibrium relationship found for resins of this type with similar background concentration (Fig. 6).

A Type II strong-base resin, Ionac A-651, gave similar results to those given by the Type I resin but with less efficient stripping. This resin was studied only in alkaline systems for high chloride liquors, but a programme of tests on acid-leaching systems is under way and should be completed in the near future.

The vinyl pyridine resin was studied extensively in the acid cycle⁶. Nitrate was found to be particularly efficient. Typical loading and elution curves are given in Figs. 7 and 8 for Ionac A-580, and show that nitrate anion has a significant effect on the function of the pyridine exchange site.

The weakly basic group has a similar attraction for nitrate as can be seen in Figs. 9 and 10⁸. The effect of nitrate as compared with that of chloride is almost

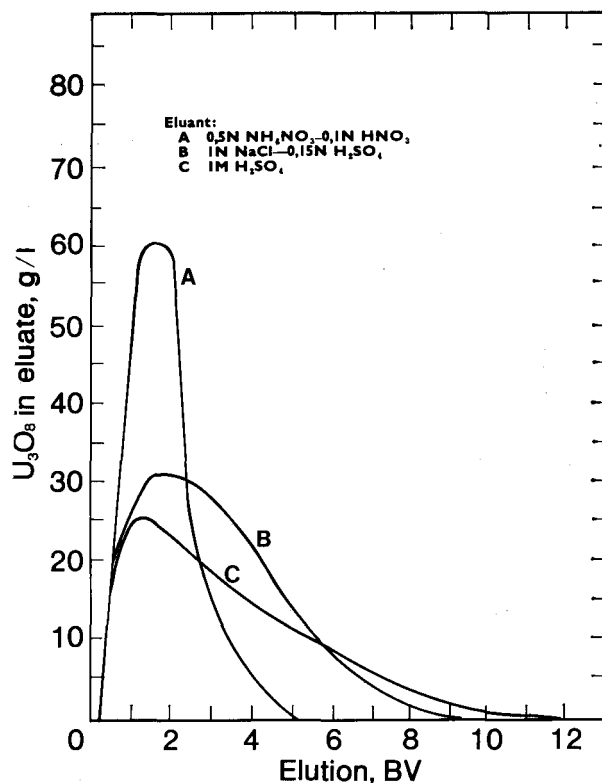


Fig. 8—Stripping form vinyl pyridine Ionac A-580 acid cycle (after Greer et al.⁷)

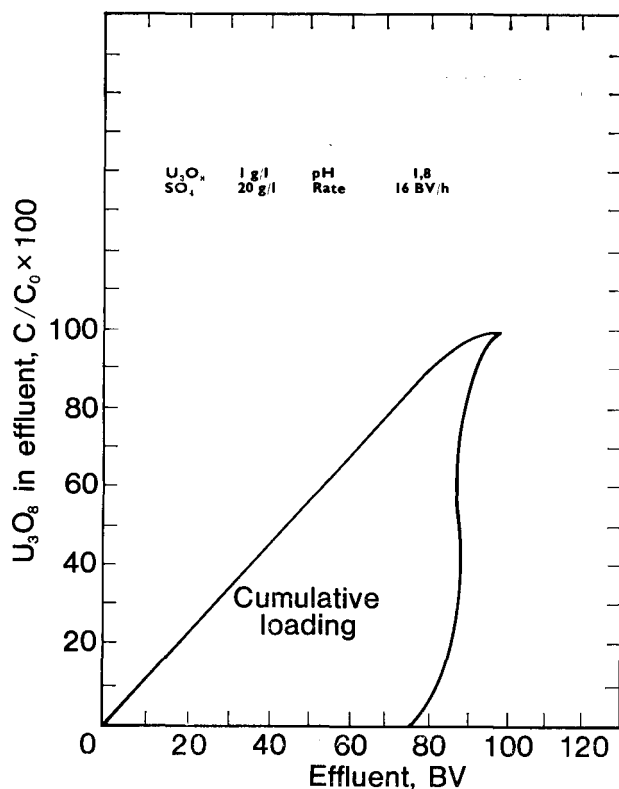


Fig. 7—Typical loading curve for Ionac A-580 (after Greer et al.⁷)

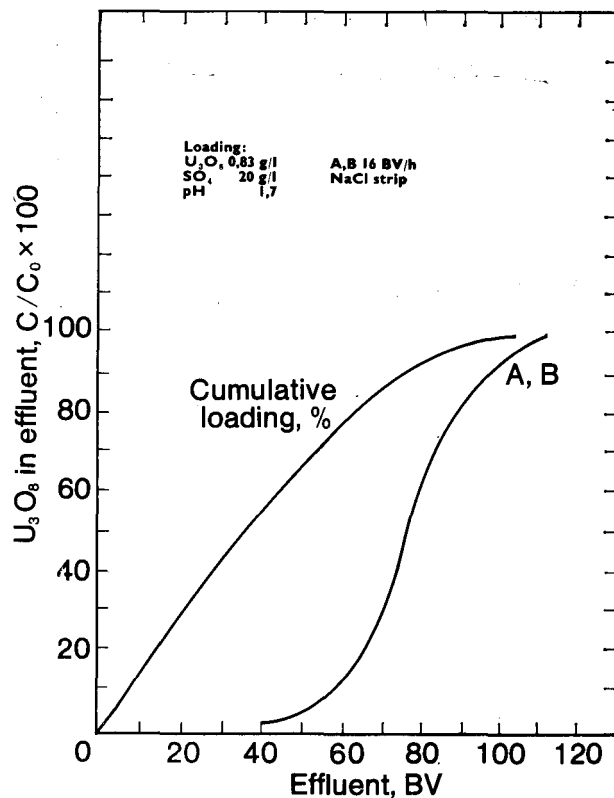


Fig. 9—Loading of a weakly basic anion exchanger (after Kunin et al.⁸)

double from the standpoint of elution peak. The use of sulphuric acid as a stripping agent is even less efficient in these resins but still remains economically rewarding in some cases.

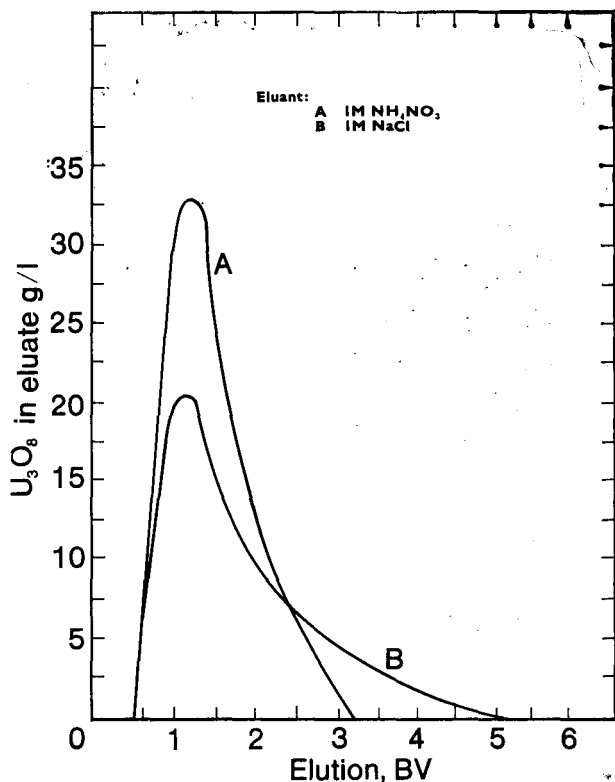


Fig. 10—Elution of a weakly basic anion exchanger

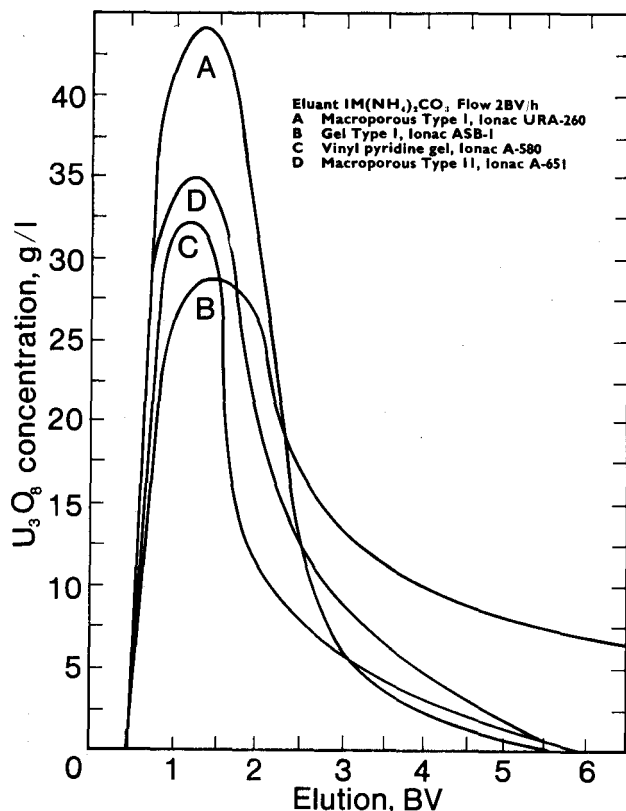


Fig. 11—Comparison of elution volumes

Carbonate Leach Liquor

Similar studies were carried out with alkaline leach liquors using ammonium carbonate for stripping. Since carbonate liquors contain no iron complexes, the competition for the sites is less. The loading is somewhat confused by the presence of divalent carbonates as well as $[\text{UO}_2(\text{CO}_3)_3]^{-4}$. Where the carbonate content is fairly low, very high loadings were measured, and in some cases even uranium was precipitated in the resins, which resulted in difficult stripping.

Type I strong-base resins were loaded rather similarly to their loading in the acid runs. However, there were substantial differences in stripping, as shown in Fig. 11. These results indicate that diffusion in the gel phase controls the stripping. A highly cross-linked gel tends to strip poorly owing to the slow diffusion of the uranyl complexes, which are of large molecular mass. The high-capacity macroporous resins are much faster owing to diffusion into pores in which there is liquid diffusion. Naturally, these pores must be carefully sized so that silica and other precipitates do not accumulate there, thus greatly reducing the rate of diffusion for the uranyl complexes and other stripping chemicals.

Carbonate Leach Liquor with Chloride Elution

When resins loaded with uranium from carbonate leach liquors are stripped with chloride, the tendency to build up chlorides in the mill liquor becomes a real problem. Type I strong-base resins and vinyl pyridine resins both show extensive sensitivity to increased chloride levels. Figs. 12 and 13 show loading and stripping curves for Type I, Type II, and vinyl pyridine

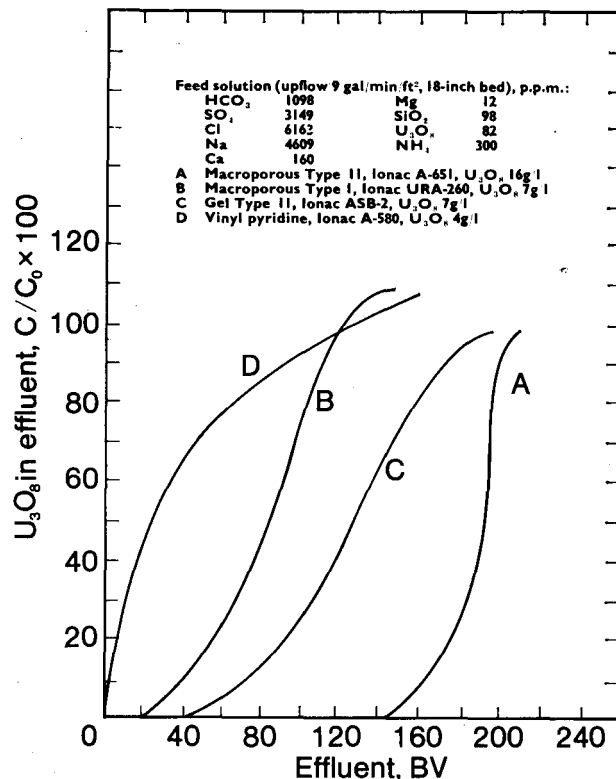


Fig. 12—Loading from liquors containing 6100 p.p.m. of chloride

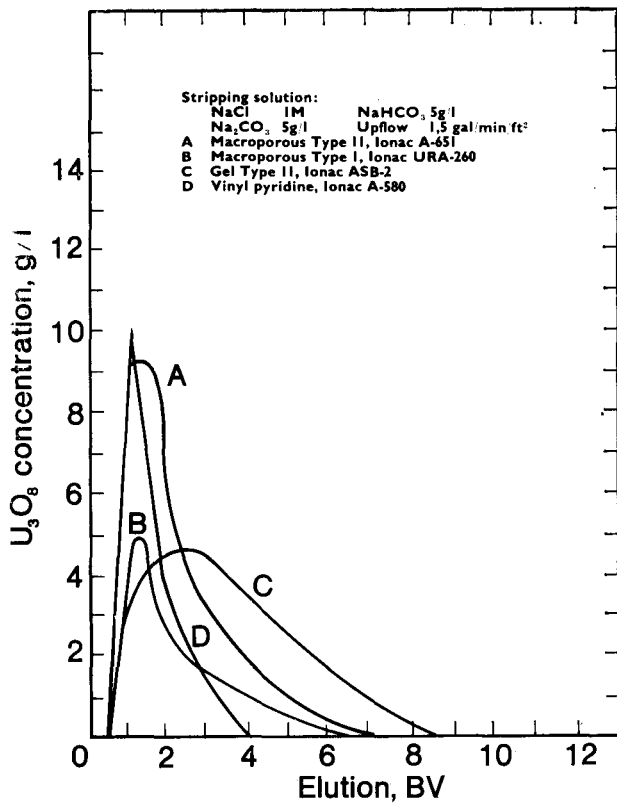


Fig. 13—Elution of loading solutions containing 6100 p.p.m. of chloride

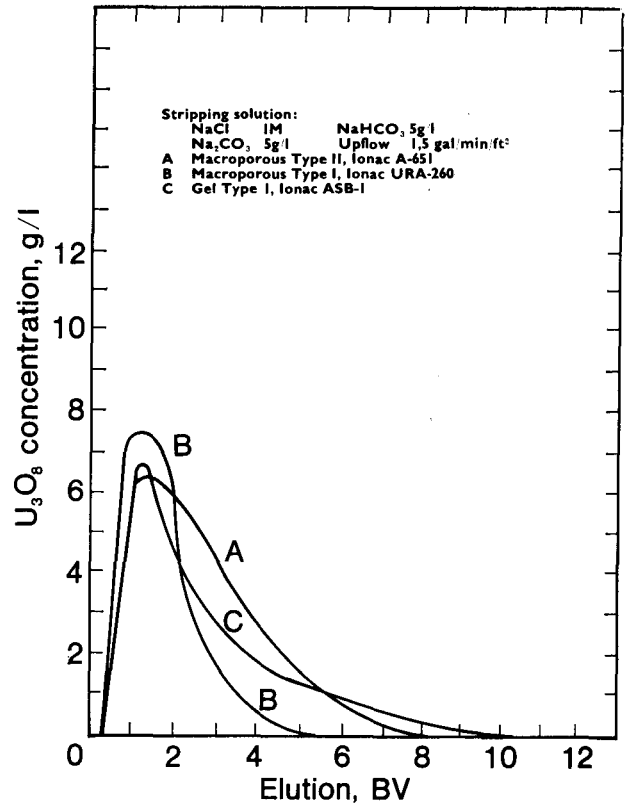


Fig. 15—Elution of loading solutions containing sea-water concentrations of chloride

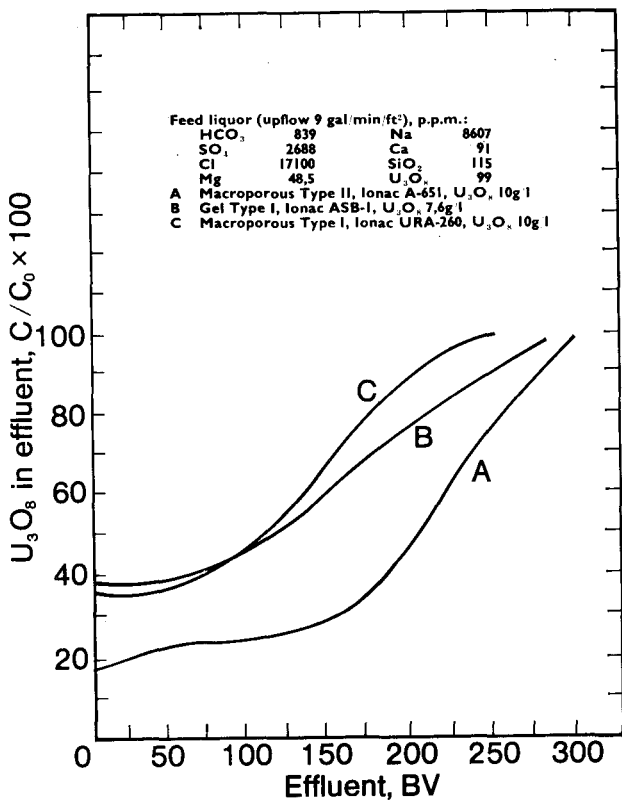


Fig. 14—Loading from liquors with sea-water concentrations of chloride

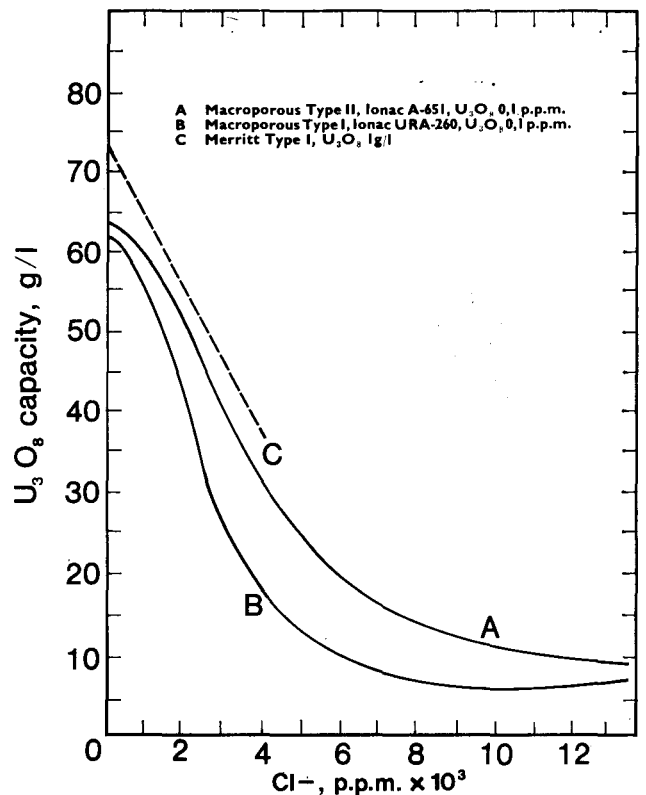


Fig. 16—Summary of capacity data on liquors high in chloride

resins when the liquors have 6000 to 7000 p.p.m. of chloride. The study was extended to resin performance when sea-water concentrations of chloride (17000 p.p.m.) were used. Figs. 14 and 15 show the loading and stripping curves for these resins. Fig. 16 summarizes the effect of chloride for Type I and Type II anion exchangers.

Economics

The costs of recovering uranium on ion-exchange resins depend on the elution process, the method of precipitation, and the various options related to pollution control. In addition, the rate of resin replacement becomes an increasingly important factor. Initially, resin losses due to fouling and attrition were very dependent on the nature of the pregnant liquor. In South Africa fouling by cobalt was a major factor, while in Canada fouling by metals was unknown and only silica fouling was considered. In the U.S.A., some difficulties were experienced from fouling by molybdenum and silica. Most of these mechanical fouling problems were solved by chemical treatment. Fixed-bed attrition rates were very low, less than 3 per cent per year.

Since some 35 per cent of plant costs is in the clarification steps, the use of various countercurrent processes has come into being. These processes can tolerate substantial amounts of slimes, but they are dependent on resin of large particle sizes. Under good conditions, these units replace resin through attrition and carryover at the rate of about 30 to 50 per cent per year, with some plants reaching 200 per cent per year. These losses are counterbalanced by the cost of clarification.

In a simple case, a plant costing 25 million U.S. dollars would require an additional 8 to 9 million dollars for clarification processes. If the costs of fixed-bed and fluidized-bed equipment are the same, the saving becomes largely the investment value of 8 to 9 million dollars not employed. At an annual interest rate of 10 per cent, a saving of 800 000 to 900 000 dollars per year can be visualized if various tax situations and other loan conditions are ignored.

A plant processing 3000 t/d requires about 1500 ft³ of resin, valued at \$125 per cubic foot. This amounts to

some \$200 000. A good case can be made for the use of a process that has a high attrition rate, but experience shows that an annual replacement rate of more than 100 per cent is difficult to justify. Variations in plant capacity and shutdown rapidly reduce the apparent economic advantage.

Summary

The functional groups and the resin matrix have a substantial influence on the performance of ion-exchange resins for the recovery of uranium. The porosity of the gel structure plays an important role in stripping processes, but the use of this variable is restricted by the tendency of the resin to become fouled with silica. The Type I strong-base resin remains the most widely useful resin, while its Type II adduct is interesting in cases where high concentrations of chlorides and nitrates are involved. Continued development work in this area is needed before Type II strong-base resins can be used effectively in the recovery of uranium. The trend toward the control of plant wastes and the development of plants near ore-bodies where water low in solids is not available, will be projects deserving a full study of unique ion-exchange sites.

Acknowledgements

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Sheet metal forming

An International Symposium on New Aspects on Sheet Metal Forming will be held in Tokyo on 14th and 15th May, 1981. The Symposium, organized by The Iron and Steel Institute of Japan and The Japan Sheet Metal Forming Research Group, will re-examine important problems in sheet-metal formability and forming techniques resulting from the increasing demands for energy saving, and will try to find the most favourable approach to expected problems in sheet-metal forming processes. The official language of the symposium is

English.

The programme will cover as much as possible of new aspects of sheet-metal forming including formability, forming severity, and ductility service behaviour, and the properties of sheet-metal surfaces.

Further information is obtainable from The Symposium Secretariat, NASMF 1981, The Iron and Steel Institute of Japan, Keidanren Kaikan 3rd Floor, Otemachi 1-9-4, Chiyoda-ku, Tokyo 100, Japan (telephone: 03-279-6021, telex: 02228153 ISIJTK J).