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ION EXCHANGE TECHNOLOGY IN THE NUCLEAR FUEL CYCLE

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FOREWORD

Since the dawn of the nuclear energy development, the ion exchange process has been used as a key technology for the production of nuclear materials. Nuclear grade uranium and ultra-pure water required in the nuclear industry have become technically available by use of ion exchange technology. The application of ion exchange has recently been expanded to various parts of the nuclear fuel cycle. Major applications are:

- in uranium production facilities; concentration of uranium from leach solution, refining of uranium, recovery of uranium from various sources, etc.

- in nuclear power plants; chemical controls of coolant water, e.g. controls of pH and boron concentration, condensate polishing, quality control of water in spent fuel storage pools etc.

- in spent fuel reprocessing and waste treatment; separation of uranium and plutonium and their purificaton, separation of transplutonium, removal of actinides and specific isotopes from radioactive wastes etc.

Furthermore, application to isotope separation has been under development. Special enrichment technology applicable only for the production of commercial-purpose uranium fuel has been intensively studied by using ion exchange resins, and recently regarded as quite promising. The enrichment of ^{10}B, which is used as the neutron absorption material, is another promising field of ion exchange application.

The ion exchange process is well established for water treatment and incorporated in most industrial plants using pure water. Efforts have constantly continued to expand its application to various fields in the separation and controlling of chemical substances. Numerous technical papers have been reported on scientific and engineering aspects of ion exchange. A number of scientific books on the general uses of ion exchange have been published in different languages. Information on the nuclear application of ion exchange has been dispersed among these numerous publications. For the recent needs of the information of this kind, this technical document was planned to describe state-of-the-art of the ion exchange technology applied to the processes in the nuclear fuel cycle. It is hoped that this document would be useful not only for the specialists who are working in the field of ion exchange or nuclear chemical engineering, but also those who are concerned with various fields of the nuclear industry.

The Agency wishes to thank all the authors who contributed to this document: Ms. S. Fisher (USA), Mr. F. X. McGarvey (USA), Mr. A. Himsley (USA), Mr. J. D. Navratil (USA), Mr. I. Dobrevsky (Bulgaria), Mr. B. Czeglédi (Hungary) and Messrs. Y. Fujii, M. Okamoto and M. Kakihana (Japan). Special thanks are due to the ion exchange resin manufacturers listed in Appendix 2 for providing their resin data.

The officer of the Agency responsible for editing and finalizing the document was M. Ugajin of the Division of Nuclear Fuel Cycle. His predecessor, Mr. Y. Fujii, one of the authors of this document, began this task by organizing the initial series of Consultant Meetings.

EDITORIAL NOTE

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INTRODUCTION

Ion exchange is the reversible exchange of ions between a solid and a liquid in which there is no change in the structure of the ion exchange material.

Ion exchange technology has been widely applied to numerous processes used in the nuclear fuel cycle. Ion exchange has been used for:

1) Concentration and purification processes in uranium mills and refining facilities.
2) Fuel fabricatiopn scrap recycle.
3) Spent fuel reprocessing operations.
4) Treatment of radioactive wastes.
5) Coolant purification and pH control and boron control in reactors, and many others including stable isotope separation.

Application and development of ion exchange technology has constantly continued in the field. Furthermore, significant improvements are being made of its use in the separation of materials and in various process operations.

There have been a number of scientific publications on fundamental aspects of ion exchange processes and the specific applications of ion exchange in uranium production and other nuclear fuel cycle steps, many of which are either too academic or too specialized for general use. A general book on ion exchange processes applied to the nuclear fuel cycle has not previously been published. It is hoped that this technical document will fill that gap and assist a larger group of people dealing with the nuclear fuel cycle to better understand the processes. The expected users of this document include:

- experts on specific ion exchange processes in the nuclear fuel cycle;

- industrial engineers dealing with the general ion exchange processes;

- ion exchange resin manufacturers;

- students of nuclear chemistry and chemical engineering;

- nuclear development and nuclear fuel facilities planners.

The technical document is designed to be a guidebook or source book for ready reference containing the following scientific and engineering topics:

- implemented ion exchange processes in the nuclear fuel cycle;

- recent developments in the field;

- general scientific descriptions on ion exchange resins and ion exchange reactions;

- general engineering descriptions on ion exchange equipment;

- glossary of relevant technical terms;

- tables and specifications of ion exchange resins commercially available;

- necessary descriptions of uranium chemistry.

The chapters cover each major nuclear fuel cycle step, e.g. uranium milling, reactors and reprocessing. Analytical application of ion exchange is also important for the producition of nuclear fuel. Unfortunately there are many forms of analytical application and because of its vastness this subject is not included in this publication.

CHAPTER 1

ION EXCHANGE MATERIALS USED IN NUCLEAR TECHNOLOGY

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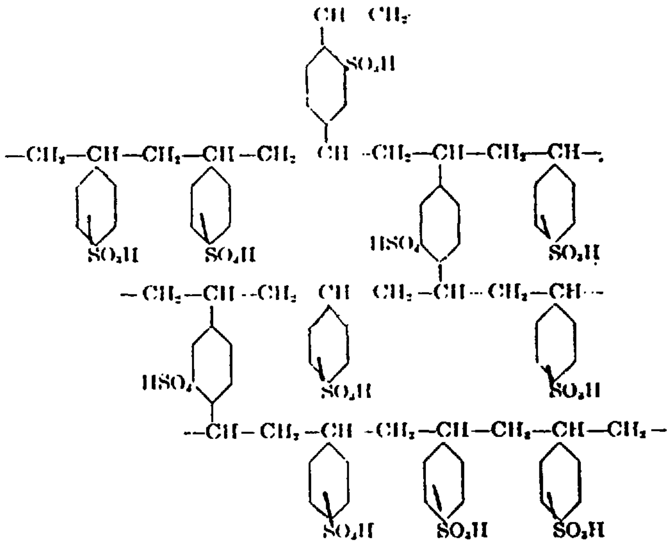
Abstract

Ion exchange materials make a dual and vital contribution to nuclear technology. From the beginning, ion exchange materials, both bead-form and liquid, played major roles in the recovery of high purity uranium from complex uranium-bearing deposits. Subsequently the development of nuclear power systems expanded the need for ion exchange processes to purify and repurify water for both steam generation and cooling and to provide a concentration process for radioactive waste from aqueous systems. As a result, a broad spectrum of resin types are now used in some aspect of nuclear technology. Indeed, without ion exchange materials power generation via nuclear technology would be impossible.

The majority of cation resins used in nuclear applications are sulfonated styrene-divinylbenzene polymers generally called nuclear sulfonic acid resins. However, methylene sulfonic acid resins are used in the treatment of some radioactive waste streams and carboxylic acid polymers based on either crosslinked methacrylic or acrylic acid polymers are used in some specialized applications in the nuclear industry.

SULFONATED STYRENE-DIVINYLBENZENE POLYMERS

Sulfonated styrene-divinylbenzene copolymers used in the nuclear industry are normally split into two broad catagories: gels and macroporous. The distinction between the two is based on the structure of the copolymer bead rather than the functionality. Both types of resins have as their exchange functionality a sulfonic group substituted directly on a six-membered unsaturated ring as an appendage to or a crosslink between two linear saturated methylene chains. This produces a three-dimensional network of the following structure:



The differences in the two polymer types arise from the solutions of monomers assembled for the bead making process. Gel structures are usually produced following the teaching of d'Alelio (1,2) wherein a mixture containing only styrene, divinylbenzene and a catalyst is suspended as droplets in a medium in which it is not soluble and heated to form solid copolymer beads.

Macroporous beads are formed when a component that does not enter into the polymerization is added to the styrene and divinylbenzene prior to the formation of the suspension of droplets. Usually a third component is chosen that is miscible with the monomers but not a solvent or swelling agent for the polymer. This process forms a finished bead, aptly described by Corte and Meyer (3) as 'sponge-like', consisting of highly crosslinked microgel polymer containing large macropores filled with the non-polymerizable third component. This component is sometimes described as having been squeezed out of the polymer as it formed but in actuality the polymer precipitates from it.

Patents have been issued covering a number of variations of the macroporous process. Those of Millar (4), Werotte and Grammont (5), Mindick and Svarz (6) and Meitzner and Oline (7) represent a sampling using a variety of starting combinations. By varying the third component, its ratio to the polymerizing monomers and their ratio to each other almost an infinite range of physical properties in the sulfonated polymer is possible. However, the basic chemical structure is the same as that of the gel polymers. Further, the polymer itself is a gel with the same characteristics as a bead prepared at an equivalent degree of crosslinking. It differs from the so-called gel bead primarily because the solution being treated permeates the macropores so that the ratio of surface to polymer is substantially larger.

GEL SULFONIC ACID RESINS

Nuclear sulfonic acid gel resins that are fully sulfonated differ from each other in their degree of crosslinking. This is primarily a function of the ratio of divinylbenzene to other monomers, such as styrene and ethylvinylbenzene, in the original monomer mixture. Other factors such as the amount of catalyst used, rate of polymerization,the thermal pattern during the polymerization, all modify the properties of the final polymer slightly. The type of sulfonating agent and the sulfonation temperature also have some effect. But these changes usually produce differences smaller than those encountered in routine replication of a given monomer ratio in commerical production of these resins.

For the user, the water retention capacity of the finished polymer in a known ionic form is the most convenient parameter for estimating the crosslinking of a gel sulfonic acid resin. Standard methodology for measuring this parameter has been developed in the United States in the ASTM system (8).

This methodology produces numbers which correlate so well with those published by manufacturers in other countries for materials described as having the same degree of crosslinking, that one must conclude similar methodology is universally used.

Although polymers prepared under research conditions will show a slightly higher capacity at low degrees of crosslinking, commercial polymers used in the nuclear industry all have a dry weight capacity in the hydrogen form very close to 5.0 milliequivalents per dry gram. All of their other properties: volume capacity, hydrated bead density, selectivity, stability, are functions of the degree of crosslinking in the polymer.

Variation of Properties with Crosslinkage

Many, many workers have published articles relating the properties of sulfonated styrene-divinylbenzene polymers with the divinylbenzene content. In some cases major differences exist between the values reported. These differences often reflect the fact that one or both investigators were working with commercial polymers and, hence, did not really know what the true divinylbenzene contents of their materials were. In other instances the polymers used were not fully sulfonated or may have been decrosslinked in the sulfonation process. Even more often the difficulties of producing a pure ionic form were not clearly understood and, hence, measurements were made on polymers only partially in the intended ionic form. These uncertainties are compounded by the fact that the methods of producing and analyzing divinylbenzene have improved markedly in the last forty years. A true 10% divinylbenzene copolymer prepared today contains a different spectrum of monomers than one produced in the middle 1940's.

However, the correlation of resin properties with crosslinkage in the sulfonic system is a very useful approach to predicting their performance. More reliable, perhaps, than using their nominal divinylbenzene content, which is difficult to measure in the final product, is the use of the water retention capacity in a known form. This parameter can be easily and reproducibly measured (8).

The correlation of selected properties with nominal divinylbenzene content and water retention is given in Table 1. Volume capacities assume that an equivalent bead size distribution has been produced at each level of crosslinkage. It will be noted that the implied precision of the numbers given is much less than those normally seen in the literature. The variation in normal commercial production of a polymer at any given nominal divinylbenzene content will produce a ±5% variation in the values selected.

Table 1

Effect of Crosslinkage on the Properties of Sulfonated Styrene-Divinylbenzene Copolymers in the Hydrogen Form (a)

Nominal % Divinylbenzene	% H_2O Retained$^{(b)}$	Volume Capacity$^{(b)}$ meq/ml	Hydrated Bead Density$^{(c)}$
2	80	0.7	1.09
4	68	1.1	1.13
6	57	1.6	1.16
8	53	1.8	1.19
10	47	2.0	1.22
12	44	2.1	1.24
16	39	2.3	1.28

(a) A composite of data by Reichenberg, Pepper, McCauley and Hale (9, 10); Glueckauf (11) and data from commercial materials accumulated by the author

(b) ASTM Method D2187 (8)

(c) Method of Kunin and Fisher (12)

This variation is illustrated by the data in Table 2. Here data from polymers of the two most commonly encountered crosslinkages from United States suppliers have been tabulated. These data are not production control data but the results of analyses of lots shipped to plant sites. The data were collected over a three year period and represent a minimum of 10 shipments from each source. As may be seen, not only are resins claiming the same nominal percentage divinylbenzene different when procured from different sources but the variation from a single source may in some cases be even greater. The nominal DVB content is based on calculated charge values so that part of the difference is due to the precision of material measurement.

Table 2

Comparison of the Properties of New Sulfonic Cation Resins from Different Producers (13)

Source	8% Gel Type		10% Gel Type		
	A	B	F	G	H
Water Retention, % (a)					
Sodium Form					
High	48.90	48.40	40.60	45.58	40.76
Low	45.77	44.83	39.44	40.72	39.86
Average	47.13	46.99	40.41	42.40	40.33
Hydrogen Form					
High	56.73	56.32	48.45	51.82	46.95
Low	52.69	52.58	46.15	48.07	46.03
Average	54.30	53.80	47.32	49.49	46.73
Exchange Capcity, H-form (a)					
meq/g dry					
High	5.10	5.11	5.16	5.10	4.95
Low	5.04	4.87	5.04	4.79	4.77
meq/ml					
High	1.88	1.87	2.12	2.06	2.09
Low	1.70	1.55	2.01	1.75	1.97
Average	1.81	1.72	2.08	1.91	2.00

(a) ASTM Method D2187 (8)

All of the properties in Table 1 are also a function of ionic form. The dependence of just one of them, water retention capacity, is shown in the data in Table 3. That the measured water retention capacity changes dramatically when one ion is substituted for another emphasizes the necessity for knowing the ionic form when polymer properties are measured.

Other properties are similarly dependent on ionic form. Bead density, for example, increases as water retention decreases. The exchange capacity per gram decreases as heavier ions are substituted into the polymer.

If the water content is calculated in a more fundamental manner as millimoles of water per milliequivalent of capacity, the water content of ionic forms from potassium down becomes a constant for a given crosslinkage. The higher values for the lighter elements indicate that the polymer matrix swells when converted, say, from the potassium to the hydrogen form. This swelling results in a decrease in the volume capacity during the transition.

Table 3

Effect of Ionic Form on the Water Retention Capacity of Sulfonic Cation Exchange Resins

	Exchange Capacity meq/g dry	% Water Retained[a]			Millimoles H_2O/Milliequivalent		
Nominal % DVB		4	8	16	4	8	16
Ionic Form							
Lithium	4.85	67.0	50.7	38.8	23.2	11.8	7.2
Hydrogen	5.00	68.3	50.0	40.5	23.9	11.1	7.6
Sodium	4.50	62.8	45.2	33.7	20.8	10.2	6.2
Ammonium	4.60	52.4	44.1	32.7	20.0	9.5	6.1
Potassium	4.20	58.9	40.6	31.7	18.9	9.0	6.1
Rubidium	3.50	54.6	35.9	27.2	18.9	8.8	5.8
Cesium	3.00	50.7	32.4	23.5	18.9	8.8	5.7

(a) Calculated from data of Bonner (14). % H_2O Retained = $\frac{\text{g } H_2O}{\text{g hydrated polymer}} \times 100$

Selectivity as a Function of Crosslinkage

Many elegant papers have been published on the measurement of selectivity coefficents of sulfonated styrene-divinylbenzene polymers. Taken as a whole, the magnitude of the numbers reported have little or no value in the designing of a water treatment plant. When used as computer feed, as they now frequently are, they sometimes generate operational fantasies which cannot be converted into operational reality. However these values are useful in cases where no column data are available.

Most of the problem arises in trying to take data derived in serene equilibrium conditions in the laboratory with two ionic species and convert it to the tumultuous multi-component, multi-variable, high flowrate atmosphere in a nuclear water treatment plant. There the concentration relationships in both phases are constantly shifting. That is not to say, however, that selectivity data is not of value in orienting one's choice of parameters for a nuclear system particularly with regard to selection of the resin phase.

The choice between materials of different selectivities in a specific exchange reaction depends first upon what the process to be operated is. In a primary loop where the resin is to be used once, a resin with high selectivity for the ions to be removed, other properties being satisfactory, is a clear choice.

In once used systems the frequently quoted data of Bonner, et. al. summarized in Table 4, is still used. Here removal of radioactive nucleides is the primary job of the ion exchange system. Rubidium and cesium are the ions most likely to be found on the cation sites. Bonner's data have been partially recalculated here to permit comparison of hydrogen and ammonium forms with the original lithium form presentation since all three forms are used in this service. On the basis of selectivity alone, the lithium form is to be prefered over the other two forms. If diffusion problems are ignored, these data also suggest an advantage in using as high a crosslinked resin as possible.

Table 4

Monovalent Selectivity Data of Sulfonated
Styrene-Divinyl Benzene Cation Exchange Resins (15)

	Compared to H^+			Compared to NH_4^+			Compared to Li^+		
% DVB	4	8	16	4	8	16	4	8	16
Cation									
Li^+	0.77	0.79	0.69	0.57	0.45	0.33	1.00	1.00	1.00
H^+	1.00	1.00	1.00	0.74	0.57	0.47	1.30	1.26	1.45
Na^+	1.15	1.49	1.54	0.85	0.85	0.73	1.49	1.88	2.23
NH_4^+	1.35	1.76	2.11	1.00	1.00	1.00	1.75	2.22	3.07
K^+	1.60	2.08	2.86	1.19	1.18	1.35	2.09	2.63	4.15
Rb^+	1.71	2.29	2.89	1.21	1.30	1.36	2.22	2.89	4.19
Cs^+	1.82	2.30	2.86	1.35	1.31	1.35	2.37	2.91	4.15

The continued use of these data after so many years reflects not so much confidence in their numerical correctness but rather the fact that they properly depict the trends seen in operating plants both with regard to ions and crosslinkage. They also predict some vital differences between the performance of condensate polishing systems in the hydrogen and ammonium forms. These systems are normally operated as regenerable, multicycle beds where the selectivity is a double-edged sword. Since high selectivity may also cause difficulty in regeneration, the reverse reaction must also be considered if the beds are to be regenerated.

In these systems, the ability of polishing beds to remove any sodium that might enter the system as a result of condensor leakage is of primary importance. These data leave no question that this removal is more favorable if cation resin in the hydrogen form is present in the system. This is particularly true if medium to high crosslinked cation resin is used. However, it also predicts that if the cation resin is decrosslinked in service its ability to remove sodium diminishes. Such decrosslinking does occur in condensate systems where oxygen removal is not complete and is frequently encountered in makeup demineralizer systems due to the presence of chlorine or other oxidants in the raw water supply.

Measurements of divalent-monovalent exchange using the same techniques were reported by Bonner at a later date (16). These values, calculated with lithium as a reference, are shown in Table 5. Of major interest are the relative differences between magnesium and calcium and the marked increase in calcium selectivity with increasing crosslinkage. Both of these are important considerations in designing make-up demineralizer systems. However, application of these data to engineering design is not an easy task as was shown by Frisch and McGarvey (17).

Table 5

Divalent Selectivity of Sulfonated
Styrene-Dinvinylbenzene Copolymers
as a Function of Crosslinkage (16)

Ion	Selectivity Relative to Li^+=1.00		
	4% DVB	8% DVB	16% DVB
UO_2^{++}	2.36	2.45	3.34
Mg^{++}	2.95	3.29	3.51
Zn^{++}	3.13	3.47	3.78
Co^{++}	3.23	3.74	3.81
Cu^{++}	3.29	3.85	4.46
Cd^{++}	3.37	3.88	4.95
Ni^{++}	3.45	3.93	4.06
Ca^{++}	4.15	5.16	7.27
Sr^{++}	4.70	6.51	10.1
Ba^{++}	7.47	11.5	20.8

The major emphasis on the selectivity for divalent ions in the makeup water system is not the removal of these ions from solution but the problems of restoring the resin phase back to the hydrogen form for another cycle. A wealth of data on monovalent-divalent equilibria does exist in the technical literature published by resin manufacturers in many countries. An example of this, recalculated into terms more readily understood internationally, is the Ionac Chemical Company data in Figure 1. These data compare an 8% and a 10% nominal divinylbenzene polymer for operating capacity in the hydrogen cycle on the same influent water when various amounts of acids are used in the regeneration cycle. The water used here contained 6 milliequivalents per liter total ions. Half of the cation equivalency was due to sodium and the remainder to calcium and magnesium in a ratio of two

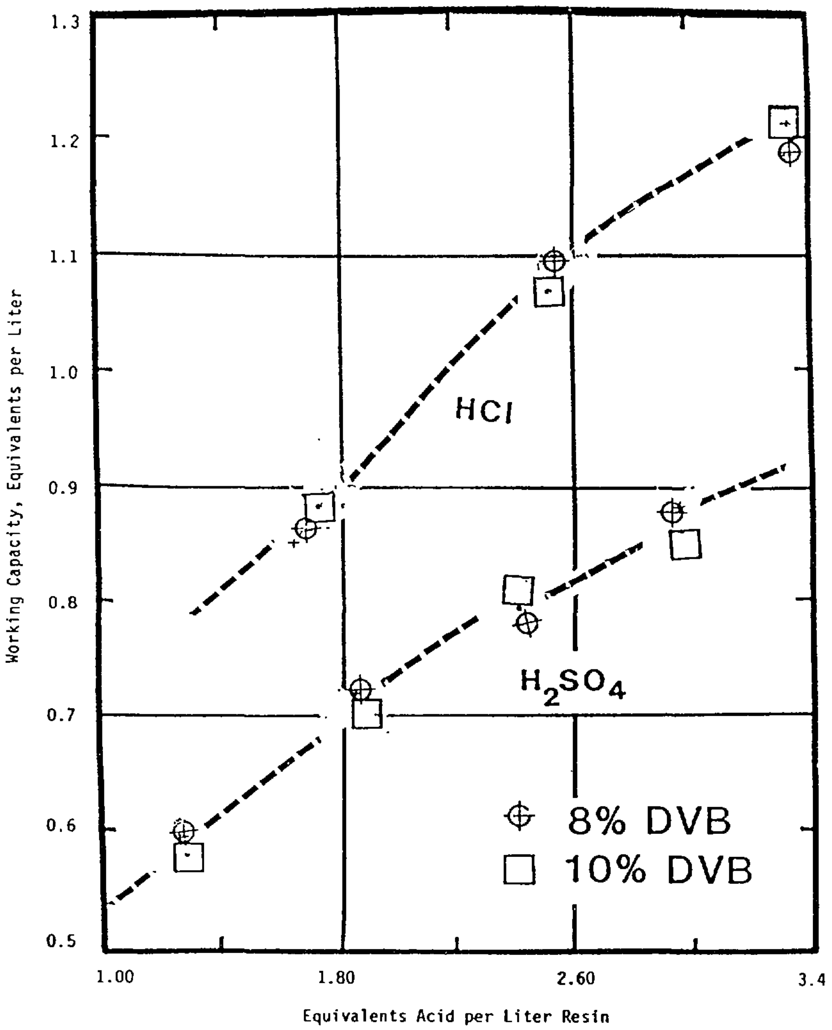


Figure 1. Effect of Crosslinkage on Resin Performance (18, 19, 20)

calcium to one magnesium. On the anion side, since the anion population does influence uptake of cations, half of the equivalency was carbonate and the remainder chloride and sulfate in a ratio of two equivalents of chloride to one of sulfate. Operating conditions so far as flow rate and temperature were the same at all regeneration levels.

The data in Figure 1 show that when both the forward and reverse reactions are taken into account the differences in selectivity due to crosslinking are so small that for practical purposes the data from the two polymers can be represented by a single line. The marked difference between the regeneration with hydrochloric acid and sulfuric acid is well known. It accounts for at least part of the differences in performance between the demineralizing systems in the United States where sulfuric acid is widely used and those in Europe where hydrochloric acid is the standard regenerant.

However, the difference in the selectivity between calcium and magnesium does influence the performance of the system. Here again, the technical literature published by the manufacturers contains very useful information. One interesting

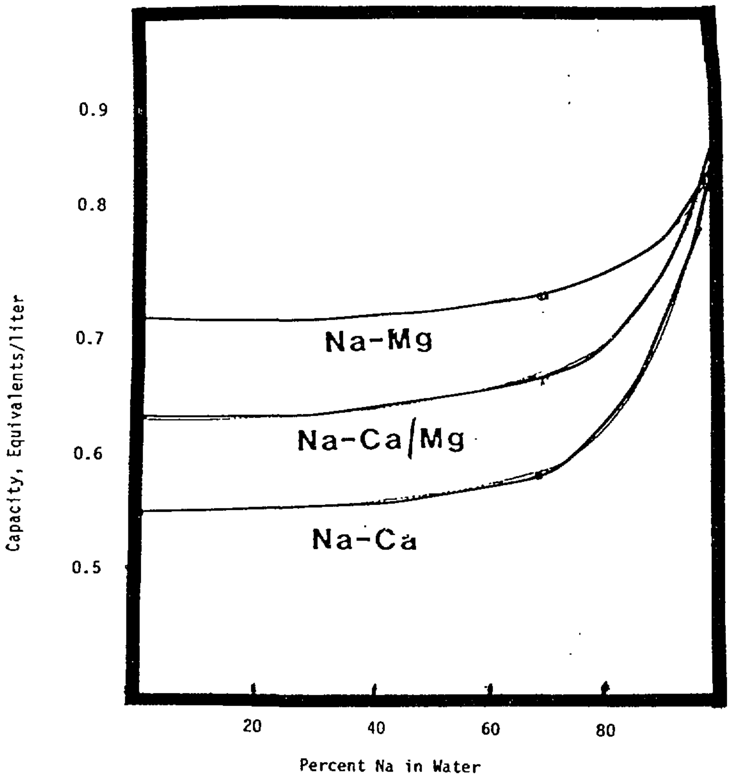


Figure 2. Variation of Operating Capacity of a Nominal 8% Divinylbenzene Sulfonic Acid Resin with the Ratio of Influent Ions (18) Regenerated with 1.5 equivalents H_2SO_4/Liter Resin

mode of presentation of such data is illustrated in Figure 2. This is one of a family of curves developed to define performance in the three component system of sodium-calcium-magnesium. Unlike the data in Figure 1, it represents the performance of a single polymer, in this case a nominal 8% divinylbenzene sulfonic resin, at a single acid regeneration level. The variable here is the ratio of cations in the influent water.

Figure 2 shows the marked affect of changing the ratio of calcium to magnesium in waters containing only divalent ions. All other parameters are held constant. On the other hand, if calcium-sodium or magnesium-sodium waters are deionized the presence of the monovalent ion exerts no influence until it is present at approximately a two-to-one equivalency ratio. And even there, in the case of sodium-magnesium the effect on the operating capacity of the system is small.

Curves like those in Figure 2, when supplemented by data on the effect of the total equivalents in the influent water, the effect of the accompanying anions, the flowrate, the concentration of regenerant and temperature serve as Programming data for computers. These programs, when given supplied with appropriate leakage limits, permit the performance of a given system for a specific water supply to be forecast. Thus it may be seen that overall performance depends on many variables some of which assume more importance than the selectivity of the resin for ions being exchanged.

Kinetics as a Function of the Crosslinkage

Data such as that presented in Figures 1 and 2 reflect the kinetics of the ion exchange process as well as the selectivity of the resin itself. It is generally believed that the cation resin reaction in sulfonic acid resins is extremely rapid once the ion to be exchanged reaches the exchange site. Indeed, it is very difficult to set up experiments to measure the exchange rate alone.

Many elegant theoretical papers have been published developing the equations for the overall ion exchange reaction including the diffusion of ions in and out of the particles. Experimentally, much of the work on the kinetics of the cation reaction dates back to the studies done in the 1940's and early 1950's in connection with the development of the separation of the lanthanides. Although much of this work was done with sulfonic resins no longer commercially available the simple conclusions drawn are applicable to present day resins.

For example, the observation by Boyd, *et al* (21) that "the magnitude of the internal diffusion constants are from five to ten-fold smaller than the diffusion constants for the same ions in solution" has stood the test of time. This paper also contains data confirming the inverse relationship between the square of the particle radii and the fraction of sites used per unit contact time.

Another interesting and instructive set of data, this time on modern resins, is that of Soldano (22) shown in Figure 3. These data, for example, measure the exchange of sodium in solution with sodium in the resin by the use of radioactive sodium in one of the starting phases. Not only is the effect of selectivity for practical purposes eliminated but the fact that the exchange reaction is dynamic is clearly demonstrated. There are, to be sure, exchange reactions where the selectivity of the anionic group of the resin is so great that once the cation approaches it the probability of it moving away spontaneously is very small. The behavior of barium in a sulfonic resin is a classic example

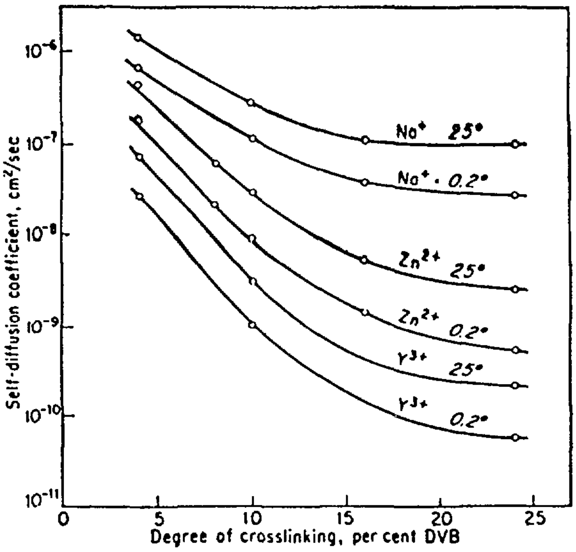


Figure 3. The Self-Diffusion Coefficients of Sulfonated Styrene-Divinylbenzene Polymers as a Function of Crosslinkage and Temperature as Determined by Soldano (22)

of such behavior. But a given sodium ion may be visualized as moving from site-to-site, sometimes deeper into the bead and sometimes back into the free liquid to attach itself eventually on a neighboring bead.

These data have added value in that they show that diffusion is faster as the temperature rises. That is not a startling finding but it must be remembered that it refers to movement both in and out of the bead. If, as many believe, exchange in a high flow rate polisher takes place primarily at the readily available surface sites, the dynamic nature of exchange reaction indicates that there will be an increased tendency for the sodium, for example, to return to solution if the temperature is raised. Although the existance of a sodium shell in these sulfonic systems has never been demonstrated experimentally, corresponding data with the much slower carboxylic resins has been obtained by Schmuckler (23) to show that an exchange gradient from surface to core is reality.

While there are many ion exchange systems where the cation kinetics are limiting, in nuclear systems cation kinetics are most important in the condensate polishing operations where ammonium is used for pH control. This is particularly true if the system is monitored by sodium leakage. In these high flow rate systems, reaching in the United States as high as 50 gallons/minute/ft^2 (2 meters/min) of bed surface, the residence time of an increment of water in a bed can be as little as 20 seconds. The fact that when these beds are run to a conductivity endpoint all of the available hydrogen capacity is seldom utilized suggests kinetic limitations as well as selectivity problems. When run to a sodium breakthrough 7-10% bed loading with sodium is normal. Sodium exchanged at the surface certainly has a higher probability of returning to solution than diffusing into the still available groups. Certainly this low degree of bed utilization is accentuated by the large size of the beads popularly used in these applications.

Stability Toward Radiation

A discussion of radiation stability is probably considered a standard portion of the properties of resins for the nuclear industry. However, only in situations where resin is reused such as in the separation, concentration, and recovery of radioactive isotopes or in cases where the resin is to be used for the long term storage of radioactive wastes is the matter of the radiation stability of a sulfonic acid resin of primary importance in resin selection.

However, the effect of radiation is an intriguing thing to study and many workers in many countries have done so. A comprehensive review of the work done prior to 1977 is available in the report by Gangwer, et al (24). This report clearly illustrates the problems inherent in evaluating data from publications where the resins are identified only by trade names.

Despite the conclusions of Gangwer that "the fundamental processes involved in radiation damage to ion exchange materials are not understood", the practical results in gel sulfonic resins are well established. Exposure of sulfonic acid cation to radiation can result in three different types of attack on the polymer structure. It is likely that all of these mechanisms occur to some degree simultaneously. Hence no significance should be attached to the order in which they are discussed here.

Loss of Exchange Capacity. Since these are functional polymers, the first change that one tends to think of is the possibility of the loss of functional groups. Such a loss does occur at high dosage levels as is shown by the data assembled by Simon (25) in Figure 4. These data indicate that once the critical dosage level is reached, neither the degree of crosslinking nor the ionic form of polymer make significant differences in the rate of capacity loss. However, inspection of some of the data from which Figure 5 is drawn (29) does show that fully hydrated polymers are slightly more suspectable to loss of capacity than those that have been dried.

Formation of Gases. A second possible result of exposure of sulfonic acid ion exchange resins to radiation involves the formation of gaseous materials. The most commonly measured gases from the sulfonic resin have been sulfur dioxide, carbon dioxide, carbon monoxide and hydrogen. The work of Mohorcic and Kramer (34) provides insight into the relative amounts of these gases formed from the lithium and hydrogen forms of the sulfonic acid resin in different degrees of hydration. These forms are the most commonly used in primary loop water purification.

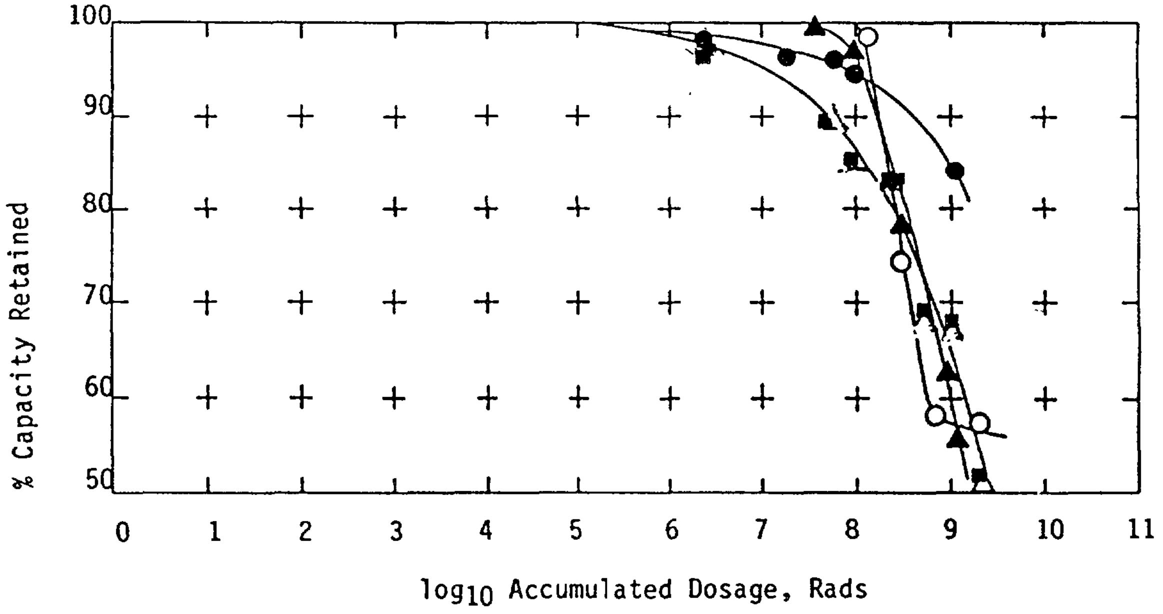


Figure 4 - Capacity Loss as a Function of Radiation Dosage for Styrene-Divinylbenzene Sulfonic Resins. Data from references 26 to 33 integrated by Simon (25)

○ = 2% DVB, Na$^+$ form

● = 6% DVB, Na$^+$ form

■ = 8% DVB, Na$^+$ form

▲ = 8% DVB, H$^+$ form

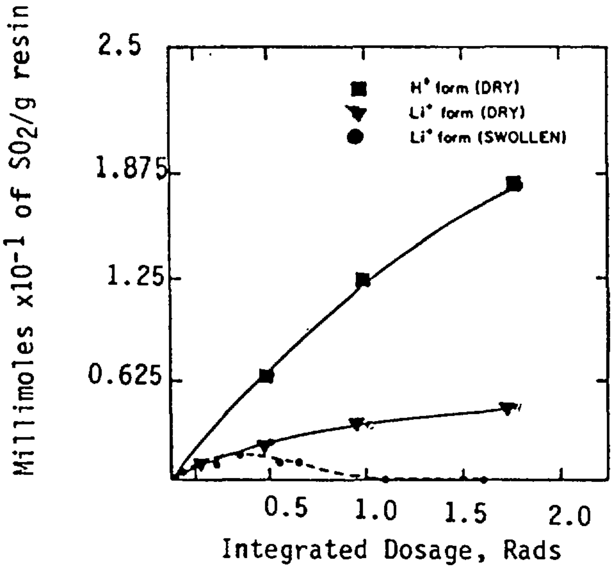


Figure 5 -Sulfur Dioxide Formation as a Function of Radiation Dosage (34) 10% DVB Sulfonic Resin

These results obtained, redrawn by Gangwer (24), are shown in Figures 5 through 8.

It will be noted first that the evolution of gas in measurable quantities begins at the same cumulative dosage as the loss of exchange capacity shown in Figure 4. Although sulfur dioxide was measured in the highest yield (Figure 5), its rate of formation is approximately one-tenth of the rate of capacity loss suggesting that the majority of the sulfur lost from the polymer is not liberated as a gas. Indeed, it should be noted that liberation of sulfur dioxide from dry resin greatly exceeds that from swollen resin and that the hydrogen form in this case is more liable to attack than the salt form.

Formation of hydrogen (Figure 6) could indicate the formation of unsaturation in the polymer chains. However, the fact that resins in water are a source of markedly larger amounts of hydrogen than dry or moist resins suggests a mechanism involving the water molecule. This may not involve the formation of unsatuation

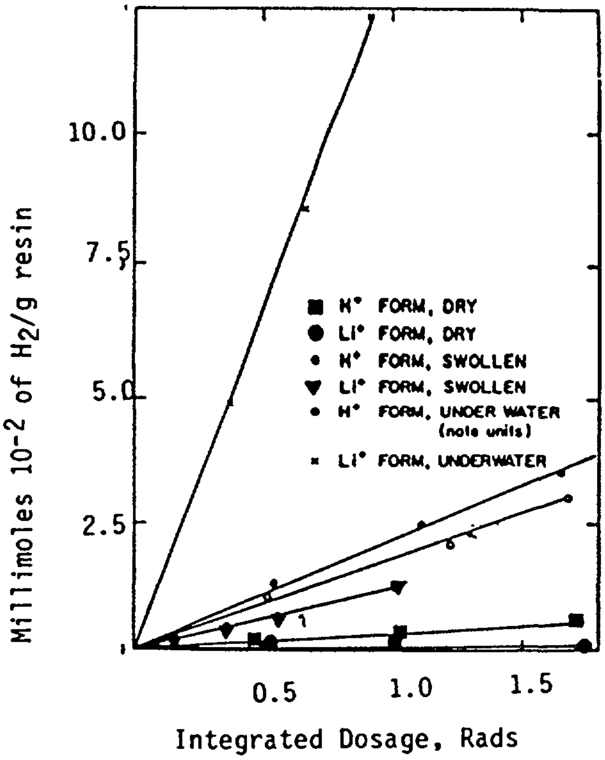


Figure 6 - Hydrogen Formation as a Function of Radiation Dosage (34)

10% DVB Sulfonic Resin

H^+ form under water = Millimoles x 10^{-1}

but rather an oxidative reaction. Such reactions usually involve the carbon on the polymer chain alpha to the benzene ring. If a peroxide is involved, as is likely here, a hydroxyl group is added to the chain and hydrogen liberated. This is usually the first step in reactions which break the polymer chain. It should be noted that the hydrogen form of the resin is more susceptible to this type of attack than the lithium form. This follows the same pattern as susceptibility to damage by chemical oxidants.

At a given dosage rate, the amount of carbon dioxide liberated is approximately a hundreth of the amount of sulfur dioxide as may be seen in Figure 7. Again water obviously is a partner in the process with the dry resins being substantially lower in gas formation than the wet which are in turn lower than those evaluated in water. Again the relative instability of the hydrogen form compared with the lithium form is shown. Carbon monoxide is formed at about half the rate of carbon dioxide (Figure 8).

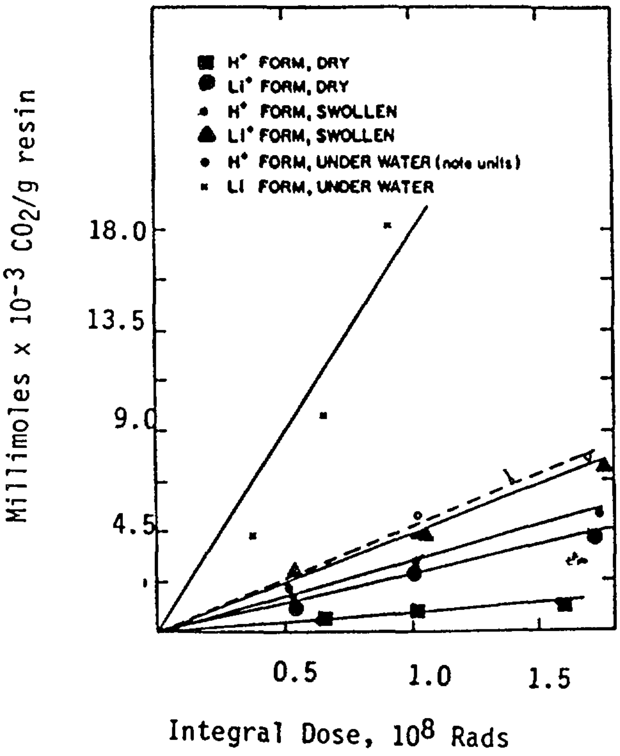


Figure 7 - Carbon Dioxide Formation as a Function of Radiation Dosage (34) 10% DVB Sulfonic Resin; Broken line Millimoles x 10^{-2}

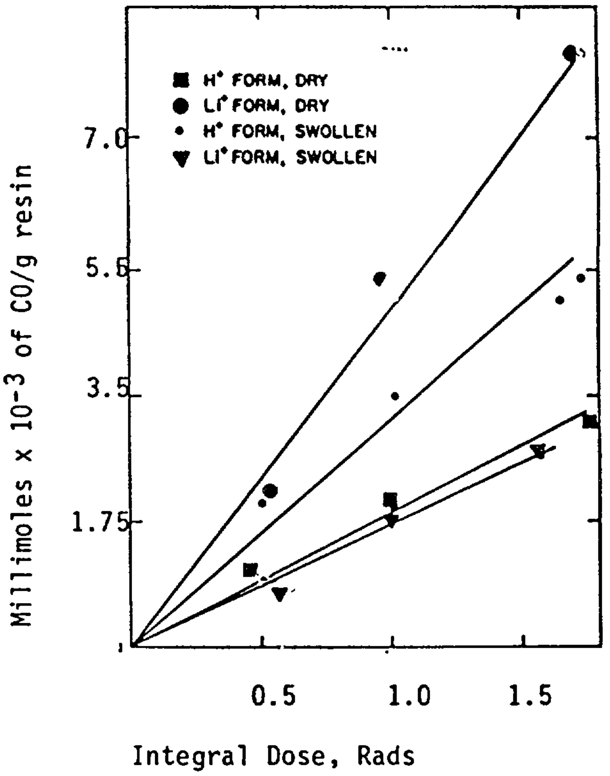


Figure 8 - Carbon Monoxide Formation as a Function of Radiation Dosage (34)
10% DVB Sulfonic Resin

Decrosslinking. When the resin is attacked by radiation at high dosage levels, the polymer chains are broken and it effectively assumes the characteristics of lower crosslinked polymers. This change is shown in Table 6. Regrettably these data are for the sodium form of the resin since it was not appreciated at the time they were obtained that the hydrogen form would be much more liable to this mode of attack. However, they do show that the presence of water is a factor in chain breakage and it is generally believed that the mechanism involves formation of peroxides in the water. (35)

While decrosslinking of this sort is not a factor in nuclear water treatment plants, it is of importance if the resins from such units are to be stored with the nuclides on them. The decrosslinking reaction may eventually proceed to a point where sufficient bonds have been broken so that the beads become water dispersable. Decrosslinking is also a factor to be considered when solutions of highly radioactive species are being processed on a cation exchange resin.

Table 6

Effect of Radiation on the Water Retention Capacity of Styrene-Divinylbenzene Sulfonic Acid Resins (29) All Sodium Form

	Percent Water Retained			
Nominal % DVB	4		8	
State During Exposure	Dry	Wet	Dry	Wet
Total Dosage (Rads)[(a)]				
None	65.8	65.8	43.9	43.9
10^6	65.3	76.0	44.6	44.6
10^7	69.5	76.4	44.9	45.3
10^8	74.7	80.5	48.8	52.2

(a) Conversion to rads approximate

Table 7

Isotope Loading on Typical Spent Mixed Bed From a BWR Plant (36)

Nuclide	μ Ci, g dry resin[(a)]	Specific Activity Ci/g nuclide	g x10^{-9} Nuclide g dry resin	meq Nuclide g dry resin
^{54}Mn	0.87	7.98x10^3	0.11	4x10^{-6}
^{60}Co	7.3	1.13x10^3	8.2	2.6x10^{-4}
^{65}Zn	6.3	8.20x10^3	0.77	2.3x10^{-4}
^{134}Cs	2.4	1.30x10^3	1.8	1.3x10^{-4}
^{137}Cs	7.3	87	84	0.61x10^{-3}

Bonding of these materials in a discrete zone on the resin column can subject a small portion of the resin to high radiation dosages. Such decrosslinking has been a contributing factor to at least one accident involving reprocessing on a sulfonic acid exchange cation resin.

That radiation stability plays such a small role in the choice of resin in the nuclear water systems reflects the fact that all experimental data shows that radiation damage is a function of the cumulative dose of radiation encountered by the resin. Even when the resins are used in the primary loop in a BWR plant the amount of radioactive species accumulated by the resin before leakage reaches the point where its removal from service is mandated is small. This is shown in the data in Table 7 which is typical for spent once-use resin in such an application.

The exhaustion data for radioactive systems is usually given in terms of the radioactivity of the isotopes on the resin. In Table 7 these data have been translated into milliequivalents of the various entities since these numbers will be more meaningful to those whose primary experience is in resin technology. As may readily be seen, the extent of cationic exhaustion so far as radioactive species is concerned, is very small indeed. This particular set of data does not include radiation from potentially anionic Carbon 14 which has been reported present in other systems. In actuality, rubidium and cesium are probably the principal radioactive isotopes that are exchanged with the cation resin since most divalent metal activity appears to be associated with the crud filtered out by the resin bed.

Chemical Stability as a Function of Crosslinkage

In the beginning, people believed that sulfonated styrene-divinylbenzene cation exchange resins were so stable that their operating life could be measured in decades. Situations do exist where this dream has become a reality. However, it is now well recognized that oxidizing agents augmented by high temperatures do rupture the polymer chain. The result, no matter what the specific oxidant, is generally termed decrosslinking because the resins so attacked assume all of the characteristics of polymers made at lower nominal divinylbenzene contents. It should be noted that the observable result, an increase in water retention capacity, is the same whether the chain breaks between two former styrene monomers or between a former styrene and a former divinylbenzene.

The rate of decrosslinking by any oxidant is dependent upon its concentration and the ionic form of the polymer. The hydrogen form of a sulfonic acid polymer is markedly more susceptible to decrosslinking than any of the salt forms. Since this is the form most commonly used in large scale installations both in nuclear and in fossil plants, it is the form that has been studied most extensively in recent years although early results were all sodium form (37).

The damage in terms of chains ruptured per unit oxidizing agent has never been established experimentally. Many papers have been written showing the qualitative effect of a specific amount of oxidant on resins of various degrees of crosslinkage. Typical data for uncatalyzed peroxide attack at two temperatures, are presented in Figures 9 and 10. These data, which were all obtained at the same ratios of dry resin to peroxide using the hydrogen form of the resin, are of interest not only because they compare the increase in hydration as a function of crosslinkage but more so for the dramatic temperature effect. Degradation that requires 20 days at 25°C is matched in less than 2 hours at 45°C under otherwise similar conditions.

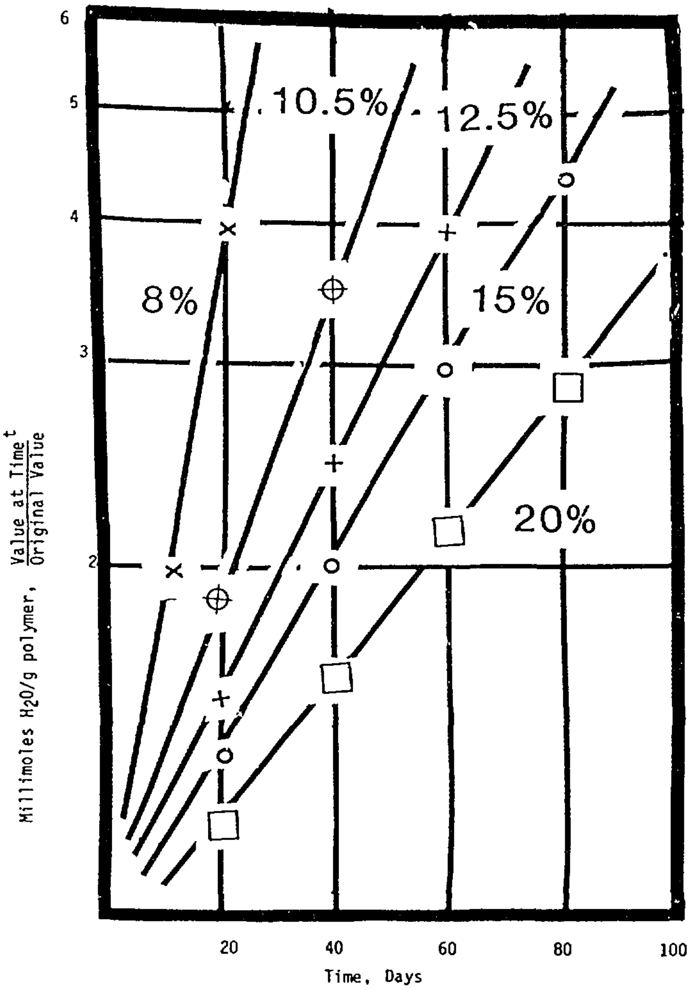


Figure 9 - Comparative Degradation of Sulfonic Acid Polymers in 3% Hydrogen Peroxide (38). Temperature = 25°C

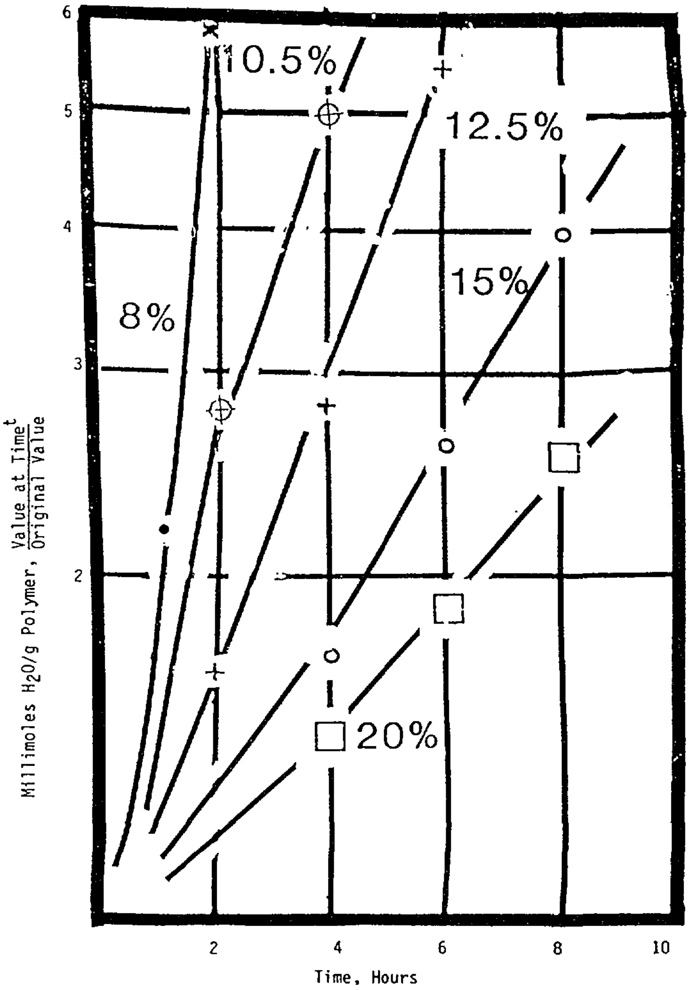


Figure 10 - Comparative Degradation of Sulfonic Acid Polymers in 3% Hydrogen Peroxide (38). Temperature = 45°C

These data do not take into account the catalytic effect on the rate of decrosslinking by such metals as iron, copper and manganese. The effect of iron precipitated in the polymer is shown by the data of Downing and Kunin (38) which is presented in Figure 11. This catalytic effect is important not only in makeup demineralizers but in condensate polishers as well.

Results such as those shown in Figures 9 to 11 have generated a belief that high crosslinked sulfonic resins are less suspectable to attack by oxidants than low crosslinked. This thinking is actually in error. The number of chain bonds broken by a given amount of oxidant in any sulfonated styrene-divinylbenzene polymer is probably statistically identical. However, the effect of breaking a specific number of bonds in a given weight of polymer is greater in a polymer with less

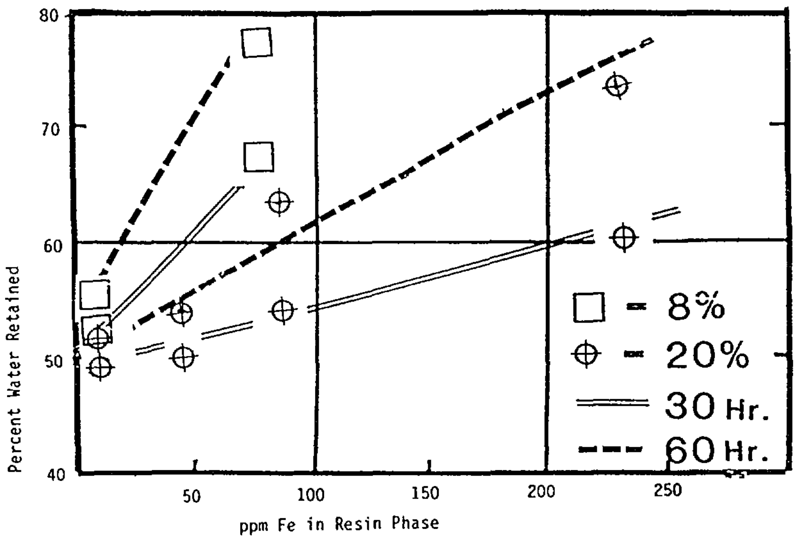


Figure 11 - Effect of Iron on the Rate of Decrosslinking of Sulfonic Acid Resins in Hydrogen Peroxide. Data of Downing and Kunin (39). Recalculated and Redrawn.

divinylbenzene since it represents the rupture of a larger percentage of the cells present. Further, the method of following this breakage involves monitoring either the increase in swelling or in water retention, both of which increase logarithmically as the mole percent effective crosslinkage decreases.

Indeed, the effective life of a resin that starts with a high percentage of crosslinking is longer in a given set of oxidizing conditions than one that has fewer bonds initially. This is shown clearly in the data of Downing and Kunin (38). Resin life is an important consideration in both makeup demineralizers, which sometimes are subjected to severe oxidative conditions, and in condensate polishers where the operating temperature is higher.

Resin life is often estimated in terms relative to that of the 8% nominal divinylbenzene polymer. To make this estimate it is assumed that the resin in a typical condensate polisher is a candidate for replacement when the water retention of the hydrogen form has reached 56%. Beyond that point changes in the bead density may effect the separability of cation from the anion resin.

In makeup demineralizers the value for replacement is usually 60% water retention in the hydrogen form. Data based on this assumption is shown in Figure 12.

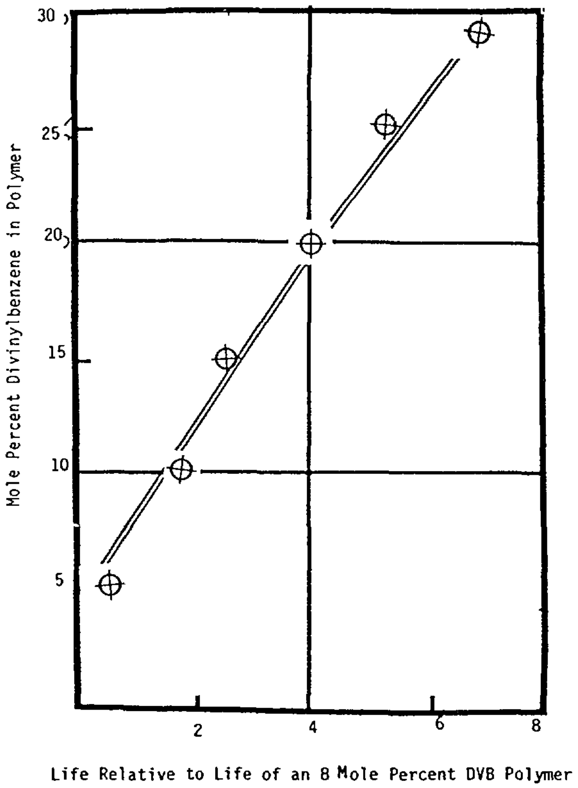


Figure 12 - Approximate Resin Life in Makeup Demineralizer Compared with 8 Mole Percent DVB Calculated from Data in Figures 9 and 10 (38) and Assumptions in Text.

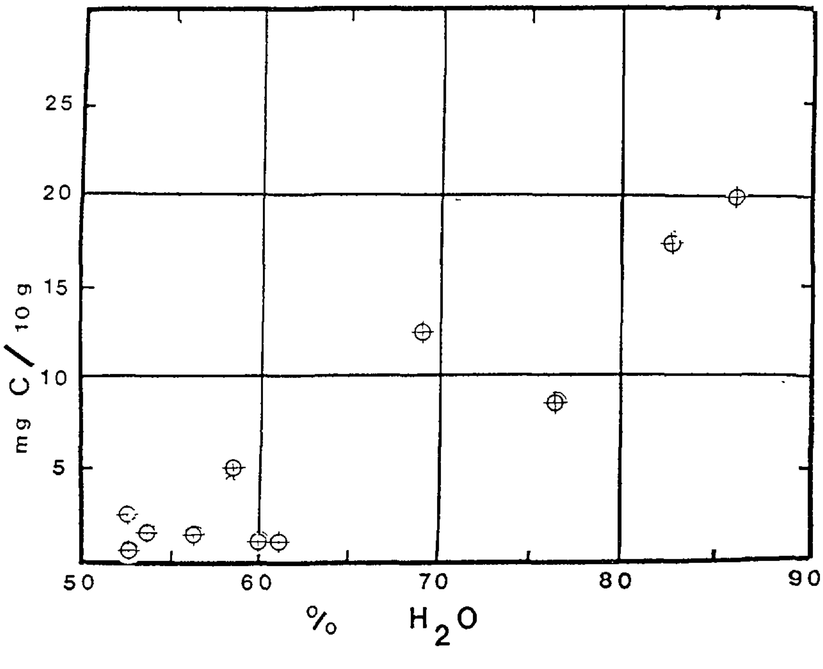


Figure 13 - Sloughage of Organic Carbon from the Hydrogen Form of Decrosslinked Sulfonic Cation Resins (39)

This value is chosen there because the decrosslinking process is accompanied by an increased sloughage of organic material from the cation resin (40). This sloughage is a serious foulant for the strong base anion resin in these systems. It increases rapidly at hydrogen form water retention capacities greater than 60% as shown in Figure 13.

Physical Stability on Sulfonic Cation Exchange Resins

Concern for the physical stability of the cation resins in nuclear water treatment systems arose with the development of continuous deionization processes in the late 1950's. Bead breakage in these systems was usually attributed to mechanical shock. Tests such as rolling the resin with steel balls in a ball mill jar were advocated (12) to simulate it.

As condensate polishing systems developed, it has been generally believed that the bead breakage occurring in the cation resin is a combination of mechanical and osmotic shock. Early testing for osmotic damage involved cycling with relatively high concentrations of acid and base as described by Kunin, et al (41). The recognization that the bead breakage was a function of the swelling between forms prompted the development of a simple test where swelling was caused by drying followed by rapid rehydration (37,38). Data obtained by the latter methods are reproduced in Figure 14. The intent is not to show the differences in stability between the three types of resin since gel resins of far better stability are

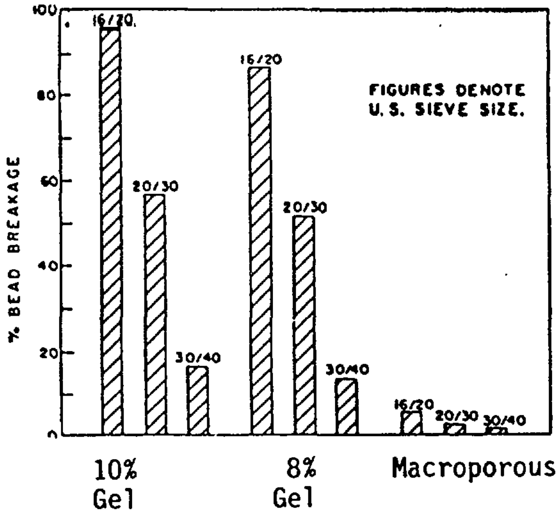


Figure 14 - Relative Physical Stability of Sulfonic Acid Cation Beads of Various Types and Sizes (37)

now produced, but rather to present testimony concerning the effect of bead size on physical stability of cation resins. That the larger the beads are, no matter what the polymer structure, the greater the tendency for physical breakage is, is an important property to remember.

Interest in bead stability was greatly accelerated by the appearance of the Chatillon test procedure in the General Electric specifications in the early 1970's (42). This is a purely physical test wherein a single bead is squeezed between two parallel plates by a known applied force until it breaks. Many manufacturers have modified their production methods, particularly of anion resins, to produce materials which give high values in this test although correlation of the results with field performance has yet to be established.

Recently a new test method utilizing a column of resin subjected to both mechanical and osmotic shock has been described by Skriba, et al (43). While this procedure was developed primarily for anion resins used in uranium recovery, it is currently being applied in modified form to cation resins as well. It has the advantage of mimicking the conditions in a packed bed under plant operating pressures and temperature and permits the use of whatever reagents are being used in the specific plant system. Results are normally evaluated by measuring the percentage of broken beads after specified numbers of cycles. Correlation with cation resin breakage in condensate systems where a portion of the cation resin may contact sodium hydroxide are following plant performance.

The Importance of Bead Size

The effect of bead size on the kinetics of the system has already been brought to attention. Further, in the preceding section its influence on bead stability is shown. Controlling the size of the beads has received increased attention as the operating flowrates in condensate polishers have increased. In general, an increase in average bead size has followed this development. As it happens, correction of one problem in an ion exchange system frequently generates others since all of the properties of the bead, both chemical and physical, work together to govern the overall properties of the system. Bead size is particularly important in understanding the hydraulics of the system and the separability of mixed beds. A discussion of its effect on these properties is a fundamental part of a discussion of the properties of the resin itself.

The factors related to pressure drop has been correlated in a recent paper (44). Over a considerable range, the pressure drop can be calculated by the following equation:

$$\Delta P = \frac{150\ U_0 L\ \mu\ (1-\mathcal{E})^2}{(Dp)^2\ g\ \mathcal{E}^3}$$

Where P = pressure difference, Pa/m

U_0 = flow velocity, m/min

L = bed height, m

μ = viscosity of the liquid at the operating temperature, poise

$\mathcal{E}$ = void fraction

g = gravitational constant

Dp = geometric average particle diameter, m

The relationship between particle size, flow rate and pressure drop implied in the above equation is illustrated graphically in Figure 15. Here pressure drop is plotted as a function of particle size at three different linear flow rates. The effect of high flow rate operation on pressure drop is clearly shown. In counteracting this by an increase in bead size, the loss in kinetic efficiency must not be neglected particularly where very low leakage is desired.

Bed Expansion. Bed expansion is an important step in the operation of a nuclear water system, both in freeing the beds from accumulated particulate material and in separating the components of a mixed bed for regeneration. If a bed expands too much, resin losses occur. If the bed does not expand sufficiently the accumulation of particulate material causes pressure drop problems and mixed bed separations will be inadequate.

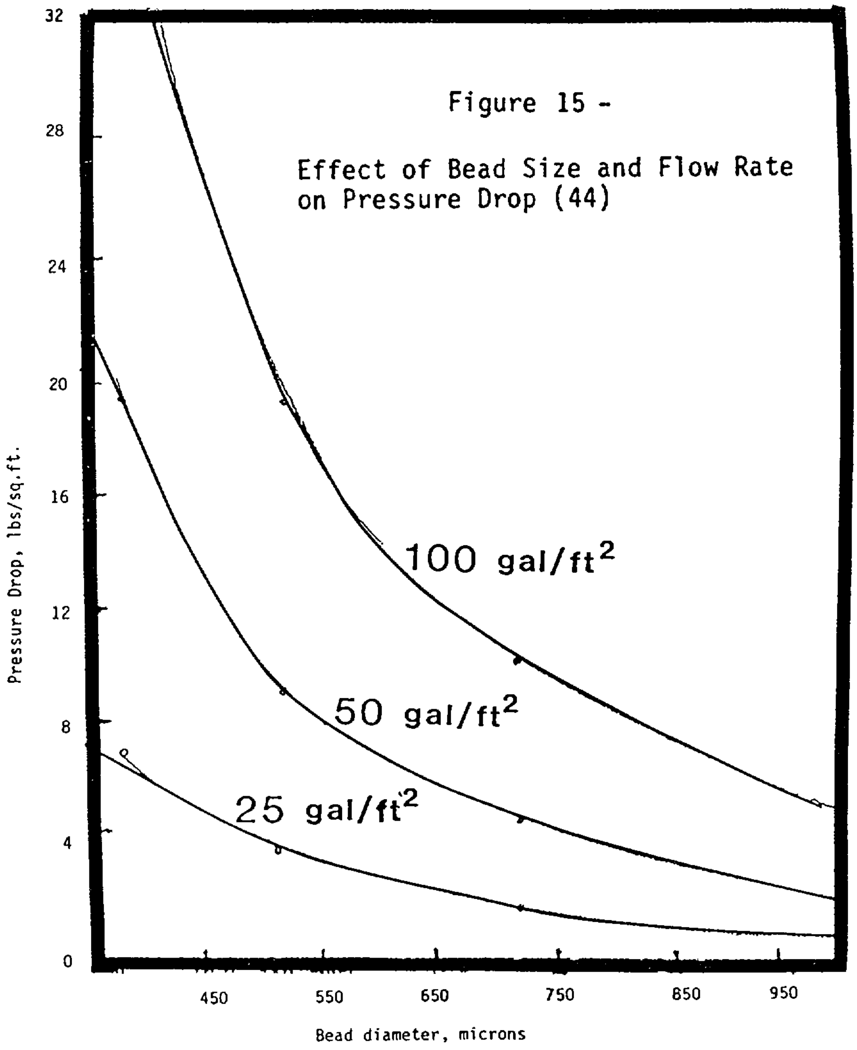


Figure 15 -

Effect of Bead Size and Flow Rate on Pressure Drop (44)

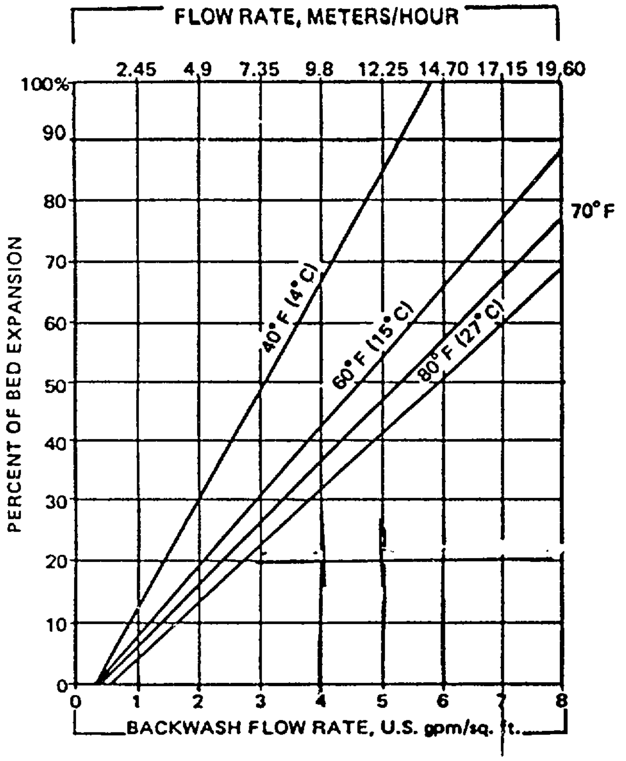


Figure 16 -

Effect of Temperature on Bed Expansion
8% Nominal DVB Sulfonic Resin
Hydrogen-Form (18)

The amount of expansion of an ion exchange material when water is passed upward through it depends upon the hydrated density of the bead itself, the size of the bead, the rate of flow of the water and the water temperature. A surprising number of systems fail to appreciate the effect of the latter. This is shown in Figure 16 with data from an 8% sulfonic acid resin (18).

The effect of bead size is shown in Figure 17. Polymer characteristics are eliminated here since all of these data were obtained on a single lot of nominal 8% divinylbenzene sulfonic acid resin in the hydrogen form. Technical grade material was selected so that a full particle size range was available.

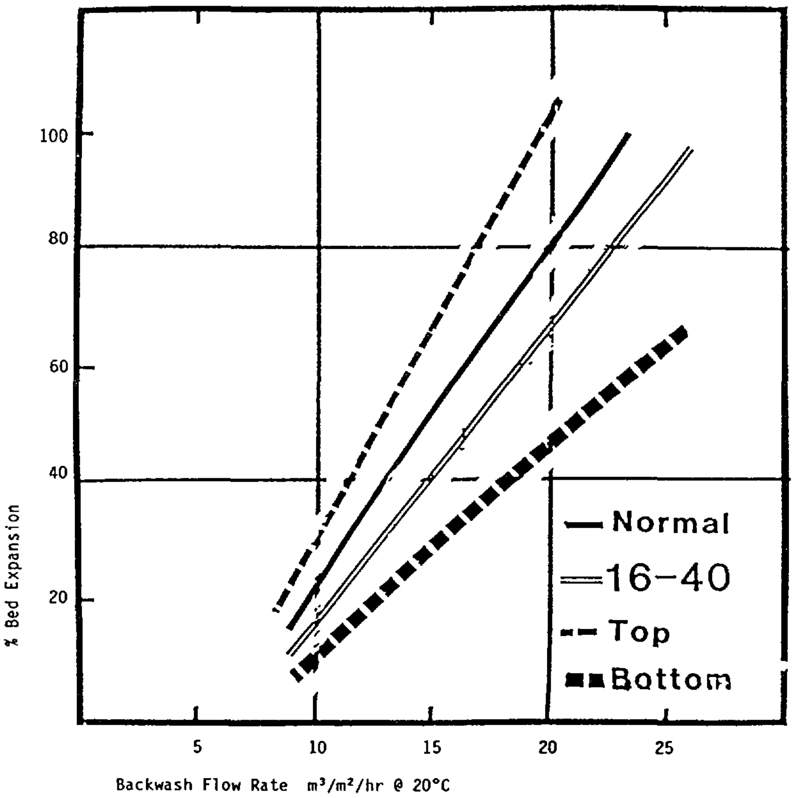


Figure 17 - Backwash Expansion of Different Particle Sizes From a Single Batch of 8% DVB Sulfonic Acid Polymer (45). Hydrogen Form. See Table 7 for Screen Analysis

The backwash expansion was first determined on the bead population as originally sold. Sieve analysis in Table 7 confirms that it did indeed have a full range of particle sizes. Next, a portion of the lot was backwashed vigorously and the fine material gradually removed until some particles retained on 40 mesh appeared in the backwash water. The bed expansion was then redetermined on the residual population whose sieve analysis is shown also in Table 7.

At the end of the backwashing, this column of material was allowed to settle by gravity and divided as nearly as possible into a top portion and a bottom portion. Backwash expansion characteristics were then determined on each of these. Subsequently both of these fractions were wet sieved (Table 7). Most backwash data published were determined on what is considered here to be the normal particle size range. When bead sizes either larger than or smaller than this are employed, hydraulic data should fit the bead size that is to be used.

Table 7

Screen Analysis of 8% Divinylbenzene Sulfonic Acid Resin
Used in Bed Expansion Tests
Hydrogen Form (45)

	Original	Fines Removed (a)	Top	Bottom
% of Total Population	100	94.4	47.1	47.3
On 16 mesh	2.4	2.5	0	5.0
Thru 16 on 20	40.7	42.9	5.8	78.0
Thru 20 on 30	45.6	48.2	81.8	16.6
Thru 30 on 40	5.5	5.2	9.9	0.4
Thru 40 on 50	4.7	1.0	2.4	0
Thru 50	1.0	<0.1	0.1	0
Effective Size, mm	0.54	0.62	0.53	0.80
Uniformity Coeff.	1.59	1.42	1.34	1.25

(a) Removed by backwashing

Separability of Mixed Beds. The development of the three-layered beds is a recognization that both the size and the density of the cation polymer is a critical factor in the separability of mixed beds. Data such as that shown in Figure 17 make this clear. Such sharp boundaries in the three-layered beds reflect use of cation resin whose bead size is very closely controlled and, hence, whose expansion can be precisely predicted.

Problems arise, however, when material made to operate in newly designed high flow rate units with proper attention to the hydraulic properties of the larger beads are put into older units without suitable modification of the backwash rates. It is not unusual in such cases to find that the bottom of the bed does not expand at all resulting in the complete exhaustion of anion resin, left in the bottom unseparated, with acid.

MACROPOROUS SULFONIC CATION EXCHANGE RESINS

Chemically, the resins that are termed macroporous are the same as the gel resins. The difference between the two classes is in the physical structure within the bead. In the case of resins termed gel, an individual bead is an essentially homogeneous polymeric spheroid. In the polymers called macroporous, this sphere contains artifically generated holes in the polymer mass which permit the external liquid phase to penetrate the sphere. Thus the effective surface area of the polymer is increased.

Chemical Properties of Macroporous Sulfonic Resins

A review of the patent literature covering the preparation of sulfonated macropolymers (3 to 7) will reveal that they are prepared using a vast variety of ternary mixtures of styrene, divinylbenzene and solvent. Each solvent, each ratio of that solvent to a given ratio of styrene and divinylbenzene, and each ratio of styrene to divinylbenzene produces a change in the final product. This vast collection of possibilities makes it impossible to correlate the properties of macroporous sulfonic resins in some orderly fashion that is possible in the pure gel resins unless one has full knowledge of the manufacturing processes. It is doubtful that two commercial products are made from identical ratios of the same starting materials. None the less, the two most widely used commercial products of this type are strikingly similar in chemical properties (Table 8). These data were collected on the same terms as those for gel resins in Table 2.

Chemically, the ratio of styrene to divinylbenzene governs the properties of the polymer itself just as it does in the gel resins. The water retention, true polymer density, selectivity, diffusion kinetics into the polymer itself,

Table 8

Comparison of the Properties of New Macroporous Sulfonic Cation Resins from Different Producers (13)

	Source A	Source B
Water Retention, %		
Sodium Form		
High	49.15	48.27
Low	46.86	46.92
Average	47.87	47.39
Hydrogen Form		
High	53.92	52.55
Low	50.91	51.84
Average	52.54	52.48
Exchange Capacity, Na-form		
meq/g dry		
High	4.34	4.37
Low	4.20	4.27
meq/ml		
High	1.80	1.89
Low	1.77	1.72
Average	1.79	1.81

and the resistance to oxidation are all governed by this ratio as they are in the gel system. The amount of artificial holes in the bead govern the surface available for the ingress of the external solution and the hydrated bead density. They also have a marked effect on the physical properties of the final bead. If the ratio of holes to polymer becomes too high the physical stability of the resultant bead will diminish.

The problem in characterizing macroporous polymers is that water retention capacity does not provide the key to the overall composition of the system that it does in gel sulfonic resins. In the macroporous system, water retention capacity is the sum of the water held in the pores plus the water retained in the polymer itself. A producer of these materials usually controls the pore volume by solvent sorption before the polymers are sulfonated. Drying curves do provide a means of characterizing these material since the water held in the macropores is lost very rapidly compared with the water in the tight polymer network. However, these are not routine measurements, since the process must be carefully controlled. For practical purposes, a simple measurement of pore volume is more readily obtained by measuring the displacement volume when the water in a small column of resin is displaced with a non-exchanging solution of electrolyte. The difference between the measured displacement volume and the theoretical interbead void volume calculated following the method of Della Valle (46) is a an approximate estimation of the volume of the pores within the beads.

Since macroporous sulfonic acid resins are made with a higher divinylbenzene content than gel resins, Bonner's data (16) in Table 5 predict that they should have a very high selectivity for calcium, as compared with an 8% gel resin, but only a slightly higher selectivity for either sodium or magnesium. In Figure 18 performance curves obtained under exactly the same conditions as

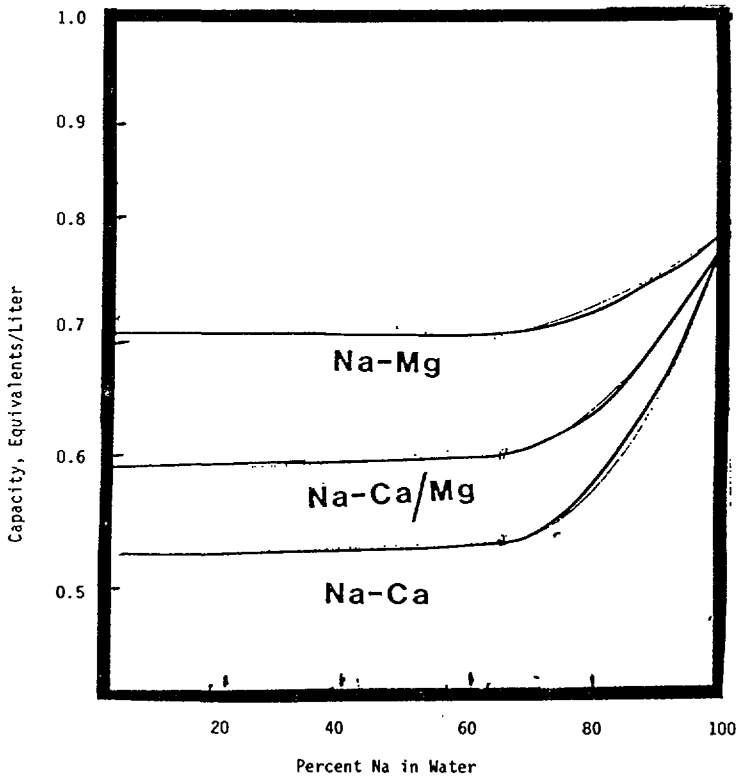


Figure 18 - Variation of Operating Capacity of a Typical Macroporous Sulfonic Acid Resin with the Ratio of Influent Ions Regenerated with 1.5 Equivalents H_2SO_4/Liter Resin (47)

Table 9

Comparison of the Operating Capacity[a] of a Gel and macroporous Resin

Ions in Influent Water	Capacity, Equivalents/liter	
	Nominal 8% Gel[b]	Macroporous[c]
100% Na	0.87	0.80
50% Na-50% Ca	0.59	0.53
100 Ca	0.56	0.52
50% Ca-50% Mg	0.64	0.59
100% Mg	0.73	0.72
50% Mg-50% Na	0.74	0.72

(a) Both resins regenerated with 1.50 Equivalents H_2SO_4/Liter. Influent water of zero alkalinitity.

(b) Data taken from Figure 2

(c) Data taken from Figure 18

Table 10

Comparison of the Bead Densities and Surface Areas of Gel and Macroporous Sulfonic Acid Resins

	Hydrated Bead Density[a]		Surface Area
	H^+ Form	Na^+ Form	m^2/g dry
8% DVB Gel	1.19	1.27	<1
10% DVB Gel	1.22	1.31	<1
Macroporous	1.19	1.26	35-42.5 (36,48)

(a) Data accumulated by the authors from commercial materials.

the data for a gel sulfonic (Figure 2) are shown. Selection of a few points at different ratios of influent ions in Table 9 confirms the fact that the major difference in performance between the two types of polymers is in waters where calcium is a major component of the influent population. That the macroporous polymer is more selective for calcium manifests itself in a lower operating capacity since the reverse reaction of hydrogen replacing calcium is less efficient.

Despite the differences in their structure, the bead densities of commercial macroporous resins are essentially identical with those of a nominal 8% divinylbenzene gel resin (Table 10). The difference between the two types of polymers is shown primarily in surface area measurements.

The similarity in hydrated bead density of the macroporous resin and the nominal 8% gel indicates that if both are made in the same particle size range their hydraulic properties, and particularly their backwash expansion rates, should be so similar that they can be used interchangeably in a given unit without adjustment of flow rates.

Stability of Macroporous Sulfonic Resins

In the nuclear system, macroporous resins are most often utilized in condensate polishing systems to obtain the better chemical and physical stability of a higher crosslinked resin while avoiding the serious kinetic problems shown in the work of Soldano (Figure 3), by increasing the effective surface. Various papers have been published attesting to their superior physical and chemical stability, of which the data in Figures 14 and 19 taken from early work (36, 38) are typical. Like most commercial products, macroporous sulfonic resins

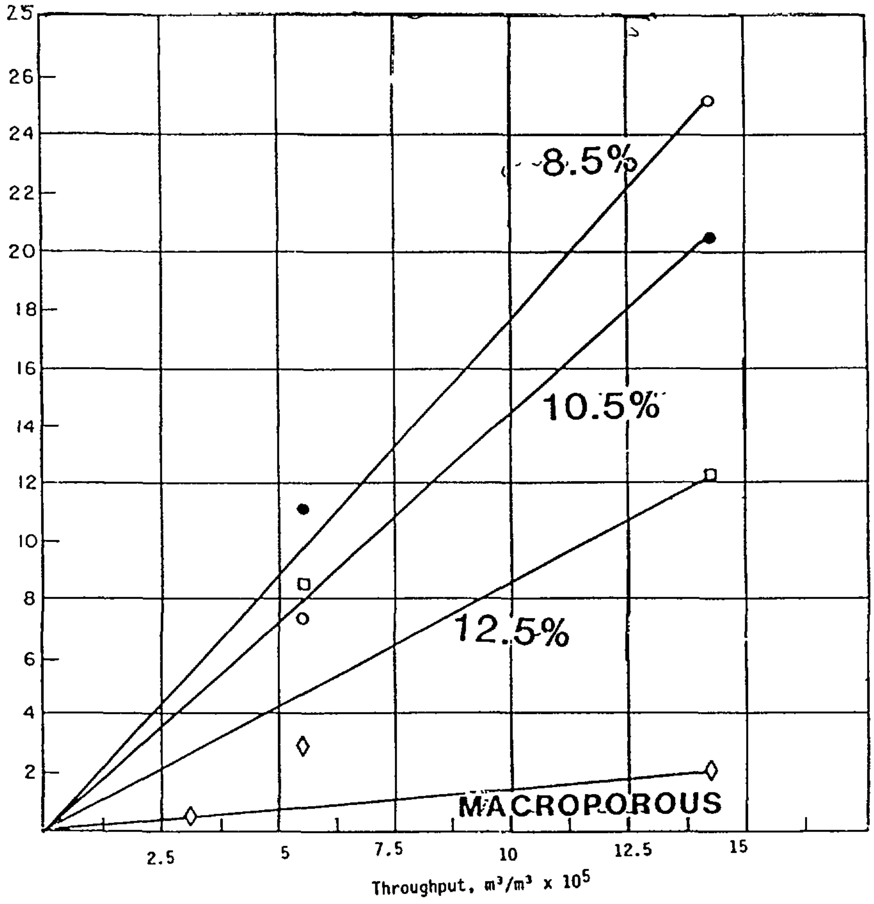


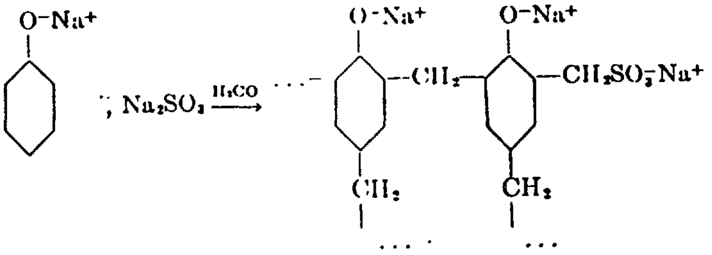
Figure 19 - Comparison of the Decrosslinking of Gel and Macroporous Sulfonic Resins in Field Tests (38)

presently sold represent a compromise in properties and the materials made now are not identical to those first marketed under similar trade names. The chemical stability toward oxidants of these polymers will, however, follow the curves in Figures 9 and 10. Such measurements actually provide a means of estimating what the divinylbenzene content of a given polymer is.

Although data on the subject are scarce (49), the stability of these high crosslinked materials to radiation should be superior to that of gel resins with respect to the tendency to decrosslink. Otherwise their radiation stability should depend only on dosage as has been shown above. The accessibility of their groups to large ions and colloids has promoted their use in radwaste treatment.

METHYLENE SULFONIC ACID CATION RESINS

Methylene sulfonic acid cation resins are of greater historical than current interest in the nuclear industry. Since styrene-divinylbenzene based sulfonic resins were not available until the mid-1940's, much of the earlier work was done with methylene sulfonic acid resins. Their preparation, which involves a condensation reaction of phenol, formaldehyde and sodium sulfite is described in patents by Holmes and others (50, 51). In general, their structure is represented as follows:



The properties of these materials are described by Kressman and Kitchener (52). They were a marked improvement over the earlier nuclear sulfonic acid resins formed by sulfonation of phenol-formaldehyde polymers which could only be used in the hydrogen form at temperatures below 40°C. Higher sulfonic capacities of the styrene-based materials (Table 11) and the ease with which bead-form polymers could be made in that system resulted in the rapid displacement of the methylene sulfonic polymers in industrial applications.

Table 11

Comparison of the Chemical Properties of a
Methylene Sulfonic Acid Polymer
With a Typical Sulfonated Styrene-Divinylbenzene Polymer
Before and After Radiation Exposure (28)
All Values for Sodium Form

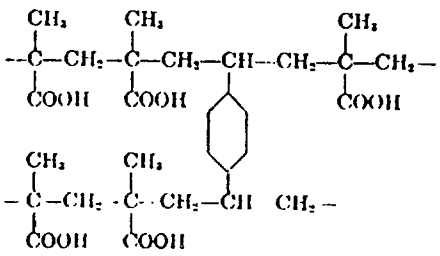
	Methylene Sulfonic		8% Nominal Styrene - DVB	
	Before	After(a)	Before	After(a)
% H_2O Retained	60.8	63.5	43.9	52.2
Total Cation Capacity meq/g dry	5.38	4.53	4.90	(b)
Sulfonic Capacity meq/g dry	1.69	1.60	4.40	4.43
Sulfate in Leach Millimoles/10 g	0.12	1.12	0.09	5.34

(a) Approximately 10^8 Rads
(b) No data given

However, numerous workers (28, 29, 53-56) have reported that methylene sulfonic materials have superior resistance to high levels of radiation compared with the nuclear sulfonic resins. This, plus their excellent selectivity for the heavy isotopes, means that they still find use in some special radwaste systems.

CARBOXYLIC CATION EXCHANGE RESINS

Although the original patents of D'Alelio (1, 57) describe the production of cation exchange resins with carboxylic acid functionality made from many monomers, those commercially available are either methacrylic acid crosslinked with divinylbenzene or acrylic acid crosslinked with divinylbenzene. The structure of the methacrylic acid polymer is represented as follows:



The acrylic acid polymer is of similar structure with the methyl group on the carbon alpha to the carboxyl group replaced by a hydrogen. Both types of polymers may be made as gels or as macroporous structures (58). Generally similar macroporous materials of both acid types and gel acrylic resins comprise the available commercial spectrum (Table 12) encountered in nuclear applications.

Table 12

Typical Properties of Commercially Available
Types of Carboxylic Acid Resins (59-63)

Acid	Methacrylic	Acrylic		
Polymer Type	Macroporous	Macroporous	Gel	
			Standard	Porous
% H_2O Retained				
H^+ Form	48	47	44	52
Na^+ Form	73	73	62	72
Total Cation Capacity				
meq/g dry, H^+ form	10.6	10	12	13
meq/ml, H^+ form	3.5	3.0-3.8	4.0	4.4
meq/ml, Na^+ form	1.7	2.1	2.3	2.2
Hydrated Bead Density				
H^+ form	1.25	1.13	1.19	1.18
% Volume Increase				
$H^+ \rightarrow Na^+$	100	85	50-70	70-100

The properties of carboxylic acid polymers are far more dependent upon crosslinkage than those of sulfonated styrene-divinylbenzene polymers. The total weight capacity, for example, is an inverse function of the mole percent crosslinking agents since only the acrylic monomers contribute functionality. Many workers have published on the effect of crosslinking on both the acidity and the physical properties of these resins (64-67). From the standpoint of the nuclear industry, however, these properties are academic since only a limited number of carboxylic polymers are used. Except for certain limitations on bead size, these are materials which have been made commercially available for other applications. These include one macroporous methacrylic acid type, gel acrylic resins which can be roughly separated into porous and standard classifications, and a macroporous acrylic type. The basic properties of these materials are summarized in Table 12.

In nuclear applications, carboxylic acid resins are used in some makeup demineralizer systems where the water has a high sodium bicarbonate alkalinity. Their advantage here, of course, is that they are easily and completely regenerated with acid which frequently can be the excess acid used to regenrate the styrene-divinylbenzene sulfonic acid resin that follows them. The standard gel acrylic or the macroporous acrylic are the resins most frequently seen in this service.

The application more specific to the nuclear industry is the use of the acrylic macroporous resin as a carrier in the recycle of Uranium-233 (68-70). The carboxylic polymer, which has a very high affinity for the uranyl (UO_2^{+2}) ion is loaded with uranium from a nitrate solution. The loaded resin particles are subsequently dried and carbonized to form kernels for use in fuel rods. The chemical properties of the resin used in this application are similar to those of resins used for water treatment but the physical properties of the beads with regard to both size and shape are carefully controlled. The fact that the carboxylic polymers have poor radiation stability (29) is not a factor here since the residence time on the resin before carbonization is short.

A somewhat related use of carboxylic polymers in uranium metallurgy is disclosed in a patent application by Kunin (71). This too depends on the high capacity of the carboxylic polymers for uranyl ion which permits its uptake by the resin as a cation from carbonate leachates. The excellent regeneration efficiency of these resins with acid permits recovery from dilute feed at high concentration factors.

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CHAPTER 2

APPLICATION OF ION EXCHANGE TO URANIUM RECOVERY

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Abstract

The application of ion exchange to uranium recovery involves the study of sorption and elution processes and the effect of competing ions upon the loading of uranium on the resin.

The equilibrium loading depends solely upon the concentrations of the various ions in the solution to be treated. The rate at which the resin reaches the equilibrium loading depends upon the competition from other unwanted ions, the concentration of ions and the ratio of volumetric flow rate to resin volume as well as the resin structure, particle size and the temperature of operation.

Efficiency of elution depends upon the type and amount of eluant used and the contact time or rate at which the eluant is passed through the bed of resin. It is also dependent upon the resin structure, particle size and the temperature of the eluant. The water retention of the resin beads, which is a measure of crosslinking and porosity also has a marked effect upon the rate of exchange both on sorption and elution.

URANIUM PROCESSING CONDITIONS

Sorption of Uranium

When solutions of uranium containing an excess of free sulphuric acid are passed through a column of strong base ion exchange resin the uranium is sorbed by the resin. The uranium on the resin could be any of the following forms:

$$UO_2(SO_4)_3^{4-} \qquad UO_2(SO_4)_2^{4-} \qquad U_2O_5(SO_3)_2^{4-}$$

Usually it is the first form, uranyl trisulphate, that is encountered with most acidic leach solutions. The second form is usually encountered when the pH is high - in the region of pH2 - and when the sulphate is low. The third form is expected to be found in solutiuons where the concentration of uranium is high. It will be noted that twice as much uranium can be taken up by the resin when the uranium is in either the second or the third form.

Resin having a capacity of 1.25 equivalents per litre would have a maximum capacity for the tetravalent ion in the region of 80 g/l as U_3O_8. However, the presence of other ions that can be taken up by the resin often reduces this sorption to values which are somewhat below this figure.

The ions generally competing with uranium for sites on the resin are the bisulphate ion which is dependent upon pH, the sulphate ion and the ferric ion.

Ferric ion also forms an anionic complex with sulphate and this can be a serious competitor particularly when the molar ratio of the ferric iron to uranium is in excess of 15:1. Chloride and nitrate also compete but they only become noticeably restrictive at levels above 1 to 2 g/1.

Whilst the uranium complex is more strongly held than the iron complex the mechanism of loading results in the resin being brought to equilibrium first with the barren solution which contains ferric iron and bisulphate. This has then to be eluted off the resin by the pregnant liquor and the more iron there is the more time is required for the resin to come to equilibrium with the uranium content of the feed liquor. When the resin is finally in equilibrium, some of the ion exchange sites would still be occupied with the iron complex and the sulphate ions depending upon their relative concentrations and selectivities.

The formation of the ferric iron sulphate complex is favoured at higher pH values and consequently the competition from iron becomes noticeably stronger at pH values above 2. It has been found that when ferric iron is present in significant quantities the optimal pH for operation is around 1.5. If the pH is much lower than this there is a reduction in uranium loading due to competition from the bisulphate iron.

Other components such as silica, polythionates and some other metal anionic complexes as mentioned earlier may cause resin fouling resulting in decreased resin capacity. This has to be remedied by special regeneration treatment of the resin at certain intervals.

Contact Time

One of the most inmportant parameters in any mass transfer process such as ion exchange is the relationship of volumetric liquid flow to resin volume. This is sometimes expressed in terms of contact time which is the calculated residence time of the liquid as it flows through the resin bed. The estimated void volume of the bed divided by the flow rate through the bed gives the contact or retention time. This however, is not considered to be the best way of expressing contact time because not always is the voidage known and in any event the rate of ion exchange is mainly governed by the volume of resin and not the voids.

The most convenient manner is to express the liquid flow in equivalent resin bed volumes per hour which obviates the need to assume a voidage in the resin bed. The resin bed volume is the volume occupied by the wet settled resin and includes the resin beads and the voids.

The rate at which the resin is eluted may also be expressed in terms of bed volumes per hour. The number of bed volumes of eluant required may be estimated based on existing data or alternatively some tests carried out to determine this value. Safety factors must be applied to allow for any fall-off in the kinetics of sorption or elution.

Equilibrium Loading of Resin

The equilibrium loading for uranium can easily be established by passing the solution to be treated through a small bed of resin in a 25 mm dia. tube at a flow rate of 4 to 6 bed volumes per hour until the effluent concentration of the ion of interest is equal to the influent concentration. The resin can then be stripped completely using perchlorate or an excessive amount of acid and the amount of uranium in the eluate determined. The amount in grams divided by the volume of resin in the tube in litres will give the equilibrium loading in grams per litre.

Rate of Uranium Loading

The rate at which resin will load with uranium can be determined by passing pregnant solution through a bed of resin about 1200 mm deep in a tube 25 mm or larger in diameter at a rate of 6 to 7 bed volumes per hour. Samples of the effluent should be taken from time to time until the effluent concentration is the same concentration as the influent. The plot of such data is known as a breakthrough curve.

The slope of the curve is a function of the rate at which uranium is being taken up by the resin. If the ratio of volumetric flow rate to resin volume is increased, the slope of the curve decreases, i.e., the curve becomes longer. Likewise, if the concentration of uranium in the feed is increased whilst maintaining the same flow rate, the length of the curve becomes longer. In all cases however, the rate at which uranium is taken up by the resin increases markedly up to a concentration around 1 g U_3O_8/l and then it begins to tail off.

An important piece of information to be obtained from such a curve is the ratio of the time when the resin is essentially in equilibrium with the feed and the time at which breakthrough occurs. This ratio has a strong bearing upon the size of equipment required to satisfactorily treat the pregnant liquor. Different resins may give different ratios and it is desirable to use a resin which gives a low ratio.

If a resin column were eluted when breakthrough occurred, the amount of uranium so eluted would obviously be less than if the resin had been allowed to reach its equilibrium or saturation loading. It is therefore desirable to have two resin columns in series so that the leakage from the first column (between breakthrough and saturation) can be taken up by the second column. This demands that the aforementioned ratio be at least 2.

Rate of Uranium Stripping

Having loaded the resin it is necessary to strip the resin to determine the amount of uranium sorbed by the resin and also the rate at which it can be eluted. It must also be decided which type of eluant will be most satisfactory from the standpoint of cost, availability, effectiveness and environmental constraints. The various eluants that can be used have already been discussed.

The rate at which the uranium is stripped off the resin is mainly controlled by the laws of diffusion. Time is therefore an essential requirement for good elution and provided adequate time is allowed the amount of eluant required to elute the resin can be kept to a minimum.

Increasing the flow rate of eluant reduces the time for elution but the total volume of eluant used increases thereby increasing cost and decreasing the strength of eluate.

The rate of elution can be increased by raising the temperature at which it is carried out but it must be recognized that degradation of the resin is more rapid at the higher temperature; also the corrosive properties of the solution are usually increased thereby demanding superior materials of construction.

Elution Curve

Having decided which type of eluant to use along with the technique to be adopted, some elution tests should be made to obtain the design data. The loaded resin column used for obtaining the sorption curve should now be used for obtaining the elution curve. Eluant should be passed down the column at a flow rate generally between 0.5 to 2 BV's/hr and samples taken at intervals so that analyses for U_3O_8 can be made for plotting the elution curve. The eluate is bulked and its volume measured.

When the eluate is at a level of 0.1 g U_3O_8/l the residual uranium on the resin is about 1 g U_3O_8/l which is considered stripped to a degree that should ensure a barren of 0.001 g U_3O_8/l from the sorption column.

The plotting of the elution curve will show the number of bed volumes of eluant to strip the resin and also the rate at which the resin is stripped. The bulked eluate is then analysed for U_3O_8 and knowing the volume, the total amount of U_3O_8 stripped from the resin can be determined.

Eluant Recycle

The operating cost of ion exchange is strongly dependent upon the efficiency of elution and the costs of the chemicals involved and therefore the design of any system must reduce the amount of eluant used to an absolute minimum.

In the case of chloride and nitrate, the amount left on the resin after elution (approx. 40 g/l and 70 g/l of resin respectively) goes out and is lost in the barren solution. However, when sulphuric acid is used for elution, the bisulphate left on the resin after elution will form sulphuric acid when barren solution is passed through it and it can therefore be recovered by returning it to leach or using it for filter washing.

To recover the uranium from the eluate an alkali such as ammonia, caustic soda or magnesia is used to precipitate the uranium as yellow cake. It is therefore desirable to use the minimum amount of acid in the eluant and also to reduce the volume of eluant used to a minimum. By so doing not only is the consumption of eluant reduced but also the amount of alkali and consequently the cost of precipitation can be kept low. One way of doing this is to recycle part of the eluate.

It may be observed from the elution curve that the second half of the eluate contains much less uranium than the first half. There is also a large amount of eluant available in this second half and consequently this may be stored and used as the first half of the next elution. In this way the consumption of eluant is reduced resulting in an increase in strength of eluate.

COLUMN OPERATIONS

Design of Fixed Bed Units

The information obtained from the adsorption and elution curves may be adjusted for design purposes depending upon the conditions of testing and the type of pregnant liquor. If there is likely to be any resin fouling from contaminants in the feed liquor then due allowance must be made in the design capacity to obviate any problems in the main plant.

As previously indicated the volume of resin in the sorption column must be such that the time required for it to reach saturation at the design flow and concentration of pregnant liquor is longer than the time required to elute a column of resin.

In addition, some time must be allowed for the backwashing and rinsing of the resin (which could take 90 mins, or so) and also some standby time which preferably should be 20% or more of the total adsorption time in order to take care of any surges in flow or increases in feed concentration.

The time required for satisfactory elution is usually the controlling factor in the design of fixed bed columns and accordingly the flow of feed solutions to the sorption columns must be such that breakthrough on the second column on sorption does not occur before a freshly eluted column is available to be placed on line.

It will be appreciated that for a constant feed flow rate in m^3/h the smaller the flow rate in BV's/h the larger is the volume of resin in each column.

Fixed Bed Systems

The first application of ion exchange for uranium recovery was in South Africa in the early 1950's. The type of system comprised three columns piped and valved in such manner as to enable any two columns to be operated in series on sorption whilst the third is being eluted. The details of this process is fully described elsewhere [1]. This has been referred to as the "Merry-go-round" system and is shown diagrammatically in Figure 1. These systems have been installed in South Africa, Australia and elsewhere, and in Canada alone over 50 such three-column sets were installed during the late 1950's. These were designed to treat clarified acid leach liquors containing 0.6 to 1.0 g U_3O_8/l some of which are still in operation in 1984. The elution is carried out automatically employing electro-mechanical equipment comprising timers and volumetric counters.

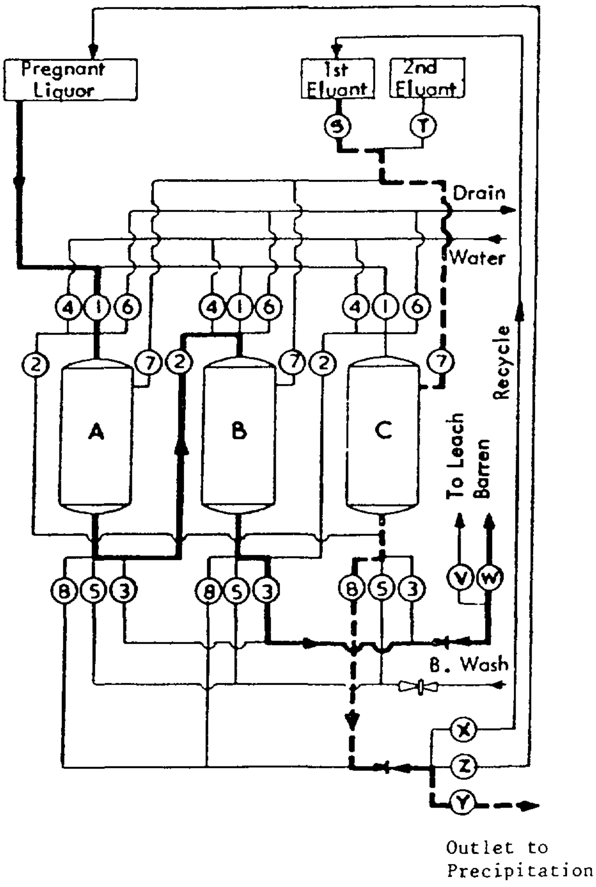


FIG. 1: THREE COLUMN SET FOR URANIUM EXTRACTION

Moving Bed Systems

Following upon the design of the fixed bed units already described in which the elution of the resin is carried out in the same column as the sorption, another approach was made to increase the efficiency of operation. This is known as the Porter-Arden moving bed system and is used at Denison Mines in Elliot Lake, Canada.

The principal departures of this system from the usual fixed bed approach are:

1. Three columns are used in series-sorption allowing for higher specific flow rates to be employed.

2. Three columns are used in series-elution resulting in lower eluant consumption and a shorter time between eluted columns becoming available.

3. A separate column for backwashing the resin and acting as a holding tank between resin transfers from the sorption sets to the elution set.

The system comprises two sets of 3 sorption columns linked to one backwash column and one set of 3 elution columns. The columns in the sorption and elution sets are piped and valved in such manner as the "Merry-go-round" concept and is shown in Figure 2.

When the resin in the leading sorption column is saturated it is transferred to the backwash column. The empty sorption column is then immediately filled with eluted resin from the leading column of the elution set and then becomes the third or trailing column on sorption. This type of system enables the ion exchange zone to extend over two sorption columns thereby allowing the columns to be operated at higher linear velocities of liquid flow.

After the loaded resin is backwashed, it is transferred to the empty elution column which then becomes the trailing column on elution. This enables the volume of eluant to be applied in three equal amounts instead of two (as practised with fixed bed columns employing recycled eluant) which increases the strength of eluate and also enables a column to be made available for sorption in a shorter space of time.

The sorption and elution columns are almost full of resin as they do not require any freeboard for backwashing the resin. Also there are fewer controls required than are customary on fixed bed systems where each set must have flow controllers for sorption, backwash and elution.

There are several of these resin movement plants installed in Elliot Lake, Canada in the late 1950's using 2450 mm dia. (8' -0") pressure vessels for containing the resin.

It takes about 20 minutes to transfer approximately 13 m^3 resin at a liquid flow of 22 m^3/h. At the end of that time it has been found that about 30 to 60 litres of resin remain at the bottom of the unit. This is of no consequence in the backwash and elution columns but it is most undesirable in the case of the sorption columns. The loaded resin left behind is immediately covered with eluted resin from the elution set and the column is placed in the trailing position on sorption. The "Royal Barren" effect so produced necessitates recycling back to leach a large percentage of the barren. The recycling of 20 - 25% was not uncommon but even so the average barren effluent to tailings

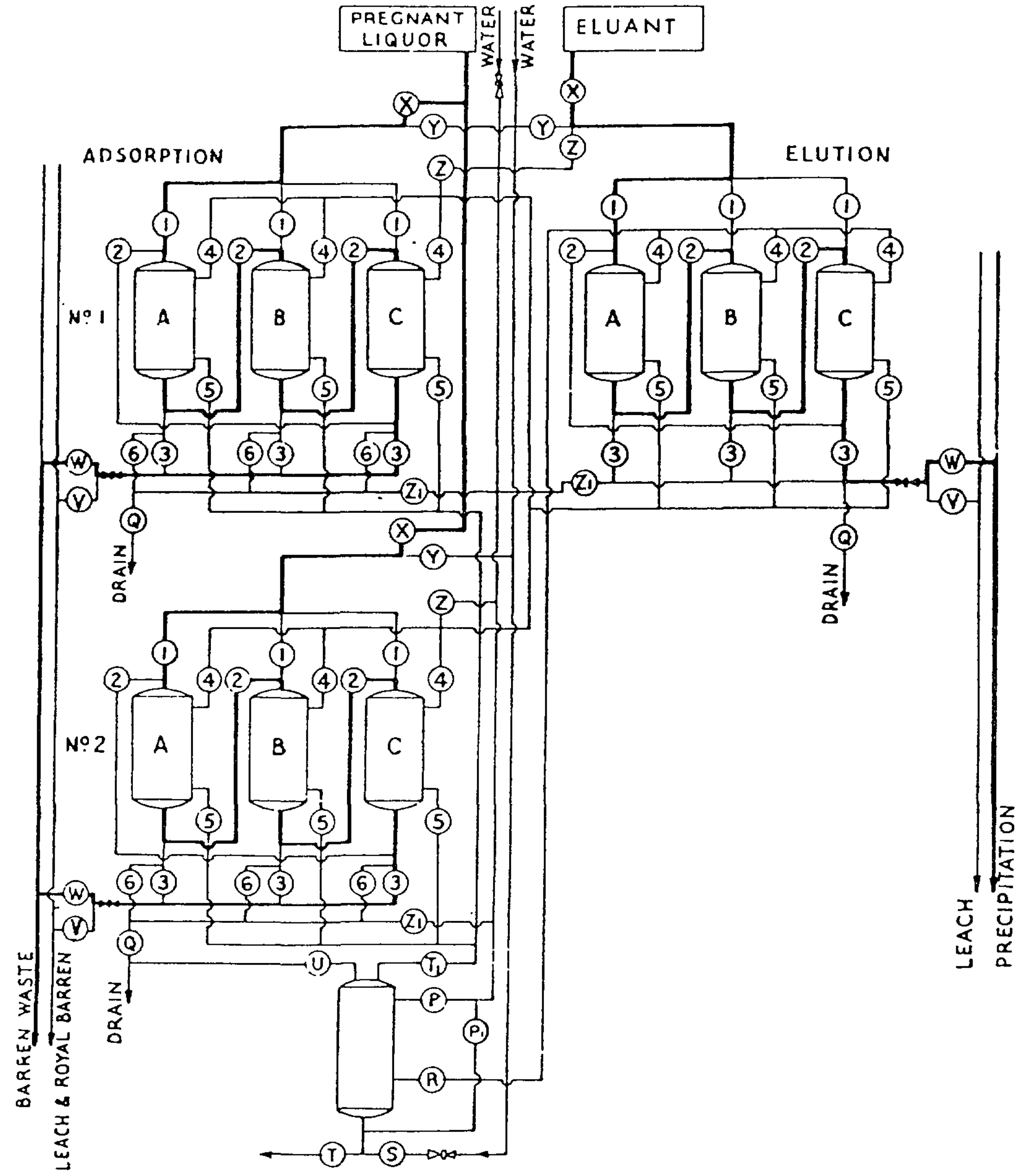


FIG. 2: PORTER-ARDEN MOVING BED SYSTEM

was often in excess of 0.005 U_3O_8 as compared with less than 0.001 g U_3O_8/l from fixed bed systems in the same area.

These systems were automated so that all the resin transfers and elutions were conducted automatically. A more complete description is given elsewhere [2].

Resin Attrition

In any ion exchange system there is some replacement of resin required from time to time. The life of resin depends upon many factors, the principle ones being:-

1. the material from which the resin is made.
2. the physical forces to which it is subjected in use.

3. the swelling and shrinking which may occur when going from one ionic form to another.

Most resins in use today are based on a co-polymer styrene and the methods used by the major resin manufacturers result in a fairly robust material. Nevertheless, it is important to minimize the rate of attrition by taking suitable precautions in the design of systems.

During the formation of the resin beads there are usually some internal stresses which result in cracks appearing in the finished material. These show up quite clearly under a microscope and it is these beads which will break down most quickly in use. When a new batch of resin is placed in operation therefore the first 30 to 50 cycles should see most of these cracked beads broken down and removed during normal backwashing as resin fines. Thereafter the rate of attrition should fall to a steady level established by mechanical and chemical effects. The fixed bed systems in Elliot Lake are reported to have a resin make-up of 2 1/2% per annum although there are no firm records to substantiate this. The moving bed systems have been shown to have a resin make-up of about 10% per annum.

The mechanical forces which affect attrition are such things as high presure losses across the resin bed. This could be the result of excessively high flow rates or an accumulation of dirt or slimes on the resin. The resin being a polyelectrolyte acts as a very effective filter and a dense mat of such arrested impurities can readily form on the surface of a packed bed of resin and cause a considerable resistance to flow. Sometimes resin fines, if not backwashed from the bed, will themselves cause a considerable increase in pressure loss. This is because these smaller particles of resin in the bed will reduce the voidage. The pressure loss through the bed is greatly affected by voidage since it varies inversely as the third power of the voidage.

It also must be recognized that the resin beads can be deformed under pressure and this decreases the void volume. For example a bed of polystyrene bead resin 1000 mm deep may be compacted by 40 mm when subjected to a superficial flow of 180 m/h (75 U.S. gpm/ft^2). If we assume an initial voidage of 0.4 then this is reduced to 0.375 and the pressure drop increases by 18%. However, any traces of suspended matter at such flow rates will increase this loss dramatically.

A point of interest here which is worthy of further study is the observation by Golding & Irving [3] that the predicted increase in pressure loss through a compacted bed is somewhat greater than that actually found in practice. An explanation they offer is that only part of the volume change is due to a reduction in voidage. The remaining volume change must be by squeezing water out of the beads thus decreasing their size. This could adversely affect the kinetics of exchange thereby requiring longer contact times.

In Elliot Lake the fixed bed systems are operating at flow rates in the region of 10 m/h superficial velocity (4 U.S. gpm/ft^2). In South Africa it is usual for fixed beds to operate at lower rates in the region of 4 to 7 m/h due to the lower rate of ion exchange caused by competition from other ions and blockage of resin pores with silica.

The larger the diameter of the resin bead the smaller is the pressure drop through the bed. However, the rate of ion exchange with coarse beads is slower because there is less surface area of the beads per unit volume of wet settled resin since this varies inversely with the diameter of the beads.

The elution or regeneration of the resin must be done so as to minimize the change in volume when going from one form of the resin to another. The sudden contraction of a resin bead brought into contact with a strong electrolyte creates stresses on the resin which can shatter the outer shell and this may then peel off like an onion skin. This type of failure generally referred to as osmotic shock, is more common when the resin is in its most swollen form, i.e. the hydroxyl form and is brought into contact with a strong acid in the region of 20% - 30% H_2SO_4.

Treatment of Eluate

As mentioned earlier the uranium is precipitated from the eluate as yellow cake and this involves raising the pH by adding an alkali such as caustic soda, magnesia or ammonia. Ammonia is most frequently used but environmental regulations are causing uranium producers to look toward lime and magnesia. Iron being less strongly held by the resin is eluted off first so that a separate cut can be made if the iron is of a significant amount. Sometimes the first two bed volumes or so containing the iron and some uranium are returned to leach.

A two stage precipition of the eluate is generally employed, in the first of which a small amount of lime is added along with ammonia (or other alkali) to raise the pH to around 3.5. This causes the precipitation of gypsum for reduction of sulphate and the ferric iron. By adding more alkali the uranium is precipitated around pH 6.5 which is used to make up fresh eluant.

This barren eluate contains sulphate that has been eluted off the resin with the uranium and this should not be allowed to build up to more than about 30 g/l when nitrate is used for elution. Chloride can elute satisfactorily at somewhat higher levels but the gypsum precipitation can conveniently keep the sulphate under control.

Eluex

When sulphuric acid is used as an eluant, the amount of free acid in the eluate is generally such that some recovery system is required to reduce the cost of operation. It is usual for fixed bed systems to send the strong eluate to a solvent extraction plant to extract and further concentrate the uranium and return the acid raffinate for further use as an eluant. The solvent used also makes a satisfactory separation of any ferric iron and other impurities that may have been taken up by the resin thus obviating the need for the precipitation of iron. This treatment of eluate by solvent extraction is referred to as an Eluex system in North America and as Bufflex in South Africa.

Royal Barren

When the resin is eluted the majority of its active sites are occupied by the ions that have displaced the uranium. However, there will still be some uranium left on the resin as it would require an excessive amount of eluant to strip off all the uranium. The amount usually left on the resin is about 1 g U_3O_8/l or below which is the level at which barren effluents in the region of 0.001 g/l or less can be achieved.

The eluted column of resin is placed in the trailing position of the sorption columns so it receives barren solution from the preceding column. The exchangeable anions in the acidic barren solution displaces the eluting ion from the resin and depending upon the type of ion used for elution will form hydrochloric, nitric or sulphuric acid until all the eluting ions have themselves been eluted. This wave of acid passing through the bed along with any residual eluant left in the resin bed will strip off some of the few remaining uranium ions on the resin and result in what is termed a "Royal Barren". Because of the uranium content the first few bed volumes are usually returned to the leach circuit. It will be perceived that this will also introduce chloride or nitrate ions in the leach liquor. Since chloride and nitrate ions compete with uranium for sites on the resin the build-up in the leach circuit of such ions must not be allowed to reach such levels as to reduce the loading of uranium to any serious degree.

The concentration of nitrate in the Royal Barren can range from 10 to 15 g NO_3/l resulting in the uranium content being around 0.05 to 0.1 g U_3O_8/l. When this is returned to the leach circuit the nitrate content in the pregnant liquor may fluctuate between 0.7 to 1.0 g NO_3/l.

Sorption from Alkaline Solutions

The sorption from alkaline leaches depends upon the concentration of uranium, carbonate and bicarbonate in much the same way as in acid leaching where it is dependent upon uranium sulphate and bisulphate. High concentrations of carbonate or bicarbonate result in low uranium loadings on the resin. At ambient temperatures the best uranium loadings are obtained around pH 10 and above.

Interference in the loading of uranium is also experienced from sulphate, chloride and nitrate ions but for a given concentration they depress the uranium loading to a greater degree than in the acid leaching process. This reduces the possibility of re-circulating any "Royal Barren" to the leach circuit since the build-up of chlorides, nitrates or sulphate could seriously affect the loading of uranium.

Anionic complexes of phosphate, aluminate and molybdate are much less strongly held than the uranyl tricarbonate complex so that a fairly good separation is effected by ion exchange from such solutions.

The competition from vanadium in alkaline solutions depends upon the pH of the solution and when vanadium is present it is preferable to operate in the region of pH 11 or so. At pH 9 vanadium can displace the uranyl tricarbonate ion quite effectively and as suggested earlier, it presents an interesting possibility for the recovery of uranium and vanadium in separate fractions.

Elution of Uranyl Tricarbonate

As already known, chloride, nitrate and sulphate will displace uranyl tricarbonate ions and the lowest cost anion of these is chloride. As a result, sodium chloride is often used as an eluant but suitable care must be taken to prevent the concentration of chlorides building up to such levels in the leach circuit that it interferes with uranium loading. Ammonium chloride with some carbonate is another type of eluant in use.

In much the same way as acid is added to the eluting agents of uranyl trisulphate so is it found desirable to add some bicarbonate to the chloride solution for most effectively eluting uranyl tricarbonate.

Chloride eluants usually are between 1 to 1.5 molar and the amount of bicarbonate to insure good stripping is in the region of 0.2 to 0.5 molar.

Ammonia can also be used for elution along with CO_2 for the formation of bicarbonate. Such a technique enables recovery of ammonia from the eluate to be obtained for recycling. It also overcomes the problem of contaminating the leach liquor with competing anions.

Types of Resin in Use

The most common resins used for uranium recovery in North America and South Africa are the gel type strong base polystyrene bead resins examples of which are Rohm & Haas IRA 400, Dowex 21K, Duolite A101D and Ionac 641.

There has been some application of macroreticular weak base resins with the intention of obtaining a better separation of iron and uranium. However, such resins are relatively slow in sorption and elution rates and the uranium loading of the resin has been found to be somewhat less than for strong base resins; levels of 30 - 35 g U_3O_8/l are not uncommon when treating a 1 g/l pregnant solution. Being a macroporous resin, it is prone to blockage with silica which contributes to its slow exchange rates. Because of its tertiary ion exchange groups it can make a better iron separation on the average leach liquor than the quaternary groups of the strong base resins and it can be eluted with a lower volume of eluant. However, the weak base resins presently available do not appear sufficiently attractive for use in uranium extraction at this time.

The particle size of the resin must be chosen to suit the particular application for which it is intended. The smaller the particle size, the more rapid are the exchange rates but the pressure loss through a packed bed of small resin beads becomes significantly greater at any given flow rate as it varies inversely with the square of the diameteer of the bead.

If the resin is to be used in a fluidized bed, then some consideration must be given to its density and particle size from the standpoint of its fluidization properties. For dilute solutions, a large bead resin with its slower exchange kinetics may enable uranium to be extracted at a faster rate than using a smaller bead for which the flow rate must be restricted to prevent elutriation of the resin from the column.

The settling rate of the resin becomes more important when dealing with leach liquors containing large amounts of suspended matter. Leach pulps containing 7% to 10% solids have not only a higher apparent density but also the viscosity may be affected by the nature of the solids in suspension.

Recognizing this fact,there has been some attention given over recent years to the development of an ion exchange resin having a greater density than those presently available. In recent years Sentrachem Limited in South Africa have developed a heavy resin named Senbrix but no commercial experience is available at this time.

Resin-in-Pulp

For many years considerable attention has been given to methods whereby ion exchange resin beads can be loaded with uranium without first having to clarify the pregnant solution thus saving space, capital and operating costs [4].

Early attempts were made employing stainless steel baskets moving up and down in tanks arranged to operate in a counter-current fashion [5]. At the Anaconda Company's Blue Water plant 14 tanks 5' x 6' x 50' long were installed in series each of which contained ten 4' cubicle baskets. When the resin in the first tank is saturated, the tank is drained and rinsed and a new tank containing eluted resin is added at the end of the series. The tank containing the loaded resin is then added to the series of tanks forming the elution section in which it becomes the last tank on line. When the resin is completely eluted it is rinsed and made available for use in the sorption section. These installations were very cumbersome and the resin attrition was found to be excessive. The high maintenance costs for the baskets and associated mechanism led to the abandonment of the process and in 1983 there could have been only one of those installations in service.

A different approach was made by Homestake Mining in treating a large volume of mine water from a drainage ditch. Downflow operation was unsuccessful because the slimes blinded the resin bed. They used two 14' dia. x 8' deep tanks each containing 400 cu. ft. of resin. Upflow operation in series was carried out and when the first column was loaded the resin was removed and taken by truck to the mill 16 miles away for elution [6].

Other fluidized systems have been installed for treating acid leach liquors comprising a series of tanks through which the slurry and resin passed in counter-current direction. Agitators in each tank keep the resin mixed with the slurry and an air lift or a pump is used to take the resin from one chamber to the next. The tanks are at different elevations to obtain gravity liquid flow but the resin is carried up by an air lift (or pump) to some stainless steel Sweco screens which separate the resin from the slurry. The slurry is transferred downstream to the next tank and the resin is transferred upflow to the preceding tank. A typical screen-mix resin-in-pulp system is shown in Figure 3 [7]. Western Nuclear installed eight sorption vessels 13' dia. x 14' high operating at 3.75 gpm/sq.ft. and loadings of 2.5 lbs. U_3O_8/cu. ft are reported. There are fifteen 7' dia x 8' deep elution vessels operating at 1.25 gpm/sq.ft. producing a strong eluate of around 12 g U_3O_8/l.

Other installations of equipment employing a number of tanks with air lift similar to Western Nuclear are Atlas Minerals Corporation, Moab Mill, Federal American Partners' Mill and Union Carbide Corporation Gas Hill's plant. The latter has six stages

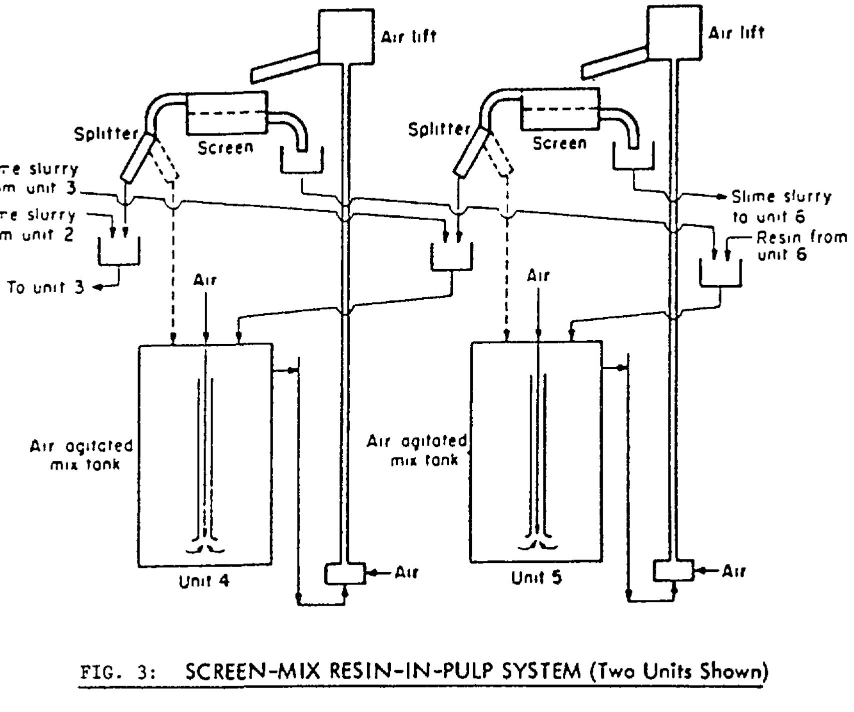


FIG. 3: SCREEN-MIX RESIN-IN-PULP SYSTEM (Two Units Shown)

on sorption and ten on elution and the average loading of the resin is 3 lbs/cu. ft. These systems have been well described and illustrated by Merritt [8].

Most of these mills are in the United States in areas where the slimes are very difficult to separate as compared to the Elliot Lake area where separation is somewhat simpler due to the structure of the ore.

Advantage of Fluidized Beds

There are some distinct advantages in using a liquid fluidized bed of ion exchange resin instead of a packed bed, among which are:

1. Low pressure drop - approximately equal to the weight of the suspended particles per unit area of bed.

2. Suspended solids can pass straight through the bed - thus avoiding the need for prior filtration when solids removal is not mandatory for other reasons.

3. Any change in volume of resin resulting from mass transfer can easily be accommodated. This avoids possible crushing of resin in those cases where the resin expands in volume during its loading cycle.

Continuous Ion Exchange

For many years there has been an interest in ion exchange systems which can operate continuously instead of the batch type process characterized by fixed bed systems. Continuous ion exchange processes offer economic advantages in those cases where large amounts of ions are required to be exchanged per day. This is because the resin inventory in a continuous system would be much less than that required by a well designed fixed bed system for the same recovery process. Such systems therefore are particularly suited to hydrometallurgical processes or any other application where the product of flow and ionic concentration is high.

The fluidized bed systems described earlier employing a number of tanks arranged horizontally in series could, when automated, be considered as a continuous ion exchange system. However, the amount of space taken up by the tanks along with the provision of screens for separating slimes from the resin with the consequent maintenance of those screens and the number of pumps or consumption of air for resin transfer resulted in attempts being made at having one tall column containing fluidized resin.

It is known that when the density difference between the fluid and particles is small, the entire bed expands uniformly and particulate fluidization is achieved. Any differences in settling velocities of particles due to size or density lead to segregation or classification and when dynamic equilibrium conditions are achieved the larger particles are below. There is no gross mixing other than the disturbances created within the fluid stream lines and the small amount caused by the coarser particles passing through the bed during the segregation.

The moving and fluidized particles create a "choke " effect upon the rising liquid and a steady state turbulence is achieved.

This is local and much less circulation of particles occurs than is generally observed with gas fluidized beds. If there is no excessive disturbance apparent on the surface then it is an indication that good flow distribution is achieved.

In 1951 a process was investigated in which a vertical fluidized bed ion exchange column containing a strongly acidic bead type cation resin was used for the extraction of copper [9]. It was observed that the degree of longitudinal mixing of the resin is influenced by differences in diameter or density of the particles in the bed. From the principles of elutriation a bed is classified with the largest beads at the bottom Such classification is undesirable in a continuous system and it is therefore necessary that resin particles of nearly uniform diameter should be used. However, in a continuous ion exchange system it is necessary that the resin be moved around from the sorption section to the elution section and therefore some resin attrition must occur which will destroy any initial uniformity of resin particle size.

Over the years a number of systems have been proposed and many patents taken out of various designs. These have included systems in which the resin bed is compacted as well as many systems where the resin is fluidized.

Many of these have been reviewed by Slater [10] but only a few have been used in full scale commercial plants. It is proposed to mention only those which are presently being applied to recovery of uranium from leach liquors.

Higgins Column

The first of these is a packed bed system which was invented around 1950 by I. Higgins at Oak Ridge National Laboratory.It was developed by Chemical Separations in Tennessee and has been used for water softening and chemical recovery systems. The description of the process has been given by Higgins [11] and it is depicted by Figure 4.

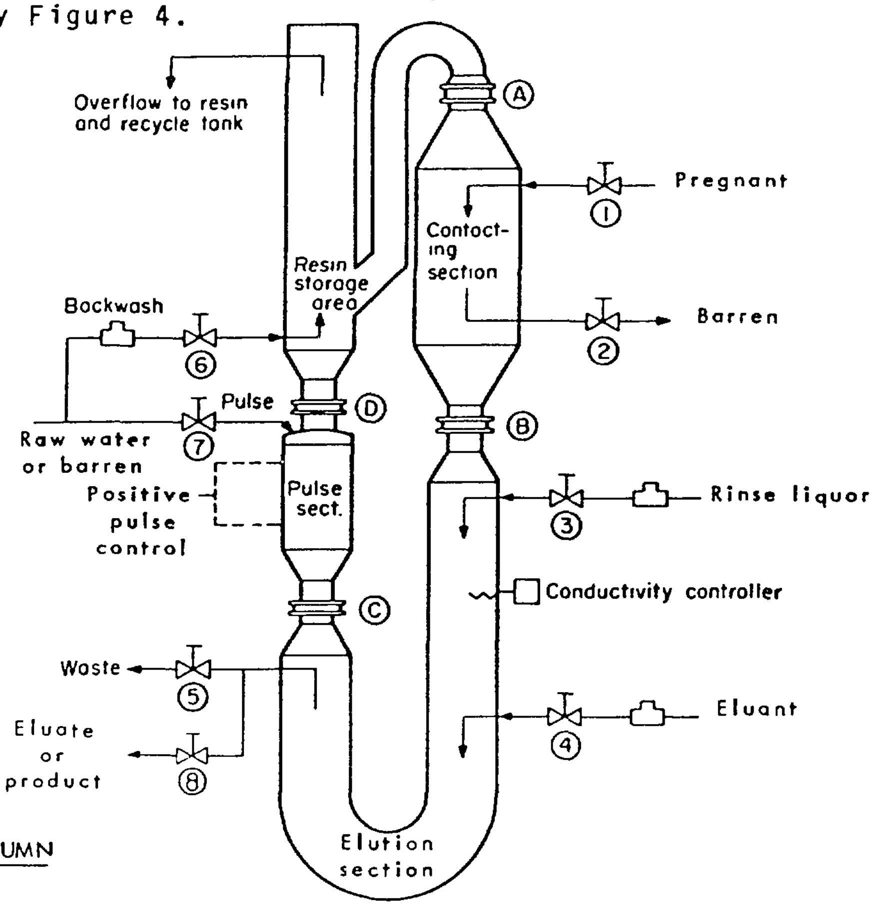


FIG. 4: HIGGINS COLUMN

It comprises a loop around which resin is moved in slugs. The resin moves upwards in the Contacting Section where sorption takes place and the flow of liquid is counter-current to the flow of resin. At the same time eluant is passing through the eluting section of the loop again in a counter-current direction. The sorption and elution sections contain horizontal flow distributors and collectors of the Johnson Well Screen type and are usually made of 316 stainless steel wedgewire with suitable reinforcement.

The feed and eluant flows are interrupted after several minutes of operation to allow eluted resin to be pulsed into the bottom of the contacting section. The period of the sorption cycle may be from 5 to 20 minutes or more depending upon the feed flow rate and concentration. During this time valves A, B, C and D are closed and elution is proceeding. At the end of the sorption cycle valves A, B and C are opened and water under pressure from an hydraulic accumulator is introduced into the Pulse Section through valve 7 which forces resin to move smartly around the loop. Valves A, B and C are then closed and the feed solution and eluant solution flows are resumed. The time for movement of resin is usually less than a minute so that the ratio of sorption time to resin movement time is large.

When the resin is pulsed around the loop, the liquid in the eluant loop is also displaced with resin. This requires a flow of rinse water to enter through valve 3 until the eluant is restored to its proper position as indicated by the conductivity controller. The eluting solution displaces the pulse water through the waste valve 5 which then closes and valve 8 opens to allow product or strong eluate to be recovered. This displacement is also controlled by a conductivity probe.

The resin that was displaced from the Contacting Section goes to the Resin Storage area in which it is backwashed by opening valve 6. The washed resin is allowed to fall intermittently by gravity into the pulse section by opening and closing valve D. When the pulse controller senses that the correct volume of resin has settled in the Pulse Section the cycling of valve D ceases and the resin is ready for transfer on the next resin movement cycle.

As the resin is in a packed form, the flow rates can be somewhat higher than are achieved in systems which employ fluidized beds of resin. However, the pressure loss across the bed at very high flow rates can result in short resin life. Also, the pressure required to drive the resin around the circuit, through butterfly valves and converging cones and around the flow distributors and collectors can be very high. This is usually between 400 to 550 kilopascals (60 to 80 psi) and indicates the high frictional forces in the loop. The butterfly valves operate in the resin stream and these open and close rapidly on the resin which must be extremely tough if the resin attrition is to be low. Nevertheless, there are some situations where such a system has been shown to have merit and these are usually when the flow rate and the frequency of pulses are low and the liquid going through the system contains very little suspended matter.

Two 2400 mm dia (8'-0") units for uranium recovery were installed in 1977 for Wyoming Minerals Corporation to extract uranium from copper leach solutions at the Bingham Canyon Mine of Kennecott Copper Corporation [12]. These were designed to treat a flow of 7600 U.S. gpm (1727 m_3/h) containing about 6 to 7 ppm U_3O_8 which shows a specific flow rate of 67 U.S. gpm/ft^2 or 163 m/h. It was found that the high flow rate resulted in excessive pressure losses which resulted in crushing the gel type resin. To correct this the length of the sorber section was reduced from 8'- 0" (2440 mm) to 5'-0" (1525 mm) and an additional unit was added which brought the flow rate down to 45 U.S. gpm/ft^2 (110 m/h). Also the gel resin was replaced with macroreticular or macroporous resin. The resin is regenerated with 3 N H_2SO_4 and produces an eluate of 0.5 to 1.0 g U_3O_8/l which is subsequently upgraded by solvent extraction (Eluex) to around 35 g U_3O_8/l. The barren effluent is usually around 0.5 mg U_3O_8/l. Resin replacement due to attrition and loss of kinetics is reported to be about 70% of the inventory per annum.

U.S. Bureau of Mines Column

In the 1960's two systems were developed in which a vertical column is divided into separate compartments by horizontal perforated baffle plates. One of these units as developed by the U.S. bureau of Mines is shown in Figure 5 [13,14].

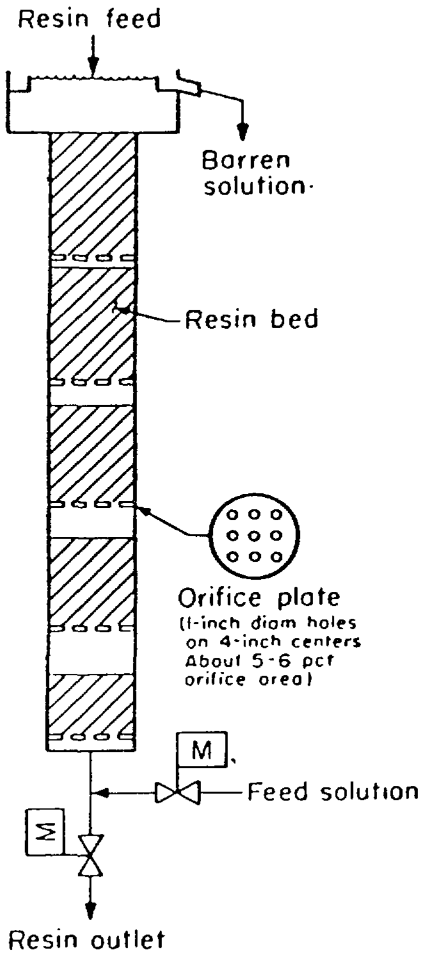


FIG. 5: Multiple compartment ion exchange column,

U.S. BUREAU OF MINES

The perforations in the baffle plates, dividing the compartments represent about 5% of the cross-sectional area of the column.

Each of the compartments contains resin and the upward flow of liquid prevents the resin from falling through the holes in the baffle plates.

When breakthrough occurs at the top of the column, the flow is stopped and a reverse flow enables loaded resin to be removed from the bottom of the column to be eluted. At the same time, resin falls down the column from one chamber to another and eluted resin is fed into the top.

The loaded resin is fed into the top of a tall elution column of similar design to the sorption column where it meets an upward flow of eluant. The strong eluate passes from the top of the column whilst the eluted resin is drawn from the base of the column.

Detailed descriptions give performance data on various solutions ranging from 0.009 g U_3O_8/l to 0.74 g U_3O_8/l. Resin loadings from 37 g/l to 76 g/l are reported and strong eluates of 23.8 g U_3O_8/l were obtained when eluting resin containing 72 g U_3O_8/l. On dilute solutions (9 ppm U_3O_8) flow rates up to 19.5 gpm/ft^2 were achieved with a 98% recovery of U_3O_8 when loading the resin up to 46 g U_3O_8/l.

Messrs George and Rosenbaum [14] state that "an essential requirement for the successful operation of the multiple compartment column is a resin of uniform particle size... Resins of conventional mesh size 0.3 to 0.8 millimeters diameter (20 to 50 mesh) cannot be used because the resin particles classify according to size and the finer particles either accumulate on the upper sections or overflow". The accumulation of small, partially loaded resin particles in the upper sections militates against obtaining low barren values. A durable and closely sized resin is therefore desirable for use in this system.

Systems of this type are in operation in various locations of the United States. Operational data has been published by George [13].

Cloete-Streat Column

A somewhat similar column was developed in England at Imperial College by Cloete and Streat [15,16].

The sorption column is divided into a number of sections by horizontal perforated plates. Two perforated baffle plates for each compartment are placed fairly close together with the open holes offset. The purpose of this is to ensure that when flow stops the resin does not all fall through the perforated plates and settle at the bottom of the column. Liquid enters the bottom of the column and eluted resin is fed into the top of the column. See Figure 6.

When solution is flowing up through the adsorption column each compartment will be filled to the full depth by the expanded resin bed. If the flow increases the excess resin moves up into the next compartment whilst if the flow decreases the compartment will be only partly filled by the fluidized resin bed.

Periodically the resin is removed from the bottom of the column and fed into the top of an elution column. To move the resin from the sorption column the liquid flow is first stopped to allow the resin to settle in each compartment. A valve is then opened at the bottom of the column and the liquid flows down the column thereby allowing the resin to flow from the bottom of the column and at the same time causing resin to go downward in the column and through the baffle plates separating the compartments. This downward flow is timed to allow only a portion - say 20% to 25% - of the resin from each chamber to pass down the column.

The resin from the bottom of the column is slurried to the top of an elution column and the carrying liquid is separated over a screen at the top of the column. The resin is eluted by an upward flow of an eluant and operates in a similar manner to the sorption column. Periodically resin is discharged from the bottom of the elution column, washed and sent to the top of the sorption column.

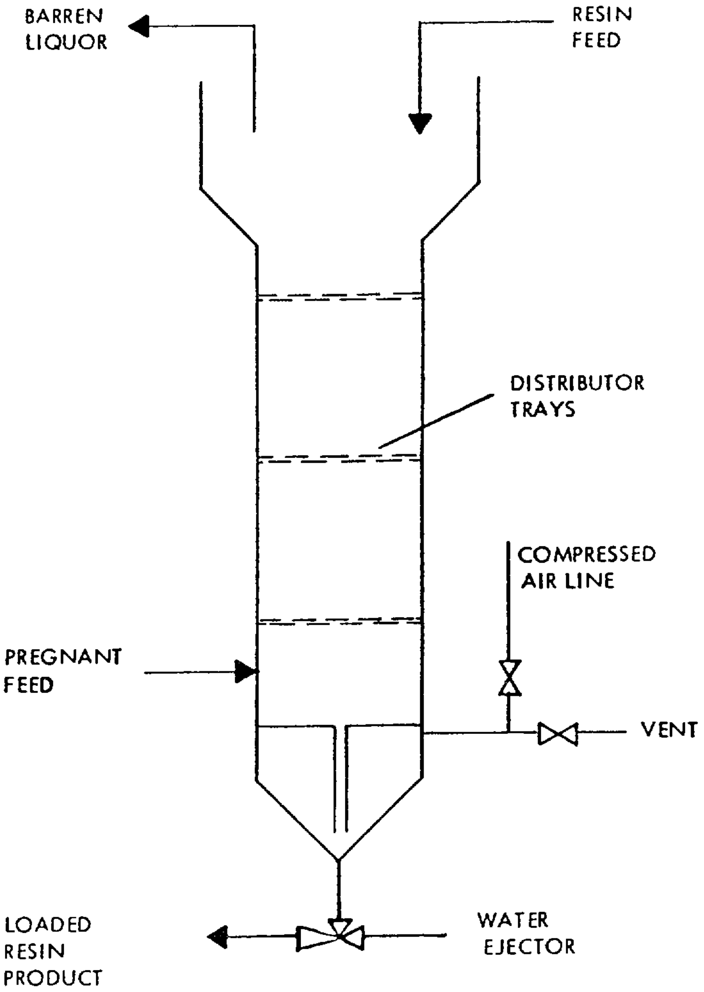


FIG. 6: SCHEMATIC DIAGRAM OF THE CLOETE-STREAT COLUMN AT IMPERIAL COLLEGE

This design has been adopted with minor modifications by Davey Power-Gas [17] and the National Institute of Metallurgy of South Africa. An installation by D.P.G. is in operation in South Africa at the Randfontein Millsite Plant and another at their Cooke Plant. A diagrammatic arrangement of the D.P.G. system which is typical for all systems based on the Cloete-Streat design is shown in Figure 7.

National Institute of Metallurgy Column (NIM) South Africa

A fluidized bed system based on the design of Cloete-Streat has been developed in South Africa to recover uranium from unclarified leach liquors. A stainless steel sorption column 2.5 m diameter (8'-0") was installed as a demonstration plant at Blyvooruitzicht Gold Mining Company Limited complete with fiberglass elution column. The baffle plates between the stages have smaller holes - around 12 mm diameter - and the total free area is between 1% and 2% as against 5% or so on other systems. No precautions are taken to prevent resin falling through the plates during shut down but as the holes are small the rate of resin discharge would be fairly slow.

At the design flow, the resin almost fills all chambers except the top chamber. There is a small free space at the top of each bed due to the upper particles of resin being swept up

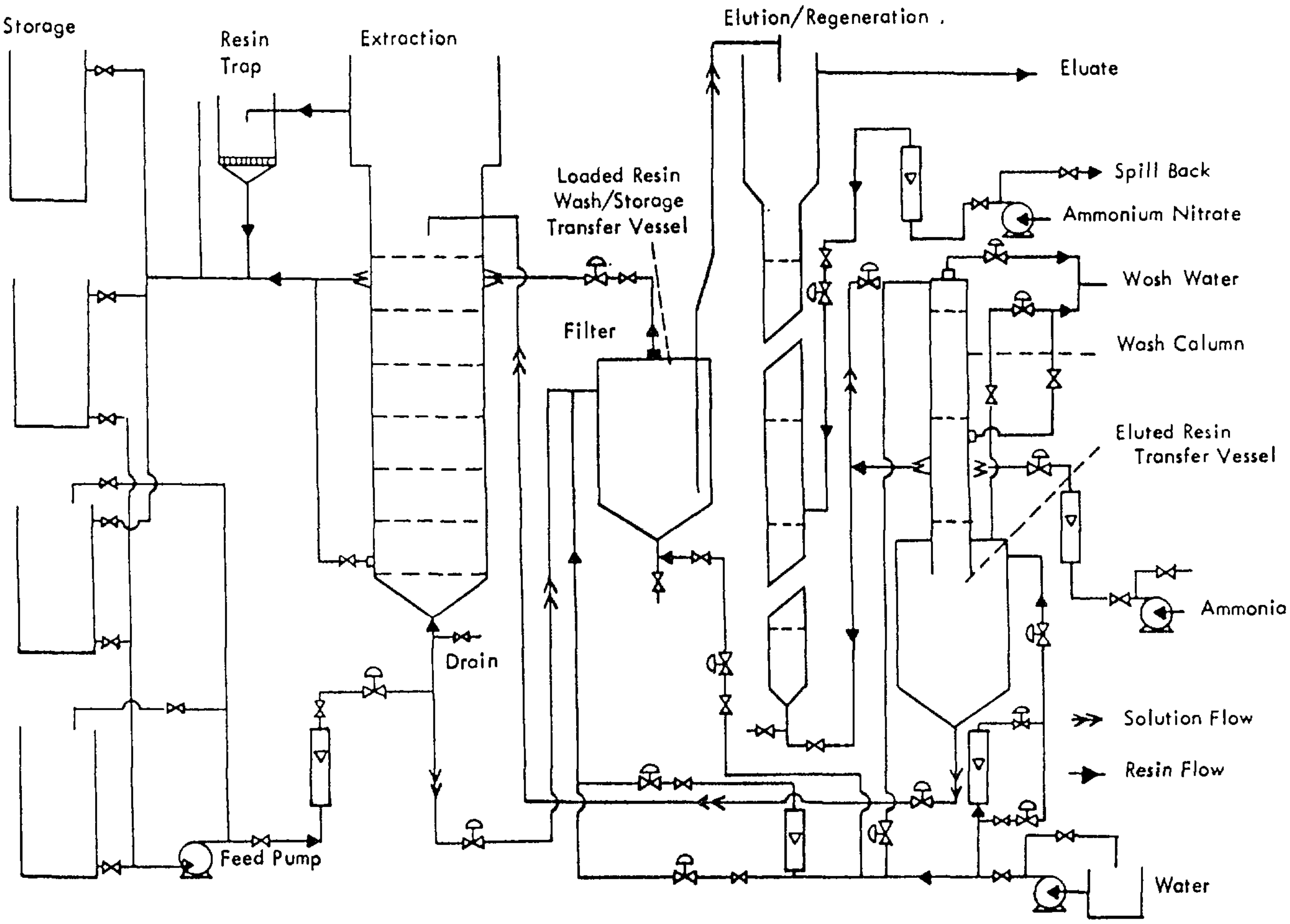


FIG. 7: DIAGRAMMATIC ARRANGEMENT OF CLOETE-STREAT SYSTEM - DAVY POWER GAS LIMITED

into the chamber above by the increased velocity as the liquid approaches the perforations in the dividing plates.

When it is required to move resin from the column, the flow is stopped and a valve at the bottom of the column is opened which allows a reverse flow of liquor to occur. This causes resin to be carried down from chamber to chamber. The bottom chamber has a restricted outlet for the resin so that the resin is transferred between the upper chambers at a faster rate. This is done to ensure that when forward flow starts again there is more resin on each stage than can be contained in the fluidized state and this excess of resin per stage is redistributed over the column length when forward flow is resumed. This causes some degree of resin and liquid backmixing but it is preferable to having unequal batches of resin in each chamber which is what would happen without the restricted outlet on the bottom chamber.

The results of the 2.5 m demonstration plant were sufficiently encouraging for two 4.25 m dia. units to be installed at Blyvooruitzicht and these have been in operation since the latter part of 1977.

There has been some data [18,19] provided on the performance of the 2.5 m diameter demonstration unit. The conclusions were that such systems are mechanically and metallurgically sound and they can handle suspended matter with a low resin attrition loss of only 3% per annum. Operational details of the 4.25 m diameter system are given in a paper by D.W. Boydell [20].

The top section of the sorption and elution columns of the U.S. Bureau of Mines and those based on the Cloete-Streat design are about 50% larger in diameter than the main body. This is so that the superficial velocity at the top of the column is reduced thereby preventing loss of resin by elutriation particularly when resin is being added to the top of the column.

Porter Fluidized Bed System

Another type of continuous system has been patented [21] an arrangement of which is shown in Figure 8. This is somewhat similar to the systems described earlier for Federal American Partners, Union Carbide and Western Nuclear with the exception that there are no screens for separating the resin and pulp in transferring from one chamber to the next. The patent states that the resin in the first vessel of the series may be removed in a batch operation which may involve the entire volume of resin in the one chamber at one time or, which is more to be preferred, there may be a continuous withdrawal of ion exchange material therefrom by means of an air lift over a period of time. This method of resin transfer results in backmixing of liquid.

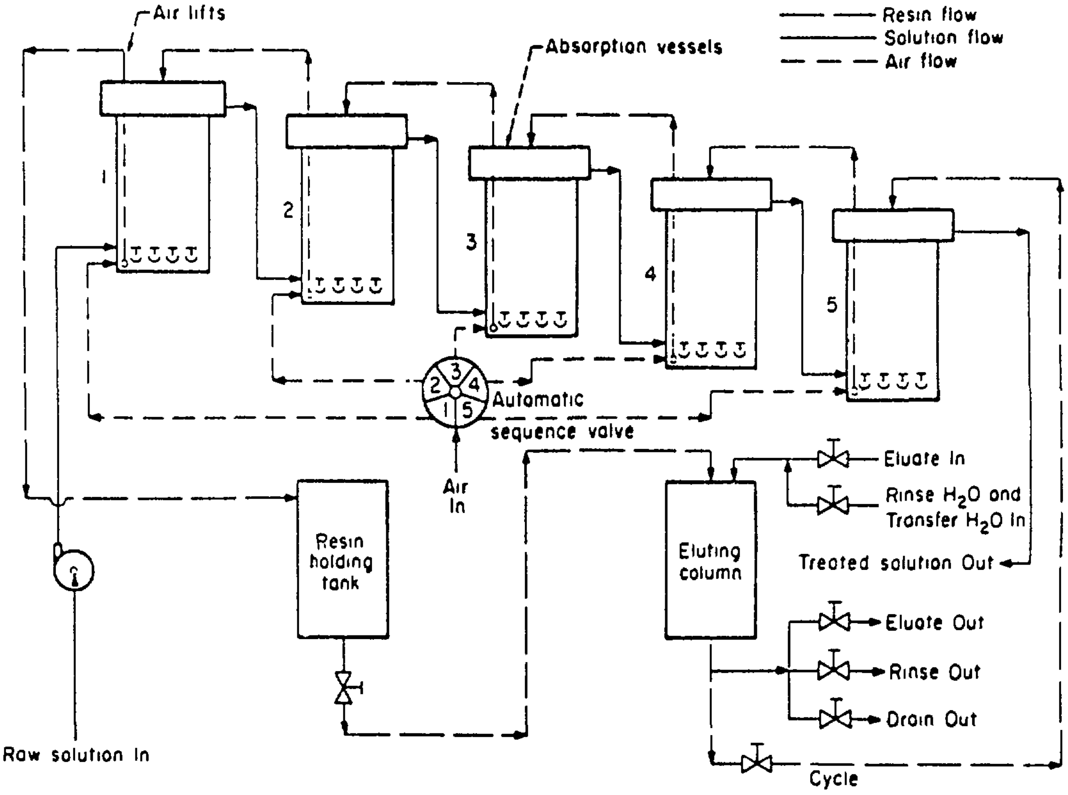


FIG. 8: PORTER FLUIDIZED-BED ION EXCHANGE SYSTEM

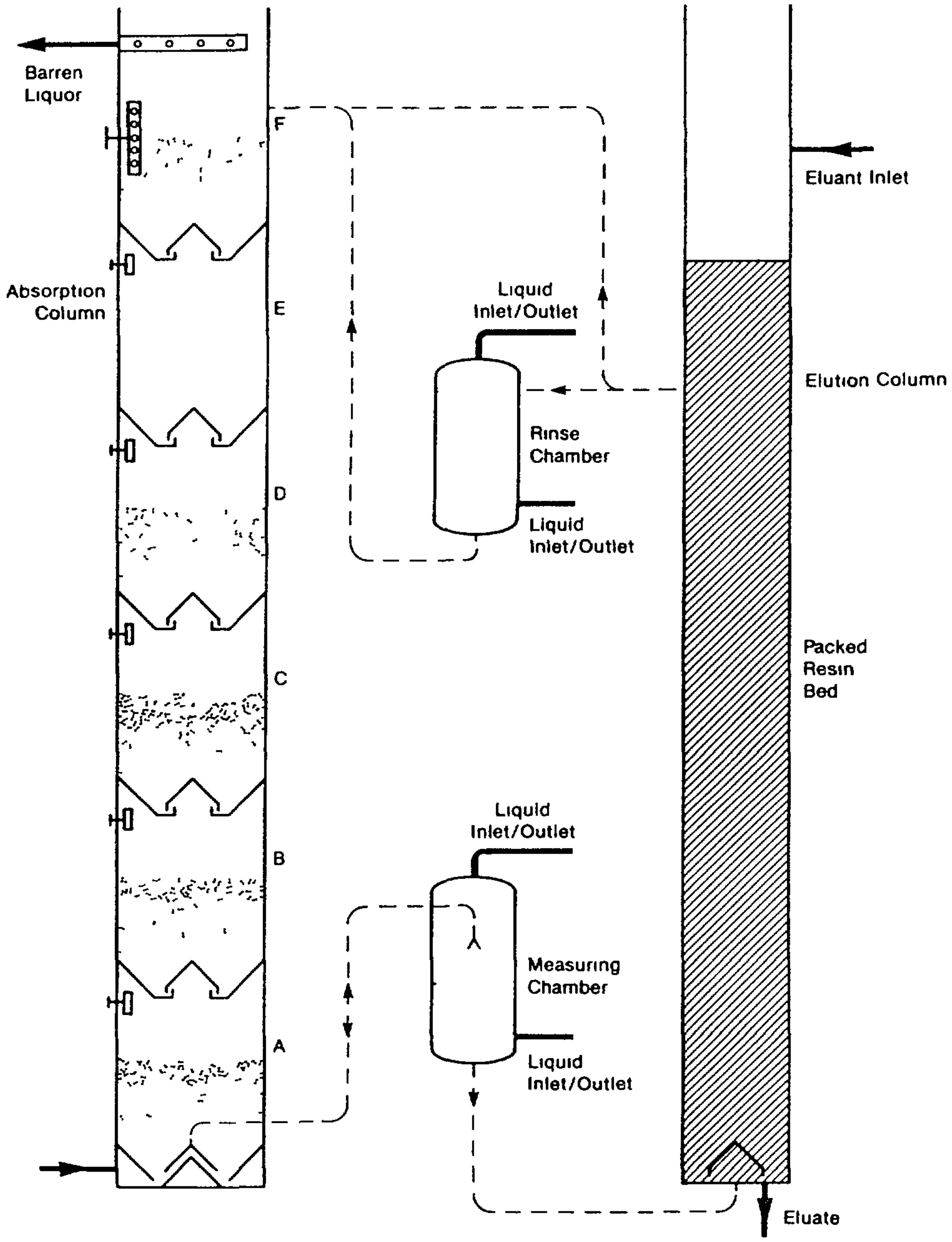
This system is installed on the large uranium extraction plant in Namibia of Rossing Uranium. The elution system there employs three columns in series to obtain a strong eluate in the same manner described earlier for the Porter-Arden resin movement plant.

Himsley Column

A more recent design of continuous ion exchange commenced operations in June, 1977 at Agnew Lake Mines in Espanola, Ontario. This system was piloted at the Quirke Mine of Rio Algom in Elliot Lake and a description of this work is given elsewhere [22]. Operating performance of systems are also available [23].

The distinguishing features of this system is that there is no interruption of the feed liquor when transferring resin from the loading column and elution is carried out downflow through several batches of packed resin. The adsorption is therefore truly continuous.

A typical arrangement of the system is shown in Figure 9 and comprises a sorption column, a resin measuring chamber, an elution column and a rinse chamber.



Typical arrangement of Himsley Continuous Ion Exchange System
Fig 9

The sorption column is divided by cones and baffles into several chambers containing resin through which an upward flow of liquid fluidizes the resin within each chamber. During normal operation all of the chambers contain resin except the one immediately below the top chamber. The number of such chambers and the volume of resin in each chamber depends upon the rate laws of ion exchange governing the particular system.

The elution column contains several batches of resin in a packed bed configuration. Loaded resin in introduced into the bottom of the column and is eluted by the downflow of eluant through the packed bed of resin. This obviates the back-mixing effect often encountered with dense eluates and resin back-mixing is also avoided because of the packed bed configuration. High strengths of eluate are obtained with this process because of the multi-stage downflow counter-current elution technique.

Each resin batch proceeds upwards through the elution column at each elution cycle and by the time it reaches the top of the column, it has been contacted with enough eluant to strip essentially all of the uranium from the resin.

The Rinse Chamber enables the resin to be rinsed free of eluant before returning it to the sorption column. It also may be used to change the ionic form of the resin e.g. from nitrate to sulphate as practised for nitric acid recovery or to treat the resin for removal of silica or polythionates.

The transfer of resin throughout the system is done in a fluidized manner requiring very little pressure. There are no valves which close on the resin and no pumps through which the resin is passed and in this way resin attrition is minimized.

When breakthrough occurs at the top of the column the resin in the lowest chamber is close to equilibrium loading with the feed solution.

At this time the resin in the top chamber is transferred to the empty chamber below and freshly eluted resin is immediately transferred to the top chamber of the sorption column. The resin from the lowest chamber of the sorption column is then transferred to the measuring chamber which is full of feed liquor. This is is done by directing the liquid flow as shown in Figure 10 without interrupting the flow of feed through the sorption column.

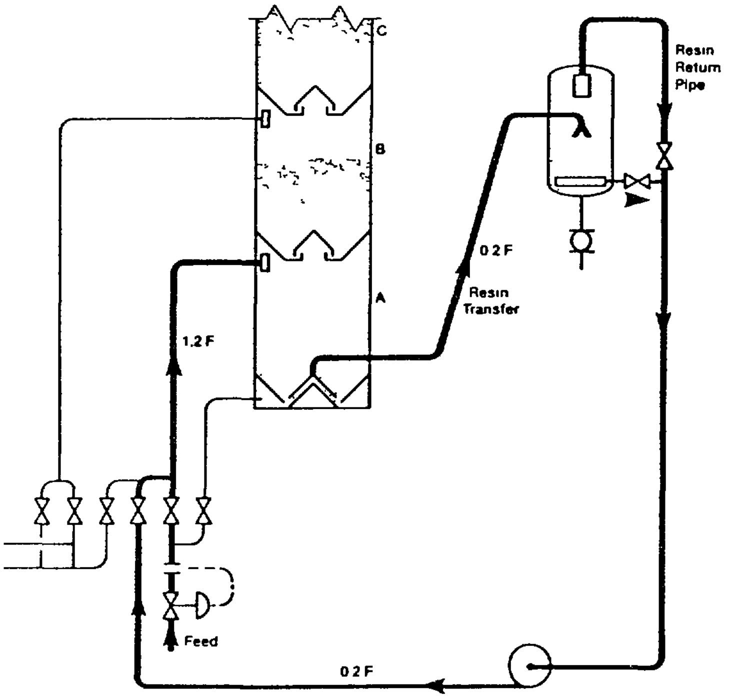


FIG 10· RESIN TRANSFER FROM ABSORPTION COLUMN TO MEASURING CHAMBER

The main function of the Measuring Chamber is to provide positive control over the batch size of resin passed around the system so that the resin in each compartment of the loading column is the same. It may also be utilized for resin pretreatment, e.g. an iron scrub prior to elution. Especially when pregnant solution with high solids content is treated, the resin may be cleaned by backwashing and if necessary an air scour can be applied.

All of the resin in chamber B is then transferred in fluidized fashion to chamber A. When chamber B is empty, it receives all of the resin from chamber C. The transfer of resin continues from chamber to chamber until all the chambers but one are empty. These resin transfers are done by directing liquid flow as shown in Figure 11.

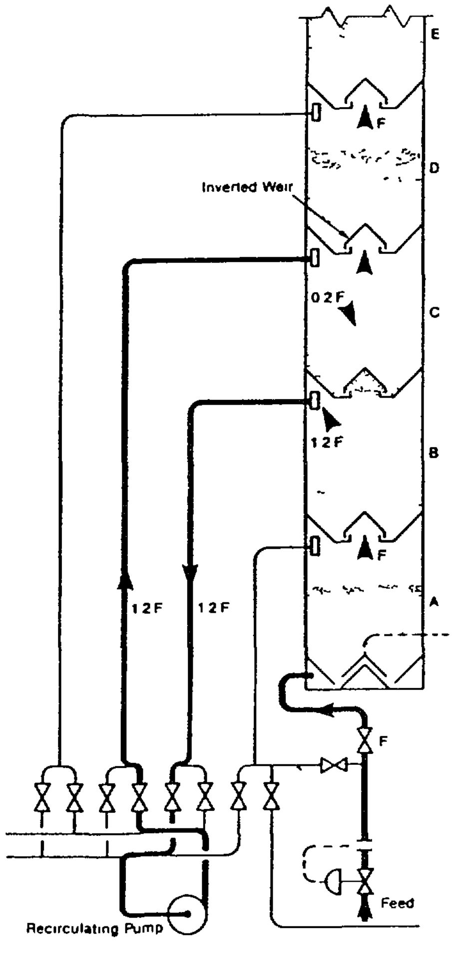


FIG 11: RESIN TRANSFER FROM CHAMBER C TO B

Strainers are provided to prevent the entrainment of resin particles with the liquid drawn from the chambers during resin transfer. Each strainer has flow going through it in one direction for 3 minutes or so and then in the opposite direction for the same length of time which keeps the strainers clean. During the remainder of the operating cycle, the strainers are not in use. There is no strainer on the outlet at the top of the column and therefore a free discharge is available for any suspended matter or resin fines. Also the diameter of the column is the same throughout which obviates the possibility of partially loaded fine resin particles accumulating at the top and raising the equilibrium concentration of the barren effluent which can occur with an upper flared section.

Requirements of Fluidized Resin Systems

Any system employing a series of fluidized beds in tanks or chambers arranged either horizontally or in a vertical column can only operate at maximum efficiency if the resin transfer is done in a counter-current direction to the liquid flow. Also the transfer of resin frome one chamber to the next must be essentially complete before it receives resin from its adjoining chamber.

Any resin left behind in a chamber will not only affect the degree of extraction from that chamber but also will create uneven resin batches in the various chambers. Such unequal distribution of resin can not only lead to poor extraction and high concentrations of the ion of interest in the barren effluent but also it can result in elutriation of resin from a chamber which contains an excessive amount of resin.

The chambers or tanks must be deep enough to contain the resin when fluidized at the design flow so that small particles of partially loaded resin are not carried along with the liquid flow into the next tank.

A further consideration in design pertaining mainly to vertical columns of fluidized resin beds is the superficial velocity. It is recognized that resins may change their density as the ion exchange process takes place e.g. a strong base resin in the sulphate form may be fluidized to a voidage of 0.7 at 15 m/h superficial velocity whereas when loaded with iron and/or uranium the velocity may be increased to 19 m/h or so whilst still maintaining the same voidage. As it is not practical on a large scale to make the column conical to change the superficial velocity a compromise is made by making the column cylindrical and allowing for a difference in the degree of fluidization as the liquid passes up the column.

Some columns provide for a larger diameter section at the top of the column so that the superficial velocity is lower because it is at the top where the resin is lightest, having been stripped of uranium. Whilst this reduces the possibility of elutriation of resin it does however lead to a concentration of fine resin beads, partially loaded with uranium, remaining in the top section of the column virtually all the time. This affects the equilibrium of the resin mass in the top chamber and can cause excessive loss of the ion of interest in the barren effluent.

Resin transfers must be made as a slurry so as to reduce resin attrition and the velocity in pipes should not exceed 2 m/s.

Pumps and ejectors should preferably be avoided for transferring resin as the high velocities incurred will lead to resin breakage and eventual loss.

Valves should not close on resin particles if resin attrition is to be minimized and the pressure loss in moving resin should not exceed 175 kPa. This latter figure also applies to pressure losses in fixed beds of resin to ensure that resin beads are not fractured.

Basis of Design

Any continuous ion exchange system makes use of a constant width ion exchange zone for favourable ion exchange processes. This has been amplified by Michaels [24] wherein he considered fixed beds and showed that the exchange zone moves down through the column at a certain velocity depending upon the feed concentration and the flow rate.

By this concept, the total resin inventory in a fixed bed system is the volume of resin contained in the ion exchange zone plus the amount of resin needed to carry on the exchange for several hours or whatever length of time is allowable before breakthrough occurs and the resin is eluted.

In a fluidized resin column the liquid moves upwards and the exchange zone also tends to move upwards. However, when the zone starts to leave the top chamber as detected by analyzing the sample from the stream leaving the top chamber, the resin is immediately moved down the column and its place taken by a batch of freshly eluted resin. The resin in the lowest chamber is then taken away to be eluted.

In this way, the upward movement of the exchange zone is limited to the distance of one chamber after which the exchange zone is brought back by moving the resin downwards and is thereby contained within the column. It is this which accounts for the efficient utilization of resin in continuous columns as compared to fixed bed columns.

It is possible to design systems regardless of size based on tests with small laboratory columns such that comparable performance can be expected provided that the ratio of the volume of wet settled resin to volumetric liquid feed rate is the same as the test work.

Fluidization of Resin

The first basic requirement in designing any fluidized bed is to see that all conditions prevail to produce a desirable degree of fluidization. In order to achieve good mixing and mass transfer it is usual to keep the voidage between 0.6 and 0.8.

The fluidization of strong base resins used for uranium extraction varies depending upon the loading of uranium. When in the sulphate form the resin has a density around 1.15 but when loaded with uranium it can be as much as 1.3 or so. Also, when the resin loads with iron its density increases but not as much as with uranium.

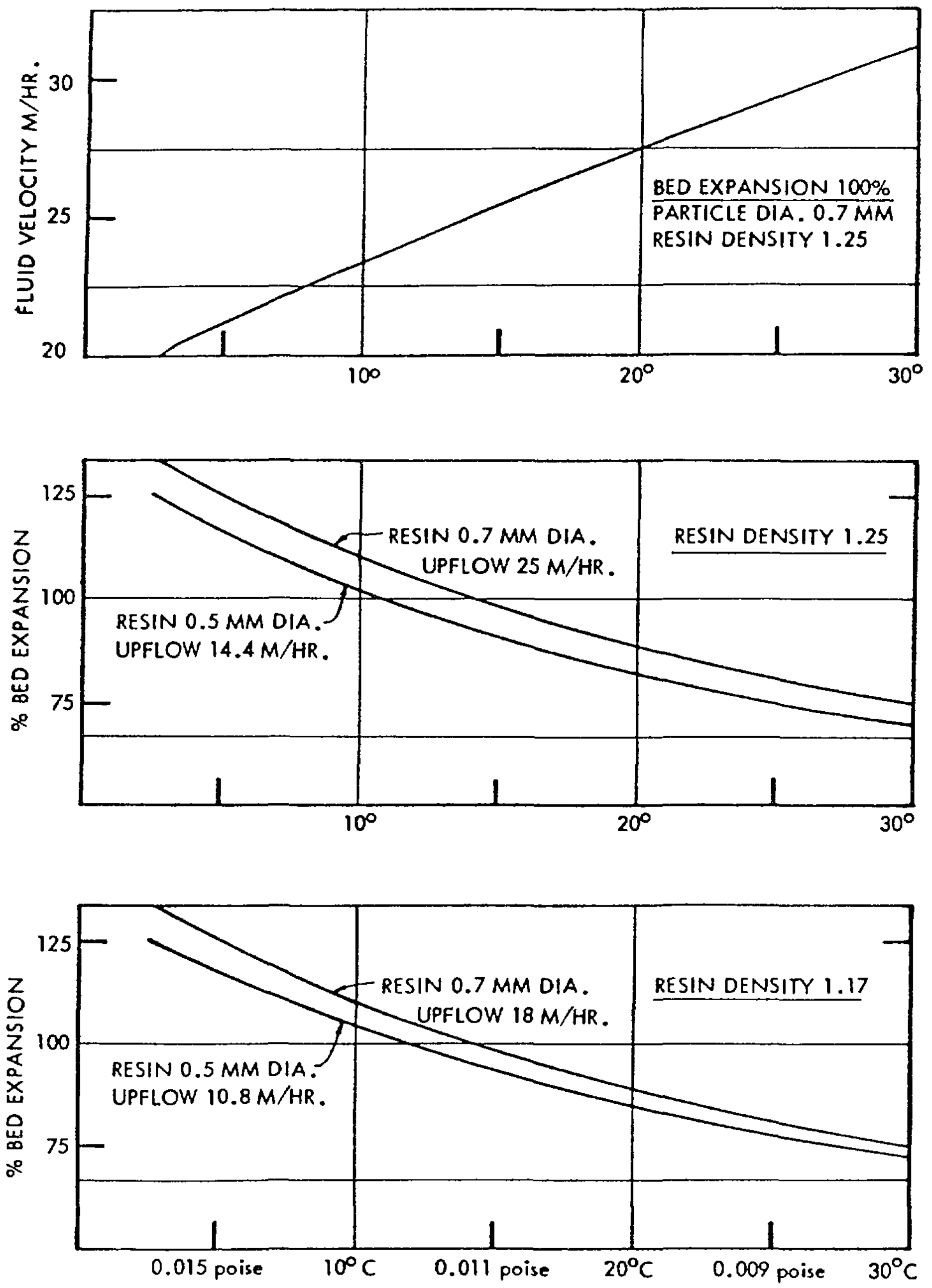
It is known that the rate of ion exchange varies inversely with the diameter of resin particles whilst the fluidizing velocity varies directly with increasing diameter of particles. As the required rate of ion exchange is the product of flow and concentration it follows that coarse bead resin can be more effectively used with dilute solutions than concentrated solutions. The limiting factor when using small resin beads for treating dilute solutions is usually the specific flow rate at which the resin would be elutriated from the system rather than the rate of ion exchange. Because of this, the smaller size resin beads are generally favoured when treating concentrated solutions.

The fluidization characteristics of resins are indicated by Figure 12 which shows the expansion of two resins having uniform sizes of 0.5 mm and 0.7 mm respectively. Also, the affect of resin density is illustrated for the two resins having specific gravities of 1.17 and 1.25 respectively.

From this it will be seen:

1. Increasing the resin particle density from 1.17 mm to 1.25 mm allows a 40% increase in flow for the same bed expansion of 100%.

2. If the bed expansion in aqueous solution is 100% at 15°C then it will expand to approximately 125% at 5°C or 75% at 30°C.



AFFECT OF VISCOSITY, DENSITY AND PARTICLE SIZE ON RESIN FLUIDIZATION IN AQUEOUS SOLUTION OF DENSITY 1.02

FIG. 12

(M/HR. x 0.41 = U.S.gpm./ft.^{2})

3. Increasing the resin bead diameter from 0.5 mm to 0.7 mm allows the flow to be increased to 170% for the same bed expansion of 100%. The rate of ion exchange, however, would decrease by about 30%.

Moving Packed Bed Ion Exchange

A modification of the Himsley continuous ion exchange system is made when treating liquids with low suspended solids such as heap leach solutions and mine waters.

The arrangement of the system is shown diagrammatically in Figure 13 and consists of the following major components:

1. Sorption Column

2. Resin Measuring Chamber

3. Elution Column

4. Resin Rinse Chamber

The sorption column operates in a somewhat similar manner to the elution column as previously described. It contains a bed of resin deep enough to contain the ion exchange zone length at the proposed maximum operating flow.

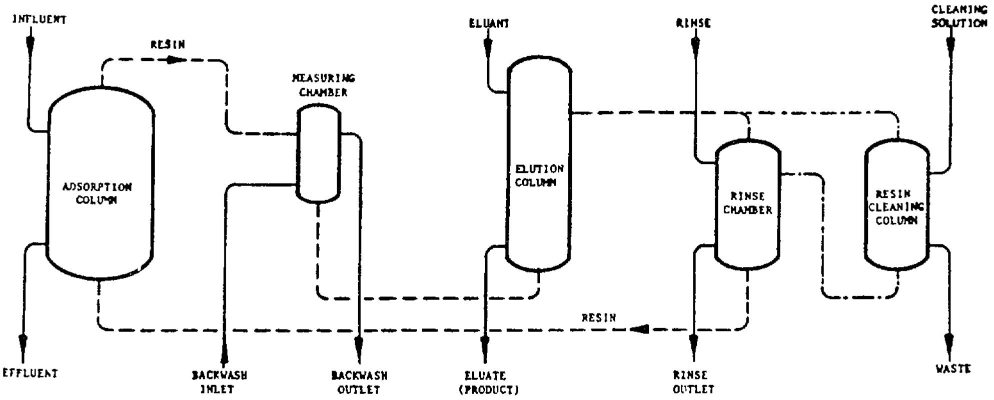


FIG. 13 TYPICAL ARRANGEMENT OF MOVING PACKED BED ION EXCHANGE SYSTEM

The water to be treated enters the top of the sorption column and passes down through the bed of resin and the treated water is drawn off from the bottom. After a given volume of feed has been treated a batch of resin is drawn off the top of the sorption column and discharged into the measuring chamber as a slurry.

The frequency of transfers depends upon the flow rate, feed concentration and the size of the resin batch. Because the resin is transferred from the top of the unit fairly frequently, this system is much less susceptible to being fouled by suspended matter in the feed than a conventional fixed bed unit.

The resin in the measuring chamber can be air scoured if necessary and backwashed to remove any suspended solids entrapped by the resin. The liquid is then drained from the measuring chamber after which it is filled with eluate. The resin is then transferred as a slurry to the bottom of the elution column using eluate.

This column is of sufficient volume to contain several batches of resin - the number being mainly dependent upon the temperature and the frequency of resin batches entering the column and also the required concentration of the eluate.

When the resin enters the elution column it lifts the bed of resin already in the column as a solid plug which avoids mixing of the previous batches of resin.

When the batch of loaded resin has been completely transferred to the bottom of the column the plug of resin is allowed to drop and form a compact bed of resin thus displacing the excess fluidizing liquor (eluate) to the eluate tank from which it came.

The resin is eluted by the downward flow of a measured volume of eluant through the packed bed of resin. Because of the multi-stage downflow counter-current elution technique the volume of eluate produced each cycle is much lower than that produced by a conventional column and this results in an eluate of high concentration.

The batch of eluted resin at the top of the column is then transferred in a fluidized manner to the rinse column for rinsing or backwashing away any resin fines. The rinsing is done with barren effluent from the sorption column after which the resin is returned to the bottom of the sorption column in a similar manner to that used for transferring resin to the elution column.

The first commercial installation of this type was commissioned in January, 1983 for treating mine water from the Schwartzwalder Mine of Cotter Corporation in Golden, Colorado, U.S.A. The ore body contains uranium and the mine water has between 2 to 5 mg U/l at a pH around 8.4.

Because this mine water discharges into a creek flowing to a drinking water storage reservoir, discussions with the Department of Health resulted in the mine management deciding to install equipment to reduce the effluent to less than 10 g U/l.

Once the equipment reached steady state conditions it produced an eluate containing 15 g U/l from a feed concentration averaging 3.9 mg U/l over a two week period which shows a concentration factor of approximately 4000. The eluate is trucked to the mill 250 kilometers away for direct precipitation of the yellow cake. A detailed description of the installation is given elsewhere [25].

Sulphate Elution

In recent years there has been some concern expressed by environmental authorities about the use of nitrate as an eluting agent. This is because the nitrate ion left on the resin after elution is displaced by sulphate and goes out in the tailings. The loss of nitrate can be reduced by using sulphuric acid to strip off the nitrate when the resin is in the rinse chamber as previously mentioned resulting in about 50% to 70% recovery of nitrates on the resin as nitric acid. Nevertheless, some risk exists of contaminating the effluent with nitrate and as a result, the industry is being encouraged to turn towards the use of sulphuric acid as an elutant.

Sulphuric acid is not as efficient and elutes much more slowly than nitrate. Actually it is the bisulphate ion that elutes the uranium from the resin and consequently, the strength of acid generally used is between 100 to 125 g H_2SO_4/l at which concentration the bisulphate ion is almost completely dissociated.

When fixed beds are employed loading resin to 50 g U_3O_8/l the sulphuric acid consumption (assuming 50% recycle eluant) would be in the region of 15 grams H_2SO_4 per gram U_3O_8. It is obviously uneconomical to consume alkali to neutralize this large amount of acid and consequently recovery of the acid is necessary. As mentioned earlier this has been achieved in the past by passing the eluate through a solvent extraction plant and this produces high grade yellow cake because contaminants in the eluate such as iron are removed and go out in the raffinate with the recovered sulphuric acid.

However, the solvent extraction process requires a relatively large area along with special fire prevention equipment and usually a separate building. It also demands a clear feed liquor to prevent difficulties in phase separation resulting in solvent losses which contaminate the effluent. These constraints of the Eluex process must therefore be recognized and evaluated against other available methods.

From the standpoint of acid recovery it has been shown that the multi-stage counter-current elution results in less than a third of the acid required by a fixed bed system employing 50% recycle eluant. At typical resin loadings the acid consumption of this multi-stage elution column is in the region of 3 to 5 grams H_2SO_4 per gram U_3O_8 which is acceptable because the neutralization of this amount of acid is less costly than the earlier processes using nitrate elution. It follows that less sulphate in the form of gypsum must be removed thus lightening the load on the filters.

The neutralization would be done in two stages, the first of which at pH approximately 3.5 would precipitate the sulphate along with iron and some other contaminants to enable a good quality yellow cake to be obtained from the second stage precipitation carried out at pH 7.

There is, however, a more recent process known as HIMIX developed for those cases where excessive contamintion of the feed liquor exists and elution is with sulphuric acid. This process [26] enables a pure eluate to be produced in one ion exchange step at a low cost. It was developed for use when 100 to 125 g H_2SO_4/l is employed as an eluant in conjunction with the Himsley continuous ion exchange system. At modest cost it results in better purification of the eluate than is obtained by the acid scrub and iron and sulphate precipitation referred to earlier. Acid consumption in the region of 3 to 5 kg H_2SO_4/kg U_3O_8 produced can be achieved by this process when using 120 g H_2SO_4/l as an eluant. A full description has been given elsewhere [27].

Materials of Construction

The greatest care that must be taken in the selection of materials and components is when acid leach circuits are used.

In cases where chlorides are low 316 L stainless steel can be used with reasonable success. However, stainless steel is not suitable under reducing conditions and consequently if polythionate poisoning of the resin is likely then materials in contact with the eluate should be of plastic or other material which is inert under such conditions.

Rubber-lined carbon steel is used extensively in acid leach circuits but care must be taken to thoroughly spark-test the lining before placing it into service. Today there is a tendency for piping to be either stainless steel or fiberglass.

In cases where an Eluex circuit is used to recover sulphuric acid there is always some organic that is returned with the acid which will attack normal rubber lining. In such cases carbon steel should be lined with Buna N or F.R.P. It must also be recognized that the solvents from an Eluex plant can attack some plastic materials and consequently a study of the particular operating conditions must be made before finally deciding upon the materials.

The returned acid from an Eluex plant may contain chlorides and nitrates which appear as hydrochloric and nitric acids respectively in the eluant. The chlorides will attack 316 stainless steel whilst the nitrates will attack Buna N rubber. This leaves fiberglass as being the most suitable material for use in cases where Eluex circuits are employed unless the chlorides can be kept low enough to enable stainless steel to be used.

The flow meters and controllers require the usual care in selection depending upon the duty, bearing in mind the comments previously made concerning the nature of solutions with which they may be in contact.

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CHAPTER 3

URANIUM PRODUCTION BY ION-EXCHANGE METHODS

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Abstract

Application of ion exchange methods is described for the recovery of uranium mainly from ores. Ion exchange processing of uranium-ore leach solution using anion and cation exchangers is explained in terms of selection of suitable ion exchanger, behaviour of uranium sorption and elution, and poisoning of ion-exchange resins. Leaching chemistry using sulfuric acid and carbonates is reviewed.

The uranium required for the nuclear energy production is yielded first of all from its ores. Besides this, uranium in a smaller quantity is gained by reprocessing of the used fuels as well, which is returned to the production of fuel elements.

Hereinafter we review development of the uranium production until now and the raw material deposits for the production.

The uranium production has continuously increased since the 1940s to the beginning of the 60s, when the quantity of U_3O_8 exceeded 30 thousand tons. Afterwards the production declined by 15-18 thousand tons U_3O_8/year but in the second half of the 70s the peak production values of the 60s were exceeded. The production in 1980 was approximately 50 thousand tons U_3O_8.[1]

In the course of time the share of different countries in the production has significantly changed. The degree of this change is shown on Figure 1.[2]

Table 1. Exploration, production, resources and production capability

Country	First exploration	First production	Total production to 1980	US $80/kgU Reasonably Assured /1000 tonnes U/	US $130/kgU Reasonably Assured /1000 tonnes U/	US $80/kgU Estimated Additional /1000 tonnes U/	US $130/kgU Estimated Additional /1000 tonnes U/	Attainable maximum production capability	Year maximum production capability reached	Qualitative potential
Algeria	Before 1961	-	0	28	28	0	6			moderate/high
Argentina	1968	-	750	23	28	4	9	700	1983	high
Australia	1947	1954	9 600	292+	301	127+	53	20 000	1990	very high
Austria	-	-	0	2	2	0	0			moderate
Bolivia	Late 1960s	-	0	0	0	0	<1			moderate
Botswana	Late 1960s	-	0	0		0	0			moderate/high
Brazil	1952	1979	100	74	74	90	90	1 000	1983	high/very high
Canada‡	1942	1938	131 500	230	259	381	770	15 500	1990	very high
Centr.Afr.Rep.	1947	1982	0	18	18	0	0	1 000	1982	moderate
Chile	1950	-	0	0	0	5	5			low
Denmark /Greenland/	1955	-	0	0	27	0	16			moderate/high
Egypt	-	-		0		0	5			
Finland	1959	1958	<100	0	3	0	<1			moderate
France	1945	1949	29 600	38	54	26	46	4 500	1986	moderate/high
Gabon	1948	1969	9 700	36	35	0	0	1 500	1982	moderate/high
Germany,Fed.Rep.	1953	1975	200	4	5	7	8	200	1984	low
India	1953	-		30	30	1	24	200	1979	high
Italy	1954	1981	0	0	1	0	2	<100	1981	moderate
Japan	1954	1970	<100	8	8	0	0	<100	1979	low
Korea/Rep.of/	-	-		0	4	0	0			low
Madagascar	1946	1955	4 000	0	0	0	2			moderate
Mexico	1957	-	< 100	6	6	2	2	90	1979	moderate/high
Namibia	1966	1977	9 400	113	122	30	53	5 000	1985	high
Niger	1954	1967	13 000	157	157	53	53	12 000	1986	high
Philippines	1953	-	0	< 1	< 1	0	0	< 100	1981	low
Portugal	1945	1945	2 200	7	8	3	3	300	1984	moderate
Somalia	1955	-	0	0	7	0	3			moderate
South Africa	Mid 1950s	1952	88 000	242	386	54	139	10 700	1986	high/very high
Spain	1952	1958	1 200	10	10	9	9	1 300	1985	high
Sweden	Mid 1950s	-	200	0	301	0	3	400	1983	moderate/high
Turkey	1956	-	0	2	4	0	0			moderate
United Kingdom*	1945	-	< 100	0	0	0	7			moderate
United States+	1945	1942	272 300	496	673	773	1 158	44 200	1990	very high
Yugoslavia	1965	-	0	5	7	5	20	400	1990	moderate
Zaire	1920s	1940s	25 600	2	2	2	2			high

Except where noted, data on resources are from Uranium Resources, Production and Demand /December 1979/, adjusted for 1979 production and updated to 1 Jan. 1980.

* Total production from 1845 for glass and ceramic colouring and radium: 200 tonnes.

\+ Source: US Department of Energy /US figures from DOE/GJO-100/80/. January 1980/.

‡ Uranium in Canada - 1979 assessment of supply and requirements - at a price of US $130/kgU and US $200/kgU.

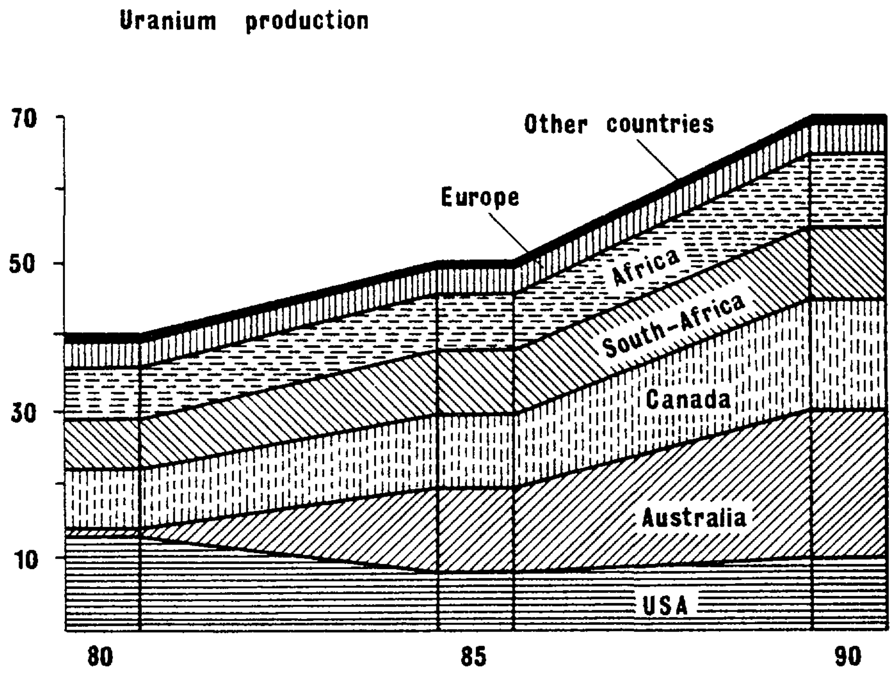


Fig. 1. Probable change of ratio of uranium production in 80s.

URANIUM PRODUCTION *
(Tonnes U)

Country	Pre-1977	1977	1978	1979	1980	1981	1982	1983[1]
Argentina	339	98	109	134	187	123	155	200
Australia	8,159	356	516	705	1,561	2,860	4,453	3,700
Belgium[2]	0	0	0	0	20	40	40	40
Brazil	0	0	0	0	0	4	290	300
Canada	112,080[3]	5,790	6,800	6,820	7,150	7,720	8,080	7,500
Finland	30	0	0	0	0	0	0	0
France	23,133	2,097	2,183	2,362	2,634	2,553	2,859	3,200
Gabon	8,464	907	1,022	1,100	1,033	1,022	970	1,042
Germany, Federal Republic of	151[4]	15	35	25	34	36	34	40
Japan	38	3	2	2	5	3	5	7
Namibia	594	2,340	2,697	3,840	4,042	3,971	3,776	3,800[5]
Niger	6,108	1,609	2,060	3,620	4,100	4,360[6]	4,259[6]	n.a.
Portugal	1,932	95	98	114	82	102	113	100
South Africa	75,332	3,360	3,961	4,797	6,146	6,131	5,816	5,800
Spain	476	177	191	190	190	178	150	150
Sweden	200	0	0	0	0	0	0	0
United States of America	209,800	11,500	14,200	14,408	16,804	14,793	10,331	7,900[7]
Zaire	25,600[3]	0	0	0	0	0	0	0
TOTAL	472,436	28,347	33,874	38,117	43,988	43,892	41,331	38,000

1. Estimated.
2. Uranium from imported phosphates.
3. Pre-1938 data not available.
4. Plus 120 tonnes uranium of foreign origin.
5. Secretariat Estimate
6. CEA - Rapport Annuel (1981, 1982).
7. Production in the US in 1983 is expected to fall between 7,500 and 8,300 tonnes.

* Supplement to Figure 1. Cited from: Uranium Resources, Production and Demand OECD-NEA/IAEA (December 1983).

Certainly there were several reasons which contributed to the change of the production and its volumes but we will not deal with them here.

Deposits of uranium production which are nowadays at our disposal can be divided into two categories as shown in Table 1. The first category contains ore deposits from which recovery of uranium is economical under the value 66 \$/kg U_3O_8 and to the second category belong deposits for which this value is between 66-110 \$/kg U_3O_8. In the first category these uranium deposits occur in 31% in sand stones and in vein form respectively, 22% of them in primary conglomerates, usually accompanied by other metals (gold, thorium, etc.), 11% of deposits are to be found in pegmatite gneisses, 2% in calcicrits, 1% in oil shales and 2% in quarries of other types. Distribution of the lower grade ores being in the second category is as follows: 30% of them occurs in sand stones, 25% in veins, 15% in conglomerates, 22% in oil shales, 6% in pegmatite gneisses and 2% in clacicrits.[4]

Besides the abovementioned categories there are several deposits containing a lot of uranium, but their concentration is very low /<0.03%/, therefore exploitation of them is not economical taking into consideration present prices. These deposits contain uranium mainly in granites, syenits and phosphorites. Enormous deposits can be found in the sea water as well, but we have no technology by which uranium can be obtained from sea water economically, so it is unlikely uranium will be extracted from sea water in the near future.

Nowadays and in the near future the uranium containing ores of the first and second categories can be considered as the raw material of the uranium production. However, in recent years the spot price for uranium has significantly decreased and at minimum point reached the value of 17 \$/lb = 37.48 \$/kg U_3O_8.[3] As a consequence production in several mines and ore processing plants was interrupted and the proportion of the exploitation of the ores with lower uranium concentration decreased. In spite of this during the following years and until the turn of the century in all probability, the raw materials belonging to the above-mentioned categories will be processed and for this mainly the current methods will be used.

Other raw materials of the uranium are not of great importance today, though e.g. the waters of world seas can be an inexhaustible source for the uranium production.

During the mining and processing of the uranium some solutions and mine waters appear as byproducts, the uranium content of which is significant. It is necessary to process them in interest of environment protection as well, but in some places even economical uranium production is guaranteed. Ion-exchange processes are applied for recovery of uranium from such solutions, but these processes are similar to the methods already in existence.

3.1. Main methods of uranium ore processing

Today mainly the sulfuric acidic leaching is used for uranium production, but the carbonate leach is also important.[27, 29]

In some places physical enrichment methods are applied depending on the mineral-rock characteristics and physical state of the ores: radiometric classification, heavy-media process and sometimes flotation.

The uranium ore and concentrate respectively is prepared usually by wet milling and the pulp of suitable grain-size is led to the leaching process. The processing methods applied nowadays as further steps for uranium ores can be classified as follows:

(a) Process using sulfuric acid:

- Leaching by sulfuric acid, processing of pulps with filtration, and by counter-current precipitation respectively, and extraction from pure solutions;
- Leaching by sulfuric acid, processing of pulps with filtration, and by counter-current precipitation respectively, and ion-exchange from pure solutions;
- Leaching by sulfuric acid, ion-exchange from pulp.

(b) Process using carbonates:

- Leaching by using carbonates, processing of pulps with filtration and by counter-current precipitation respectively, and precipitation of uranium;
- Leaching by using carbonates, processing of pulps with filtration and by counter-current precipitation respectively, and ion-exchange from pure solutions;
- Leaching by using carbonates, ion-exchange from pulp.

(c) Combined and other technologies.

Hereinafter we shall review only processes which require application of ion-exchange methods.

3.1.1. Leaching by sulfuric acid

Greater part of the uranium ores and raw materials containing uranium can be leached by sulfuric acid. This method can be limited only by degree of consumption of sulfuric acid. If the stone is rich of acid consuming components /$CaCO_3$, $MgCO_3$, etc./ it will become uneconomical, because of high acid consumption.

From its pretreated ores the hexavalent uranium is dissolved by leaching with sulfuric acid as follows:

$$UO_3 + H_2SO_4 = UO_2SO_4 + H_2O \qquad (1)$$

As uranium occurs in its minerals in tetravalent form as well which cannot be dissolved in sulfuric acid, during the leaching tetravalent uranium must be oxidized. In practice the oxidation is guaranteed by Fe^{3+} ions which are present in the leaching solution:

$$UO_2 + 2Fe^{3+} \rightleftharpoons UO_2^{2+} + 2Fe^{2+} \qquad (2)$$

For the continuous oxidation of ferrous ions pyrolusite /MnO_2/, sodium chlorate /$NaClO_3$/, etc. are used:

$$2Fe^{2+} + MnO_2 + 4H^+ \rightleftharpoons 2Fe^{3+} + Mn^{2+} + 2H_2O \qquad (3)$$

and

$$6Fe^{2+} + ClO_3^- + 6H^+ \rightleftharpoons 6Fe^{3+} + Cl^- + 3H_2O \qquad (4)$$

respectively.

The uranyl ions being formed during the leaching enter into reaction with the sulfuric acid and the result is complex uranyl di- and trisulfate ions:[5, 6]

$$UO_2^{2+} + n\ SO_4^{2-} \overset{\beta n}{\rightleftharpoons} UO_2/SO_4/_n^{2-2n} \qquad (5)$$

The equilibrium is always dependent on uranium and sulfate concentration:

$$\beta = \frac{\left[UO_2/SO_4/_n^{2-2n}\right]}{\left[UO_2^{2+}\right]\left[SO_4^{-2}\right]^n}$$

Formation constants of complexes [6]:

$n = 1$ $\beta_1 = 50$
$n = 2$ $\beta_2 = 350$
$n = 3$ $\beta_3 = 2500.$

The uranium is present in leaching solutions of uranium ores, containing sulfuric acid, in form of uranyl cation UO_2^{2+}, unionized uranyl sulfate UO_2SO_4, divalent uranyl disulfate $[UO_2/SO_4/_2]^{2-}$ and tetravalent uranyl trisulfate anion complex $[UO_2/SO/_3]^{4-}$.

If uranyl ions are step by step sorbed from leaching solution by an ion-exchanger, the quantity of uranyl complexes will decrease, they change into uranyl ions and vice versa. By increasing the quantity of sulfates the formation of uranyl complexes will be promoted and by decreasing their quantity the formation of uranyl cations and neutral uranyl sulfate molecules, respectively.

During the leaching by sulfuric acid besides the uranium other components will be leached as well which remain in the solution in different forms. Especially at higher temperature the sulfuric acid partially recovers the quartz as well (about 1%).

$$SiO_2 + H_2O \xrightarrow{H_2SO_4} H_2SiO_3 \qquad (6)$$

The produced silicic acid remains in the solution in colloidal state. 2-6% of aluminium is solved from the ore during the leaching by sulfuric acid:

$$Al_2O_3 + 3H_2SO_4 \rightleftharpoons Al_2/SO_4/_3 + 3H_2O \qquad (7)$$

Trivalent iron oxide $/Fe_2O_3/$ of siliceous uranium ores hardly dissolves in diluted sulfuric acid solution /4-8%/:

$$Fe_2O_3 + H_2SO_4 = Fe_2/SO_4/_3 + 3H_2O \qquad (8)$$

Divalent iron oxide or other compounds of iron are more easily dissolved /40-50%/:

$$FeO + H_2SO_4 = FeSO_4 + H_2O \tag{9}$$

However, in presence of an oxidant (oxygen of the air or pyrolusite) the iron is oxidized into trivalent form according to the equations (3) and (4).

At suitable pH value trivalent iron hydrolyses:

$$Fe_2/SO_4/_3 + 6H_2O = Fe/OH/_3 + 3H_2SO_4, \tag{10}$$

and at suitable sulfate ion concentration anion complexes will be formed:

$$Fe_2/SO_4/_3 + SO_4^{--} = 2Fe/SO_4/_2^- ; \tag{11}$$

and

$$Fe_2/SO_4/_3 + 3SO_4^{--} = 2Fe/SO_4/_3^{3-} \text{, respectively.} \tag{12}$$

Calcium and magnesium carbonates /$CaCO_3$, $MgCO_3$, $CaCO_3.MgCO_3$/ react entirely with sulfuric acid and calcium and magnesium sulfate respectively will be formed:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2, \tag{13}$$

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2. \tag{14}$$

Solubility of calcium sulfate is about 2 g/l in dilute sulfuric acid leaching solutions, but magnesium sulfate can be totally dissolved in practice. At the beginning of the leach the leaching solution becomes supersaturated with calcium sulfate. In further stage of leaching a precipitate of gypsum is suddenly formed, which contains besides calcium and magnesium sulfate, uranium in a rather significant quantity [5]. This makes loss of uranium at the leaching.

Vanadium and phosphorus content of the ore dissolves in dilute sulfuric acid liquor to a great extent /70-80%/. Vanadium usually occurs in carnotite form which dissolves according to the following equation:

$$K_2O.2UO_3.V_2O_5 + 4H_2SO_4 = K_2SO_4 + 2UO_2SO_4 + /VO_2/_2SO_4 + 4H_2O \quad (15)$$

In aqueous solutions vanadium besides vanadil anions occurs in form of ortho-, pyro- and metavanadil acid /H_2VO_4, $H_4V_2O_7$ and HVO_3/. In the uranium ores the phosphorus can be found either in secondary uranium phosphate minerals: otunite, torbernite, parsonsite, etc., or in original apatite $Ca_5F/PO_4/_3$, phosphorite $Ca_3/PO_4/_2$ form. In all cases during the reaction with sulfuric acid phosphoric acid will be formed:

$$Ca_3/PO_4/_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4. \quad (16)$$

Further impurities /Cu, Cr, Ni, Ti, SB, As, Mo, etc./ can be found only in a small quantity in the siliceous uranium ores, so their solved quantity will be small as well.

If the uranium occurs in complex ores the composition of the leach solution will be significantly different from the above-mentioned; for its processing a technology must be worked out in each case separately. The situation is similar to the processing of uranium containing phosphorites.

At a given uranium concentration the ratio of uranyl ions and complex forms depends on the concentration of sulfate ions. At a small sulfate ion concentration the uranyl cation and neutral uranium complexes dominate, while at a greater concentration the quantity of anionic complexes is more significant.

Depending on the circumstances of the leaching by sulfuric acid at the plant the following solutions are formed during the leaching of sandstone ores of low uranium content:

U	0,3	-	2,0 g/l
Fe/III/	2	-	10 g/l
Fe/II/	0,05	-	0,1 g/l
Al	0,1	-	6 g/l
K	0,1	-	0,3 g/l
Na	0,5	-	1,5 g/l
Ca	0,1	-	0,2 g/l
Mg	1,0	-	6 g/l
SO_4^{--}	30	-	100 g/l
PO_4^{-}	0,01	-	0,1 g/l
Cl	0,1	-	2,0 g/l

As contaminating ions even copper, nickel, chrome, manganese, titanium, antimony, molybdenum, vanadium, scandium and other ions occur in the solution in various concentrations, depending on the composition of the ore, will depend on the applied technology. The free sulfuric acid content of the solutions also depends on the applied technology, it usually changes between values 2-15 g/l.

Solutions similar to the above mentioned composition will be formed during underground leaching of the uranium ores by sulfuric acid, and at different percolation leaching processes, where sometimes bacterial oxidation is applied as well. But, there are two important characteristics in which they differ from the above solutions: first, the total salt content of these solutions - included uranyl sulfates as well - is smaller than that of liquors arising at intensive plant leaching by sulfuric acid using for example pachucas. The other difference is that the solutions from the percolation leaching are pure, almost quite free from suspended solids.

3.1.2. Leaching by carbonates

Uraninite and nasturanium content of primary uranium ores can be hardly leached by carbonates, but uranium minerals of secondary ores are easily recovered by them. However, an oxidant must be added to the leaching for the oxidation of tetravelent uranium. Soda is usually used for the leaching, but ammonium carbonate is a good leachant as well:

$$UO_3 + 3Na_2CO_3 + H_2O = Na_4\left[UO_2/CO_3/_3\right] + 2NaOH, \qquad (17)$$

$$UO_3 + 3/NH_4/_2CO_3 + H_2O = /NH_4/_4\left[UO_2/CO_3/_3\right] + 2NH_4OH \qquad (18)$$

In presence of tetravalent uranium an oxidant must be used at the leaching. Oxidation of uranium by oxygen takes place according to the following reaction:

$$UO_2 + 3Na_2CO_3 + \frac{1}{2}O_2 + H_2O = Na_4\left[UO_2/CO_3/_3\right] + 2NaOH \qquad (19)$$

In order to avoid becoming alkaline during the leaching and formation of diuranate precipitate (loss of metal) which is the accompanying event,

$$2Na_4\left[UO_2/CO_3/_3\right] + 6NaOH = Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O; \qquad (20)$$

it is necessary to neutralize continuously the hydroxyl ions which form. For this purpose sodium bicarbonate is also added to the leach liquor:

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O. \qquad (21)$$

Other minerals being present also react with sodium; the gypsum and the magnesium sulfate dissolve to a great extent, therefore they are unwanted components of the uranium ores:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4 \qquad (22)$$

and

$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4 \qquad (23)$$

respectively.

The sodium sulfate being formed causes on the one hand loss of soda and on the other hand unwanted rise of salt concentration which may disturb the sorption of uranium in case of recirculation.

To some extent the sulfides present in the ores also enter into reaction during the sodium leaching. The degree of reaction depends on the temperature, pressure and duration of the leaching:

$$2FeS_2 + 8Na_2CO_3 + 7\tfrac{1}{2}O_2 + 7H_2O = 2Fe/OH/_3 + 4Na_2SO_4 + 8NaHCO_3 \qquad (24)$$

The bicarbonate so formed neutralizes hydroxyl ions which form at the dissolution of uranium, that is why the presence of sulfides is advantageous to a certain extent. But, sulfide content of the ore above 2-4% gives rise to a signficant loss of soda, therefore it increases the cost of sodium leaching.

Even at higher temperature the quartz is leached only to a small extent during the sodium leaching, so its concentration in the leach solution rarely exceeds the value 0.2-0.4 g/l. The reaction of soda with aluminium and iron minerals is insignificant as well. Concentration of iron and aluminium in the sodium leaching solution is between 0.1 and 0.01 g/l. Calcium and magnesium carbonates do not enter into reaction with soda, that is why sodium leaching is applied on the ores of high carbonate content.

Vanadium and phosphorus pentoxides dissolve well during the sodium leaching forming vanadates and phosphates:

$$P_2O_5 + 3Na_2CO_3 = 2Na_3PO_4 + 3CO_2; \qquad (25)$$

and

$$V_2O_5 + Na_2CO_3 = 2NaVO_3 + CO_2. \qquad (26)$$

If molybdenum and arsenic are found in form of oxides in the ores they will be also recovered to a great extent.

The composition of the leaching solutions formed during plant sodium leaching of the uranium ores can be characterized by the following values (g/l):

U_3O_8	0,3-4,0	$S_{SO_4^{--}}$	0,1-5,0
V_2O_5	0,01-4,0	Fe_2O_3	0,05-0,1
P_2O_5	0,05-0,3	Al_2O_3	0,06-0,6
Na_2CO_3	2,0-10,0	SiO_2	0,05-0,5
$NaHCO_3$	2,0-5,0	$CaO+MgO$	0,05-0,1

Ionic composition of the solutions depends on the original composition of the ore and the leaching conditions, i.e. the composition of leach solution. Uranium mainly occurs in form of uranyl tricarbonate complex $[UO_2/CO_3/_3]^{4-}$, however at a lower carbonate ion concentration $/CO_3^{2-}/$ uranyl dicarbonate complexes $[UO_2/CO_3/_2/H_2O/_2]^{2-}$ can be found as well. In the sodium leach solution vanadium can be found in form of vanadate - VO_3^-, phosphate - PO_4^{3-}, silicate - SiO_3^{2-}, aluminate - AlO_2^- and iron of ferric tricarbonate - $[Fe/CO_3/_3]^{6-}$ anions.

Composition of the carbonate-containing solutions, obtained by heap leaching is essentially the same as above. But, these solutions are pure, usually free from suspended solids, which is why they can be easily processed by any kind of ion-exchange method.

3.1.3. Leaching by other reagents

For the leaching of the uranium ores other strong mineral acids /HCl, HNO_3/ can be used as well. These acids can dissolve the uranium even from ores, which are difficult to leach but in spite of this they are not widely applied, because their price is much higher than that of sulfuric acid, and what is more they would cause many technological problems at the processing plants.

Uranium ores can be leached by non-aqueous solutions as well. In this case the leaching reagent (sulfuric, hydrochloric or nitric acid) is fed in a mixture of organic and solid phases, and by agitation the solution of the uranium takes place.

For example, mono- or diisooctyl phosphoric acid, dissolved in isopropylether, has been used, to which the sulfuric acid was separately fed. As regards the carnotite-containing ores on Colorado the metal recovery was around 90%, but the organic phase loss remained 2-8 l/t after the aqueous washing of the solid phase. Industrial application of these methods has not been extensively used.

Ion-exchange accomplished simultaneously with the leaching also guarantees the good equilibrium condition of the leaching of uranium. Continuous sorption of the uranium ions, entering into solution, removes the equilibrium in direction of promoting the solving process. In spite of this their industrial application has not been widely adopted because of relatively high demand in leaching reagent.

3.2. Ion-exchange processing of leaching solutions

Introduction

In processing technology of the uranium ores the uranium, passing into the solution during the leaching, can be recovered by different methods. In this paper we review the methods, based on the application of ion-exchange processes.

To select the most suitable ion-exchange process the conditions must be examined from two points of view. On one hand the physical and chemical characteristics of the products being formed after the leaching (solution and solid residue) must be determined in detail, on the other hand properties of the ion-exchange resins must be known.

After due consideration of these two points of view optimal conditions and methods of ion-exchange can be chosen including the ion-exchange material.

There is insufficient knowledge to determine theoretically the equilibria and kinetics governing the ion-exchange process when applied to multi-component systems such as leach liquors. It is therefore necessary to conduct experiments using a typical leach solution and apply ones theoretical knowledge and experience in determining the required design parameters. Occasionally one may be able to use some data from an existing installation.

To recover uranium from its leach solution by ion-exchange, it is first necessary to choose the sorption process followed by selection of the type of eluant and finally it is advisable to study the mutual influence of the two processes (recirculation of mother lye, etc.).

3.2.1. Sorption

In the equilibrium examination of ion-exchange at sorption the apparent equilibrium constant /K/, distribution quotient /D/, separation factor /η/, i.e. as it is more frequently called selectivity coefficient, are determined.

The given ion-exchange process can be followed by graphical interpretation of equilibrium of the ion-exchange (see Fig. 2). By graphic representation of equilibrium isotherms of the uranium and different

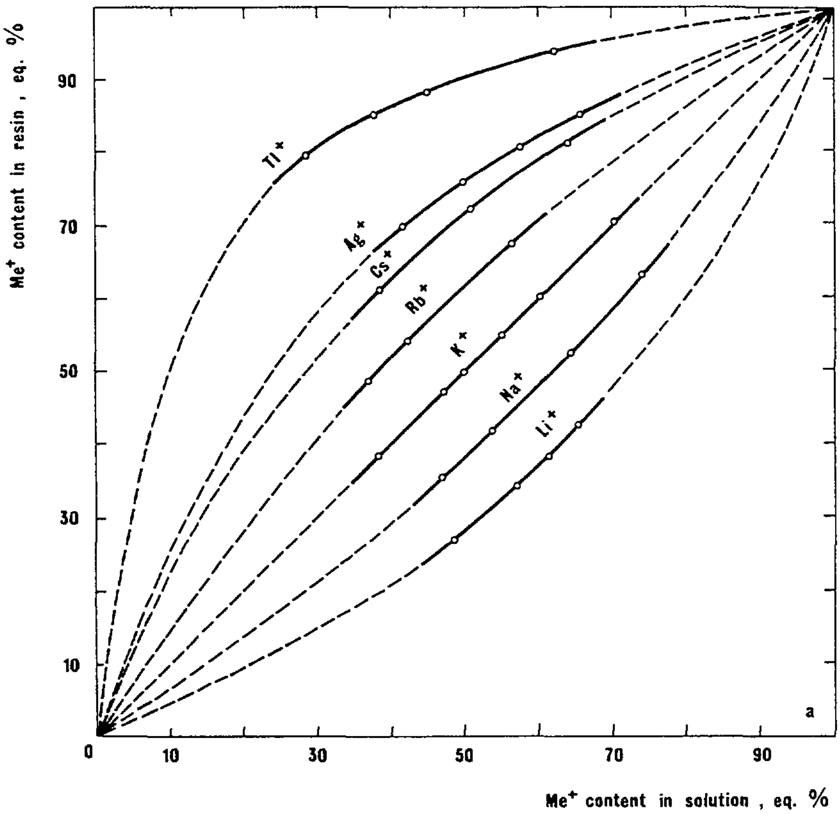
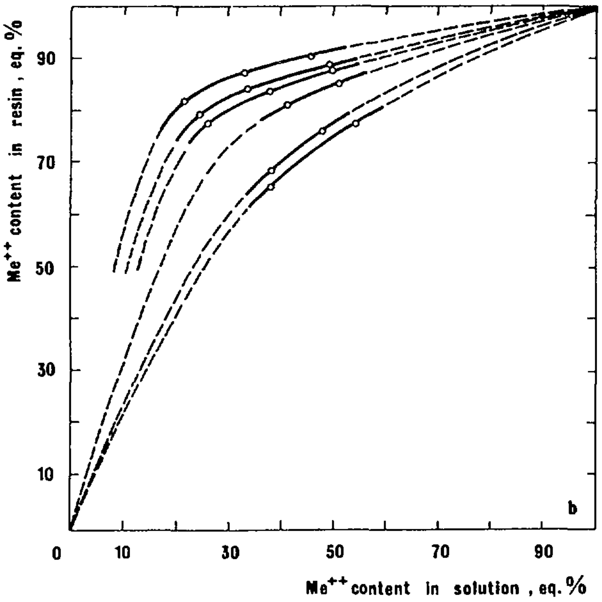


FIG. 2 a



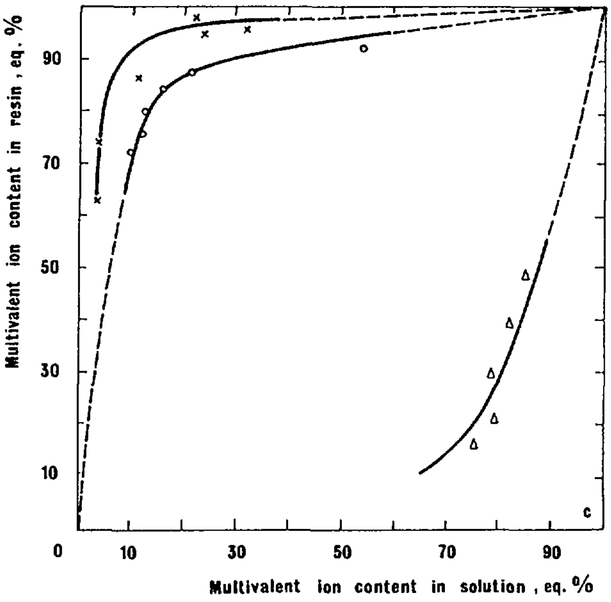


FIG. 2 b

FIG. 2 c

Graphical performance of equilibrium $NH_4R + Me^{\nu+} \longrightarrow$ $\nu = 1,2,3,4$
1 - $BaCl_2$; 2 - $SrCl_2$; 3 - $CaCl_2$; 4 - $MgCl_2$, $ZnCl_2$;
5 - $BeSO_4$; 6 - $CaCl_2$

Fig. 2. Experimental isotherms on phenol acetic acid condensation resin of ammonium form.

contaminating ions, the selectivity of ion-exchange can be extended to the examined ions, and the rank of selectivity in the process for the given ions [22].

One has to see that the selectivity ranks - otherwise determined for diluted solutions - are not always proved for the heavy physico-chemical environment of uranium technologies. They must be specified by experiments. Selectivity coefficient data from diluted solution are known for different resins [9].

On the strong-acid sulfo-cation-exchanger the ions with greater valency are sorbed earlier:

$$Na^+ < Ca^{2+} < Al^{3+} < Th^{4+}$$

Order of priority of sorption of monovalent ions on the same resin is the following:

$$Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+ < Ag^+ < Tl^+;$$

of divalent metal ions:

$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+};$$

and of trivalent ions:

$$Al^{3+} < Fe^{3+}.$$

With resins containing weakly acidic carboxyl-, amidoacetate- and phosphate active groups, there is an important difference among the ranks which will be formed. With carboxyl resin for example the rank is reversed:

$$H^+ > Ca^{2+} > Mg^{2+} > Li^+ > Na^+ > K^+ > Rb^+ > Cs^+.$$

The selectivity ranks on amidoacetate resins are as follows:

$$UO_2^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+}$$
$$> Mg^{2+} > Ba^{2+} > Ir^{2+} > Li^+ > Na^+ > K.$$

The latter ranks differ from the previous ones because of complexes formed between some cations and ions, sorbed on the ion-exchanger.

On the strong-base anion-exchangers, containing quaternary ammonia-groups the selectivity ranks are as follows:

$$F^- < OH^- < Cl^- < NO_2^- < CN^- < Br^- < NO_3^- < HSO_4^- < I^- < SCN^- < ClO_4^-;$$

and

$$MoO_4^{2-} < CrO_4^{2-} < SO_4^{2-};$$

and

$$PO_4^{3-} < AsO_4^{3-} < \text{tartarate} < \text{citrate}.$$

Concerning the weak-base resins (di and triamines) the selectivity ranks are the same as above with the exception of OH^- ions. The reason is the poor dissociation of weak-base resins and the strong sorption of OH^- ions.

3.2.1.1. Cation-exchange recovery of uranium from leaching solutions, obtained by using sulfuric acid

Because of the complicated salt- and ion composition of the sulfate-containing leaching solutions the cation-exchange recovery of uranium is possible only under certain circumstances.

In leaching solutions the greater part of cations /VO_2^{2+}, Fe^{3+}, Fe^{2+}, Al^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, CO^{2+}, Cu^{2+}, Mg^{2+}, H^+, Na^+, etc./ occur in such concentration, alongside the uranyl ions that they are sorbed to a great extent on strongly acidic cation-exchangers. Consequently, there is no possibility for recovery of uranium from such leach solutions by ion-exchange due to lack of selectivity.

From sulfuric acid leach solutions the uranium could be recovered by cation-exchange with acceptable selectivity only by using weakly acidic cation resin (e.g. of acryl- or metacryl base)[8].

But the uranium-containing solution must be of properly high ionic strength. The good result can be explained by the fact that as a consequence of low dissociation of the cation-exchanger the conditions of ion-exchange are worse, so the metal ions are sorbed only to a small extent. But, the uranium is sorbed well, because it forms complexes on the resin.

Weakly acidic methacrylic resin SzG-1 begins to sorb the uranium in important quantity between pH values 1.7-1.9. Highest loading capacity of cation-exchanger for uranium is at pH values 2.8-3.5, when the selectivity is the greatest as well. With further increasing of pH, dissociation of ion-exchanger and the loading capacity at the same time rise, but simultaneously selectivity for uranium decreases.

Elution of cation-exchanger SzG-1 loaded with uranium is made by dilute sulfuric acid solution. The volume of eluent needed for elution equals with 0.8-1.0 of the bed-volume, so 90-95% of uranium passes into eluating solution.

Uranium sorption of resin SzG-1 from complicated and concentrated solutions is advantageous, because the price of the resin is relatively low, its loading capacity is high, its mechanical and chemical resistance is good and requires a cheap eluent.

In the literature there is not any other important reference to uranium-industrial application of cation-exchange.

3.2.1.2. Recovery of uranium from sulfate-containing solutions by anion-exchange sorption

From sulfate-containing leach solutions the uranium is sorbed on strong-base anion-exchangers according to the following reactions:

$$2R_2SO_4 + UO_2/SO_4/_3^{4-} \rightleftharpoons R_4\left[UO_2/SO_4/_3\right] + 2SO_4^{2-}; \quad (27)$$

and

$$R_2SO_4 + UO_2/SO_4/_2^{2-} \rightleftharpoons R_2\left[UO_2/SO_4/_2\right] + SO_4^{2-}. \qquad (28)$$

As in technological solutions the neutral uranyl sulfate complexes can be mainly found and besides them ions with negative charge occur only at higher sulfate concentration, the following reaction plays a role at anion-exchange sorption:

$$2R_2SO_4 + UO_2SO_4 \rightleftharpoons R_4\left[UO_2/SO_4/_3\right]. \qquad (29)$$

The experimental data which prove decrease of uranium sorption and not increase simultaneously with the rise of sulfate concentration of the solution - since the condition promotes the formation of uranium complexes - indicate the fact that in practice rather the neutral uranium complexes should be sorbed on strong-base anion-exchangers. However, at high acid content bisulfate ion is also sorbed on strong-base anion-exchanger to a great extent.

If the solution is more concentrated for uranium (some g/l) $[U_2O_5/SO_4/_2]^{2-}$ anions will appear as well which also will be sorbed on the anion-exchangers.

The strong-base anion-exchangers sorb other anions as well from the solution. As the trivalent iron forms sulfate complexes, it will be also sorbed on anion-exchangers, but the degree of the sorption can be decreased by increasing the acid content of the solution without an important change in sorption of uranium (see Fig. 3). At high pH values and sulfate concentration some other metal ions (scandium, strontium, etc.) will probably be sorbed by ion-exchange on strong-base anion-exchangers besides uranium, but its degree can be neglected and it will not cause any technical problems. That is why in the above situation the uranium can be yielded from its sulfate-containing solutions, with high selectivity.

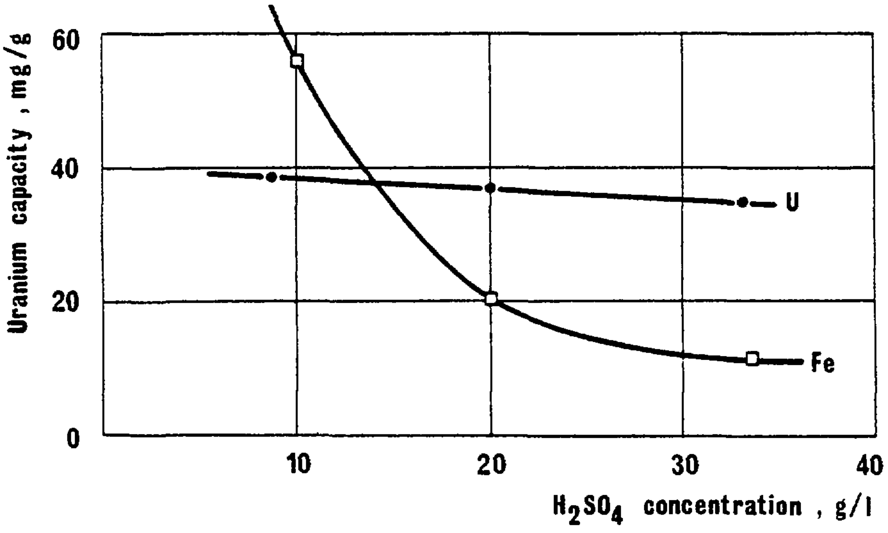


Fig. 3. Change of sorption of uranium and ferric iron depending on acid concentration on anion-exchange resin of AN-2F type.

Other anions being present in leaching solutions /Cl^-, NO_3^-, SO_4^-, $S_4O_6^{2-}$, MoO_4^{2-} and ions, polymerized in acid medium, etc./ will be sorbed on strong-base anion-exchangers under processing circumstances of the uranium ores. In spite of this anion-exchange for uranium is a more selective process than cation-exchange.

Active groups of strong acid cation-exchangers dissociate well in acid medium too, therefore they are not selective at uranium sorption. However, in sulfate-containing solution only anions of some metals occur, and of those only the sulfate complex of iron is present in any appreciable amount. The disturbing effect of iron's sorption can be overcome as well during anion-exchange sorption of the uranium.

Application of weak-base anion-exchangers is advisable first of all for ion-exchange from leach solutions of high acid content. But they sorb uranium preferentially from solutions of high phosphate content or from solutions containing anions which can be well sorbed by strong-base resins such as iron.

By increasing the acid content of the solution the sorption of uranium decreases on weak-base anion-exchangers to a smaller extent than strong-base anion-exchangers under the same conditions (see Fig. 4), and simultaneously decreases sorption of the iron as well. From sulfate-containing solutions with phosphoric acid the selectivity of weak- and medium-base anion-exchangers is also good.

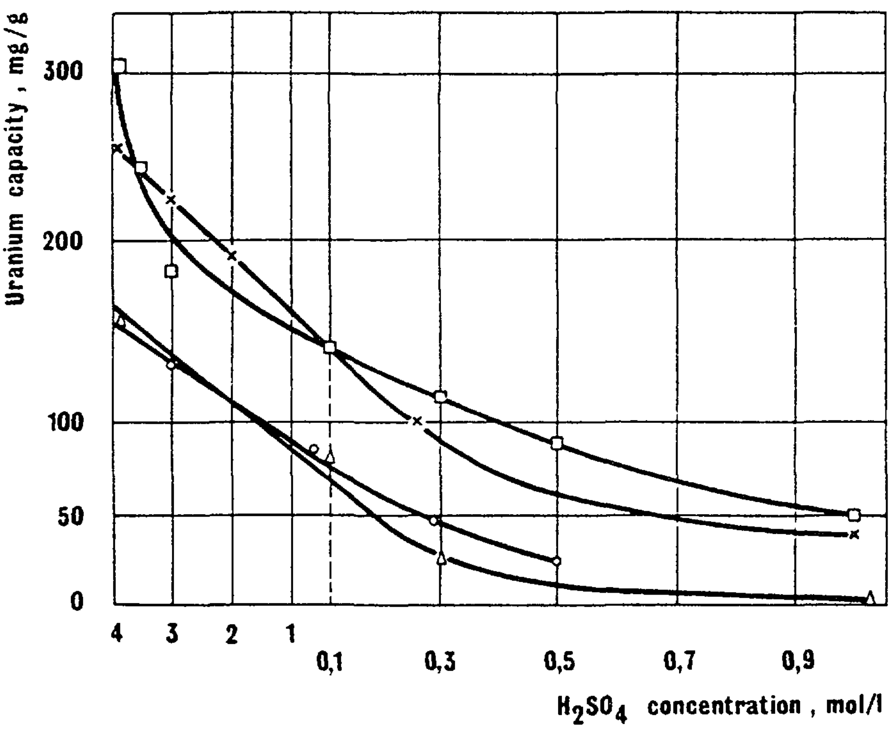


Fig. 4. Effect of free acid concentration on uranium sorption capacity of different ion-exchange resins /V = 0.5 g/l/.

3.2.1.3. Ion-exchange recovery of uranium from carbonate-containing leaching solutions

If the uranium content of the leach solution formed for recovery of uranium from carbonate ores is smaller than 2-2.5 g U/l, the precipitation by lye will not be economical. It is therefore advisable to recover uranium from weak leach solutions by anion-exchange first and then to produce the required uranium product by eluting the uranium from the resin into aqueous solution.

Sorption of uranium from carbonate solutions on anion-exchangers is very similar to the ion-exchange from sulfate-containing solutions.

The uranyl carbonate complex is sorbed on strong-base anion-exchangers of chloride form as follows:

$$4RCl + \left[UO_2/CO_3/_3\right]^{4-} \rightleftharpoons R_4\left[UO_2/CO_3/_3\right] + 4Cl^-. \qquad (30)$$

For purposes of ion-exchange it is better to use strong-base resins than medium- or weak-base ones (see Fig. 5). Uranium sorption capacity of the anion-exchanger depends on the pH value of the solution to a great extent (Fig. 6); if pH decreases, i.e. the solution becomes acidic, the uranium loading capacity will decrease as well.

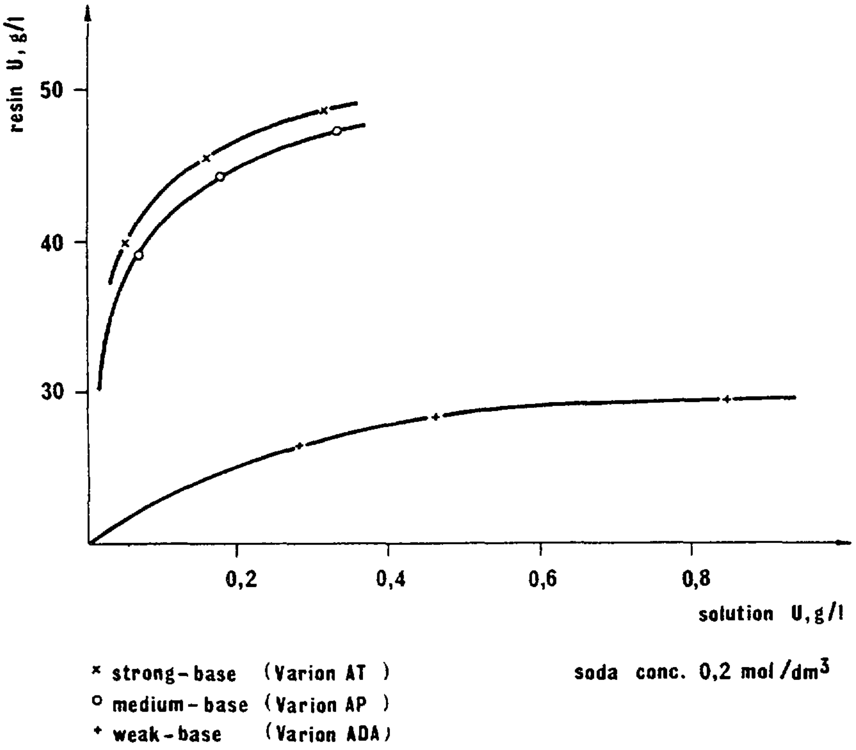


Fig. 5. Uranium sorption capacity of anion-exchange resins with different base in carbonate solutions.

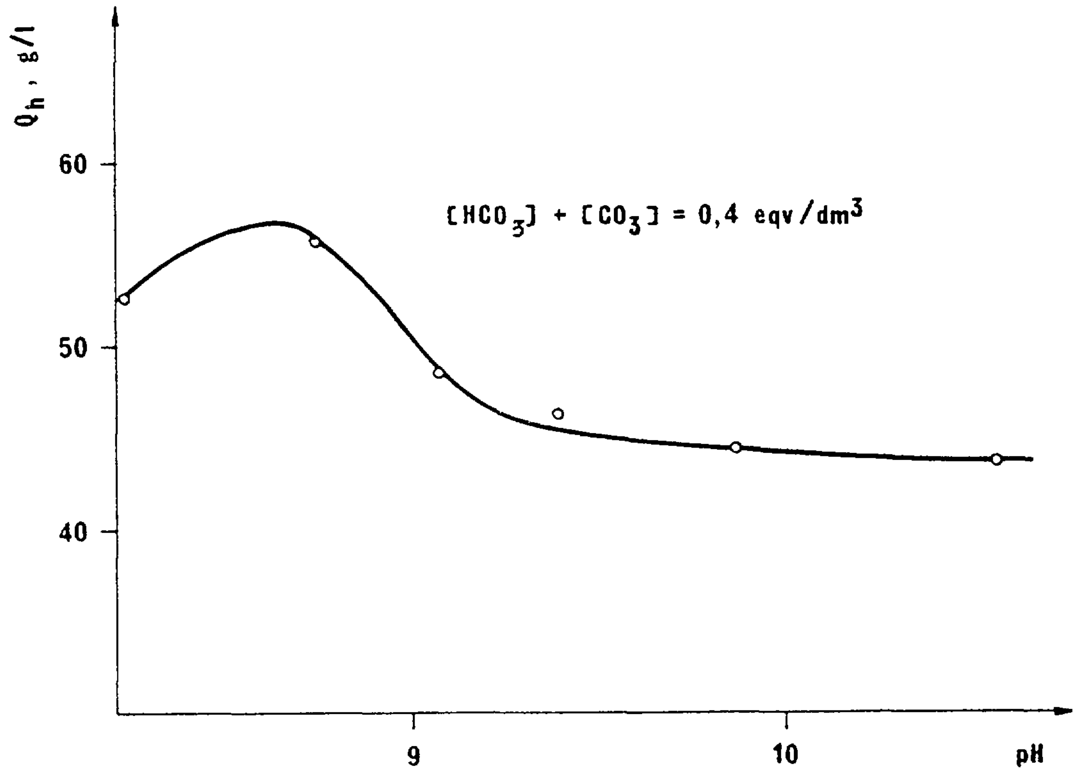


Fig. 6. Change of uranium sorption capacity of anion-exchange resin in carbonate medium depending on pH value of solution (type of resin: VARION AP).

Composition of carbonate leach solutions exerts a considerable influence on the sorption of uranium on anion-exchangers. As it is widely known these solutions contain besides anion $[UO_2/CO_3/_3]^{4-}$, anions VO_3^-, PO_4^{3-}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, maybe MnO_4^-, NO_3^-, ClO_3^-, SeO_3^{2-}, etc. and basic iron carbonate anion complexes, respectively. From the mentioned anions the sorption of uranium is signficantly decreased by Cl^-, and by NO_3^-, if present. These two are sorbed first on anion-exchange resin from a carbonate leach liquor. The priority order of sorption is as follows:

$$PO_4^{3-} > [Fe/OH//CO_3/_3]^{4-} > VO_3^- > [UO_2/CO_3/]^{4-}.$$

Contaminating anions, sorbed on the resin: phosphates, vanadates, aluminates and silicates are pushed away from the resin to a small extent under the influence of the uranium being sorbed later, but as a final consequence the sorption of these impurities decreases the sorption of uranium. But, luckily, only a small quantity of interfering ions, excluding vanadium, occurs in carbonate-containing leaching solutions, so their disturbing effect for sorption is moderate as well.

If the uranium ore contains vanadium in significant quantity the carbonate leach solution will contain both uranium and vanadium. Using fixed-column sorption for example both metals will be sorbed initially on the ion-exchange resin, as it is shown on Fig. 7. Because the selectivity of the resin for vanadium is greater than for uranium, the uranium is displaced by the vanadium until the column is loaded mainly with vanadium.

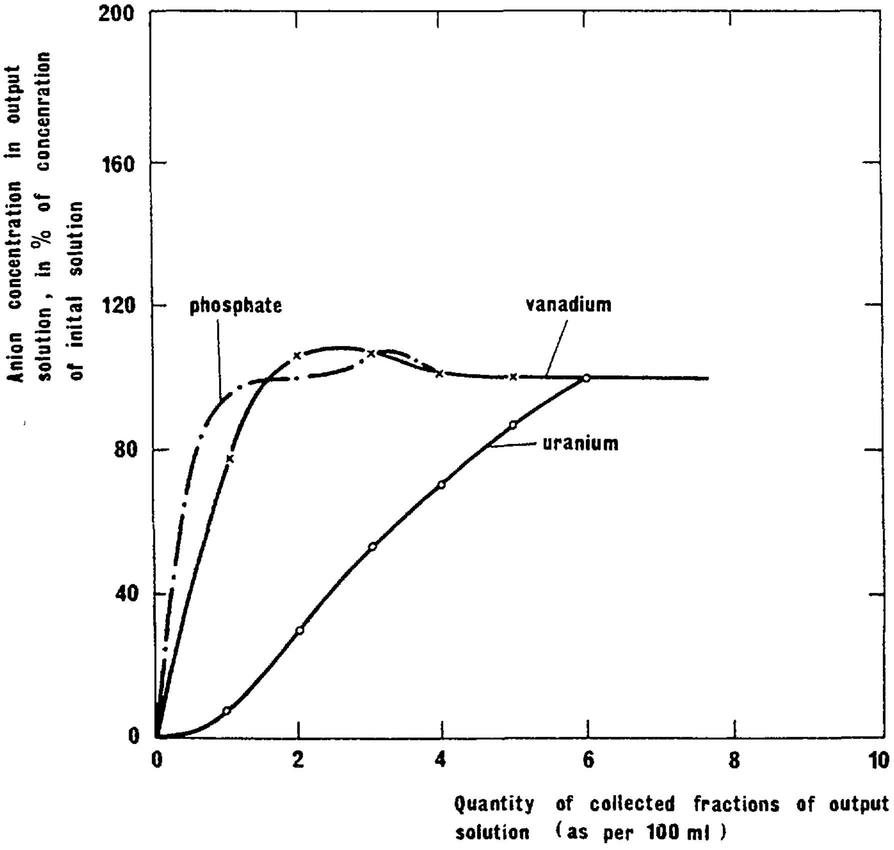


Fig. 7. Sorption of uranyl tricarbonate, vanadate and phosphate ions from solutions on ion-exchange resin of Amberlit IRA-400 type.

Carbonate leach solutions of vanadium and uranium content can be processed for its useful products in alternative way by an ion-exchanger:

- the resin is loaded until the breakthrough of uranium, then the loaded resin is selectively regenerated for uranium and vanadium;
- the column is loaded until the breakthrough of vanadium, when the uranium is sorbed in another column; vanadium and uranium can be eluted separately.

From carbonate leach solutions the aluminate /AlO_2^-/ ions are not sorbed in practice on strong-base anion-exchangers.

3.2.1.4. Recovery of uranium from other solutions (mine waters, waste solutions, etc.) by ion-exchange

Waters of the earth's crust always contain dissolved salts which can be considered as leaching reagents if they contact uranium mineralization. From this point of view the carbonate-hardness of the waters is especially of great importance: for this reason mine waters of high hardness usually contain a significant amount of uranium.

Mine waters must be purified for several reasons: from the point of view of environment protection the waters of high radioactivity cannot be led into natural water streams, sometimes these waters are needed for irrigation or for other purposes, and last but not least the uranium cannot be neglected as it can reduce operating costs.

Recovery of uranium from mine waters should be made on strong-base anion-exchange resin. The chemical process is almost the same as uranium sorption from the carbonate leach solutions. Selection of a suitable ion-exchange technique is influenced by the fact whether in neighbourhood there is a chemical processing unit or not. If there is not the sorption and elution are often carried out in one column by the method well-known from water-softening technologies. The uranium is precipitated from the eluate by lye, and the product of high uranium content, obtained in such a way, is forwarded to a mill for further purification.

In neighbourhood of chemical plants the resin, loaded by uranium, is eluted in these plants, where the uranium is processed as well. Semi-continuous ion-exchange equipment is often selected, where almost a quasi-counter-current process is carried out by frequent removal of small quantities of loaded resin from the sorption columns.

3.2.2. Elution

Ion-exchange resins, loaded in sorption processes, will be subjected to elution. Elution is the reverse process of sorption by which the uranium goes from the ion-exchange resin into aqueous phase again. It means that from chemical point of view equilibria discussed at sorption will be moved into direction of left side.

During elution almost the total quantity of uranium must be stripped from the resin, because during sorption the uranium content of the eluted resin (as a result of the equilibrium processes) determines the uranium content of the effluent or in other words, the metal loss of the sorption process. In practice the value of 0.5-1.0 gU/l is allowed on the eluted resin in order to produce a barren solution containing less than 1 mg U/l.

During elution the ion-exchange resin usually regains the form in which it was at entering into the sorption process. However, in practice it sometimes happens that some unwanted material is not removed from the resin by the normal eluant and it may build up and reduce the capacity of the resin. In such cases a separate process is used to clean or regenerate the resin. This build up of unwanted material is called resin poisoning and this will be discussed later. For uranium elution of ion-exchange resins, several methods can be applied, depending on the quality of the ion-exchanger, the state of loading and further steps of the uranium processing.

3.2.2.1. Elution of cation-exchange resins

As it is known UO_2^{2+} ions are sorbed on cation-exchange resin, e.g. of sodium type, according to the following equation:

$$UO_2^{2+} + Na_2R \rightleftharpoons UO_2R + 2Na^+. \qquad (31)$$

This equation can be reversed and the elution of cation-exchangers, loaded with uranium, is based just on this. If the ion-exchange resin is treated by solution containing a high Na^+ or H^+ concentration, the uranium will be transferred into solution.

The characteristics of elution of cation-exchange resin SzG-1, loaded by uranium, are shown on Fig. 8.

3.2.2.2. Elution of anion-exchange resin

Uranium extraction from acid or carbonate leach liquors is generally carried out using strong-base anion resins. Ion-exchangers, loaded in such a way, can be eluted by different methods.

3.2.2.2.1. Elution of anion-exchange resins in the sulfate form

When eluting anion-exchange resins loaded from a sulfuric acid leach liquor, besides uranium, mainly iron, vanadium and some other contaminating metals and sulfate anions are found. Eluting these resins the following reactions take place:

$$R_4UO_2/SO_4/_3 + 4X^- \rightleftharpoons 4RX + UO_2^{2+} + 3SO_4^{2-}; \qquad (32)$$

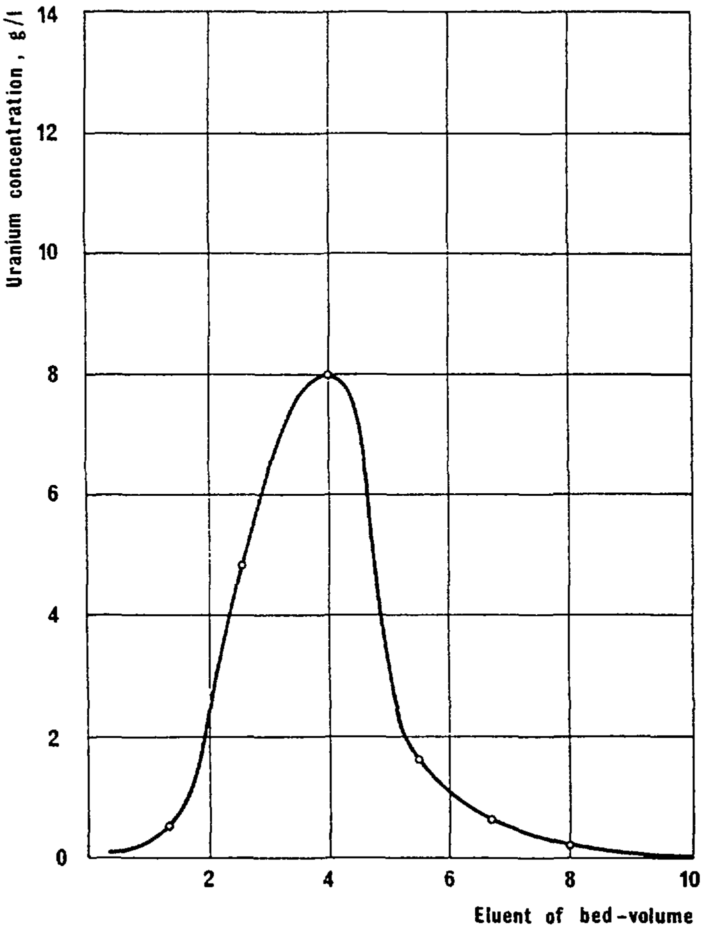


Fig. 8. Elution of uranium from ion-exchange resin of AN-2F type by nitrate-containing solution.

$$R_2UO_2/SO_4/_2 + 2X^- \rightleftharpoons 2RX + UO_2^{2+} + 2SO_4^{2-}; \qquad (33)$$

$$RFe/SO_4/_2 + X^- \rightleftharpoons RX + Fe^{3+} + 2SO_4^{2-}; \qquad (34)$$

$$R_2Fe/OH/./SO_4/_2 + 2X^- + H^+ \rightleftharpoons 2RX + Fe^{3+} + H_2O + 2SO_4^{2-}; \qquad (35)$$

$$RHSO_4 + H^- \rightleftharpoons RX + HSO_4^-; \qquad (36)$$

$$R_2SO_4 + 2X^- \rightleftharpoons 2RX + SO_4^{2-}; \qquad (37)$$

Where $X = NO_3^-$, Cl^- or $\frac{1}{2}SO_4^{2-}$ and

R = the resin.

Elution is also an equilibrium process, so all the conditions are valid for this which have already been mentioned.

Elution may be carried out by sodium-, ammonium or magnesium nitrate of 1.0-1.2 moles acidified for pH = 1 and are chosen depending on what will be used for separation of uranium from the elute, ammonia, sodium hydroxide or magnesium oxide.

Eluting by nitrates, the anionic metallic complexes and other anions sorbed on the resin are exchanged by nitrate ions, so the quantity is determined by the total capacity of the resin.

After precipitation of uranium the nitrate loss from the solution is made up, the pH value is adjusted and the solution is fed back to elution. The loss is caused first of all by the quantity of NO_3^-, sorbed on the resin and the quantity of reagent in the solution which adheres mechanically on resin. Also by the quantity of reagent sorbed by the precipitate during precipitation of uranium and iron by hydroxide.

As the elution is the main operating cost of the ion exchange process it is very important to decrease the consumption of reagent to the minimum value. Elution is promoted by increasing the nitrate concentration, but nitrate losses become larger. That is why in practice the nitrate solution of 1.0-1.2 moles acidified by HNO_3 for value of 1.0-0.8 pH is considered optimal.

Chloride ions are proved to be a good eluant for anion-exchange resins. In practice the chloride concentration of 1.0-1.2 moles is optimal as well at pH = 1.0-0.8 adjusted by sulfuric or hydrochloric acid. Here the rise of chloride concentration to a small extent also improves the concentration of elution, but in operation it proportionally increases its loss as well, similarly to elution by nitrate. But by increasing chloride concentration above 2 moles, the effectiveness of elution begins to decrease. At higher chloride concentration $UO_2Cl_4^{2-}$ complexes will be formed which are strongly sorbed on anion-exchangers.

The sorbed iron behaves in similar way, therefore elution with concentrated chloride, only sulfates will be removed from the resin; uranium and iron will remain on the resin partially or totally.

In the chloride eluate of the saturated sulfatic anion-exchanger a significant sulfate concentration could build up, especially if the mother lye of uranium precipitation is recirculated to the elution. At concentrations occurring in eluting solutions the sulfates from HSO_4^- and SO_4^{2-} ions, which can be also sorbed on anion-exchangers during elution and may take the role of an eluant. But the increase of sulfate concentration to a great extent leads to the decrease of elution - presumably because of the improvement of forming conditions of uranyl sulfate complexes; therefore sulfates must be continuously removed from the recirculating solution.

Uranium can be effectively stripped from anion-exchangers by chloride-containing eluting solutions, in quantity of 2.5-3.5 bed-volumes. Such solutions contain mainly 5-16 g/l of uranium, 5-15 g/l of iron, 40-90 g/l of sulfates and cations in a corresponding quantity. First of all the unwanted iron and sulfate ions in the eluate are separated by milk of lime solution; being neutralized to the value of pH 3.5, $CaSO_4$ will precipitate which, after filtration, is fed back to the leach circuit because of its small uranium content. The uranium is then precipitated from the filtrate by sodium- or ammonium hydroxide, and lime milk solution, respectively at pH 6.5 to 7.5.

Elution by sulfuric acid of anion-exchangers loaded with uranium is based on the principle that HSO_4^- anions might show a greater affinity for anion-exchangers, than the ions of uranium and iron sulfate respectively. So, by a stronger sulfuric acid solution (when the quantity of HSO_4^- ions is great enough) the loaded resin can be eluted.

However, the elution by sulfuric acid is less effective than chloride or nitrate. Therefore in practice it is applied as a combined method, or in a special case, where relatively high uranium content of mother lye, getting away at sorption, is not lost, does not cause metal loss and environment pollution, respectively.

Instead of eluting by sulfuric acid, Na_2SO_4 and $/NH_4/_2SO_4$ resp. is applied and only the pH value of the solution is adjusted by sulfuric acid. In practice a sulfate concentration of 1.0-1.2 moles and a sulfuric acid concentration of 0.1-0.2 moles are generally adequate.

After elution by sulfuric acid there is no possibility of decreasing the iron content of the recovered product by neutralization using lime, therefore this content must be limited even on the ion-exchanger by prewashing of the resin before the elution. Anion complexes of the iron, being sorbed more weakly than anion complexes of uranium, will be removed first from the resin.

From the sulfuric acid eluate, the uranium is precipitated by neutralization using NaOH or NH_4OH solution. The separated precipitate is filtered, dried and taken away for further processing. From the mother lye a sulfuric acid eluting solution is made again.

Compared with the elution using chloride and nitrate, the advantage of using sulfuric acid is on the one hand that the eluted resin returns to the sulfate form, and does not cause any nitrate or chloride ion contamination in the barren liquor. On the other hand in case of recirculation of wastes (waters of pulp reservoirs) they should not accumulate hindering the uranium to be sorbed on the resin.

Elution can be carried out by Na_2CO_3 and $NaHCO_3$ solutions as well. It is proved [10] that CO_2 gas should not arise at elution of loaded resin in sulfate-containing solution, if in the first step the resin was treated with a rather concentrated Na_2CO_3 solution, when only the following reaction could take place:

$$2Na_2CO_3 + H_2SO_4 \longrightarrow 2NaHCO_3 + Na_2SO_4, \qquad (38)$$

and not the following:

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2. \qquad (39)$$

As HCO_3^- ions are able to elute uranium from resin, treated in such a way, the uranium can be eluted by a solution of $NaHCO_3$. 1 N Na_2CO_3 solution of 1 bed-volume and 1 N bicarbonate solution of 2-4 bed-volumes are suitable for this process.

The advantage of the process that unwanted NO_3^- and Cl^- ions from the resin at the commencement of sorption should not pass into solution, but as the eluted resin is in the HCO_3^- form nevertheless there will be gas release during the sorption on contacting the resin with the acid solution which can affect the mechanical stability of the ion-exchange column.

3.2.2.2.2. Elution of anion-exchange resins in carbonate form

Mainly uranium anion complexes are sorbed on anion-exchangers of carbonate form arising at processing of uranium ores by using carbonates. If carnotite-containing ores are processed, vanadium anion complexes also will be well sorbed on anion-exchangers. Other metal, and other anions may be sorbed on the resin depending on the character of the ore; however these are not typical cases of the sorption by using carbonates.

For elution of loaded resins of carbonate type several reagents can be used. Elution effect of different salts, acids is shown on Fig. 9.

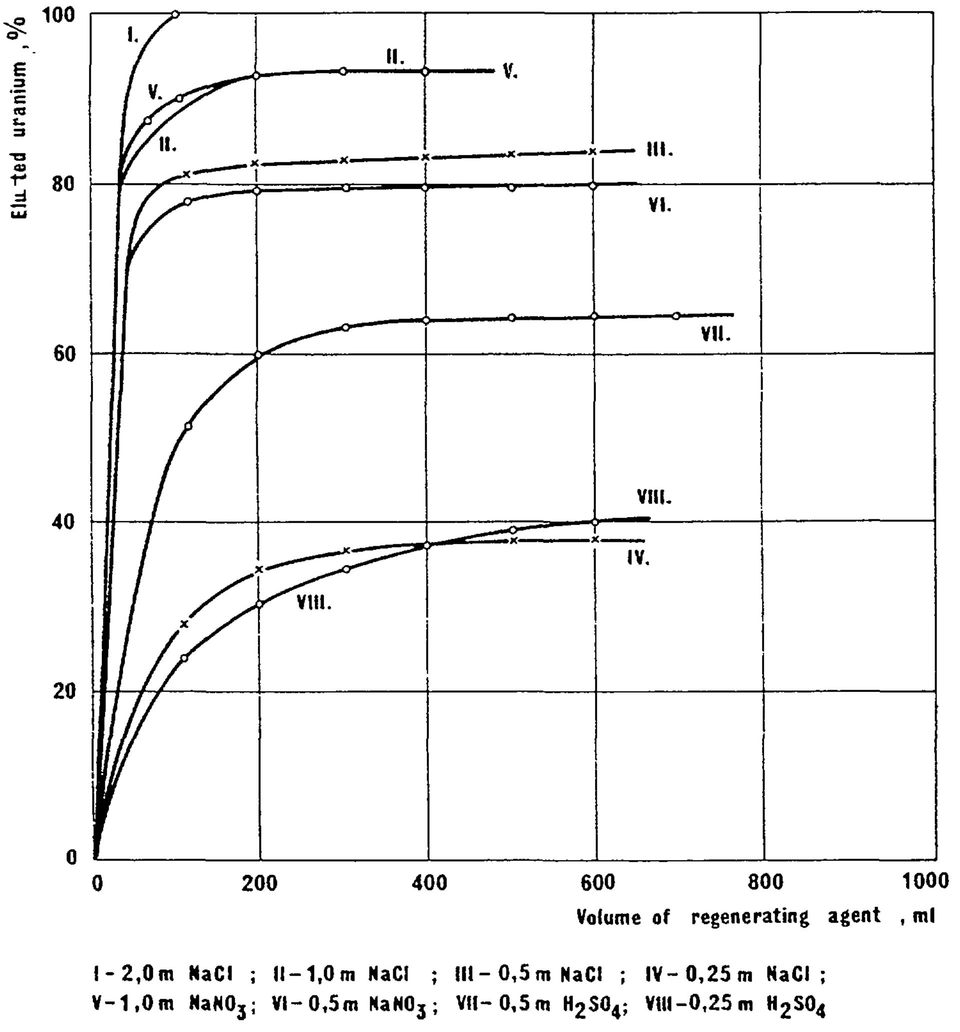


Fig. 9. Desorption of uranium from ion-exchange resin; Amberlit IRA-400 type by different solutions.

As it is proved by the Figure, $NaNO_3$ and NaCl can be considered as the most effective eluants. Efficiency of sulfuric acid and different sulfates is much smaller. The sodium elution of loaded anion-exchangers of carbonate form is also possible, but its efficiency is small, too.

In practice usually nitrate or chloride containing solutions of 0.8-1.0 moles, containing 0.1 moles soda are used for elution of carbon anion-exchange resins. It is possible to feed acid instead of soda to the solution, but in this case the uranyl carbonate complex decomposes and the uranium changes into a compound of sulfate form.

At the same time decomposition of the carbonates is accompanied by release of CO_2 gas of a great quantity which exerts unfavourable influence for the resin.

For regeneration of loaded anion-exchangers in carbonate leach solutions a loaded solution of ammonium-carbonate form is applied. Mixing the ion-exchanger with such a solution the uranium will be eluted and will form $/NH_4/_4UO_2/CO_3/_3$ crystals with the solution as third phase. After the separation of crystals the solution is loaded again with $/NH_4/_2CO_3$ and fed back to elution.

The crystals $/NH_4/_4UO_2/CO_3/_3$ formed are heated, where U_3O_8 is gained. The released gases are regenerated, so only a small quantity of reagent for compensation is necessary at elution.

3.3. Poisons of resin

Ion-exchange resins often sorb materials from the leaching solutions which cannot be removed from the resin during the usual elution. So, these materials can disturb ion-exchange processes even in a small quantity, because they accumulate on the resin if sorption-elution cycles are repeated. This reduces the useful capacity of the ion-exchanger and it will become eventually unsuitable for uranium production.

Poisons of resin can exert their influence through either physical or chemical effects.[11-15]

Polythianate ions are poisons of resin of a strong chemical effect. In practice we can meet them at leaching of ores, containing sulfides, by using sulfuric acid or when processing cyanized wastes for uranium. They arise at leaching of sulfide-containing ores by sulfuric acid, if there are strong oxidants present $/MnO_2/$ and the leaching solution contains sulfuric acid only in a small quantity.

Oxidation of pyrite in alkaline /NaOH/ solution results in ferric hydroxide or sodium sulfide, but the latest quickly changes first into thiosulfate, then into sulfate. At oxidation of pyrite in neutral and acid solutions sulfuric acid and ferrous sulfate and ferric sulfate will be formed. It is found /10/ polythionates /S_nO_6/ poison the resin; where n = 2-6, arising from pyrite at acid leaching, pH being 1. Thiosulfate arising from sulfide enters into reaction with pyrolusite as follows:

$$2Na_2S_2O_3 + MnO_2 + 2H_2SO_4 = Na_2S_4O_6 + Na_2SO_4 + MnSO_4 + H_2O \qquad (40)$$

Tetrathionate, sorbed on anion-exchangers, is a very radical poison of resin, it cannot be removed by the usual elution. Theoretically more than one reaction would be able to regenerate the resin, poisoned by tetrathianate:

- **by sulfides:**

$$S_4O_6^{2-} + S^{2-} \longrightarrow 2S_2O_3^{2-} + S; \qquad (41)$$

- **by cyanides:**

$$S_4O_6^{2-} + CN^- + H_2O \longrightarrow SO_4^{2-} + CNS^- + S_2O_3^{2-} + 2H^+; \qquad (42)$$

- **by thiosulfite:**

$$S_4O_6^{2-} + HSO_3^- \longrightarrow S_3O_6^{2-} + S_2O_3^{2-} + H^+; \qquad (43)$$

- **by mercuric chloride:**

$$2S_2O_6^{2-} + 3HgCl_2 + 4H_2O \longrightarrow HgCl_2{\cdot}2HgS + 2S + 4Cl^- + \\ + 4SO_4^{2-} + 8H^+; \qquad (44)$$

and (45)

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \longrightarrow HgCl_2{\cdot}2HgS + 4Cl^- + 2SO_4^{2-} + \\ + 4H^+;$$

- **by hydroxides:**

$$2S_4O_6^{2-} + 6OH^- \longrightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O. \qquad (46)$$

In practice, however, the last reaction is applied for regeneration of the resin. In first step the tetrathianates bound on the resin are decomposed by lye to trithianates:

$$4S_4O_6^{2-} + 6OH^- \longrightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O. \qquad (47)$$

The trithianate and thiosulfate being formed mainly remain on the resin, because OH^- ions are sorbed on the resin not so strongly. Then trithianate and thiosulfate ions may be eluted by chlorides.

Rhodanide ions are poisons of anion-exchange resins of chemical effect. Their effect is met only at plants where the uranium ores to be processed are pretreated by cyanide-containing solution for example in order to recover gold. Cyanide ions form with sulfides rhodanide ions and with uranium being present uranium cyanide complexes. From such solutions besides $[UO_2/SO_4/_3]^{4-}$ complexes uranium rhodanide complexes, and rhodanide and sulfate ions are sorbed as well on anion-exchangers as it is shown on Fig. 10. Anion complexes of uranyl rhodanide may be present in sulfate-containing solution in the following forms:

$[UO_2/NCS/_3]^-$ $[UO_2/NCS/_5]^{3-}$

$[UO_2/NCS/_4]^{2-}$ $[UO_2/NCS/_6]^{4-}$

On the free ion exchange sites of the same quantity of anion-exchangers more uranyl rhodanide complexes of low negative charge /1-3/ can be sorbed, in which 1-1 uranyl ion is present, than uranyl trisulfate anion complexes which also contains only one uranyl ion. So, the resin shows a greater total capacity than the theoretical one in sulfate-containing solution at sorption, accomplished in the presence of rhodanide ion contamination for $[UO_2/SO_4/_3]^{4-}$ than in the absence of it. So, during the first cycle the rhodanide ions could effect advantageously for the sorption. But, in reality this advantage would not appear, because

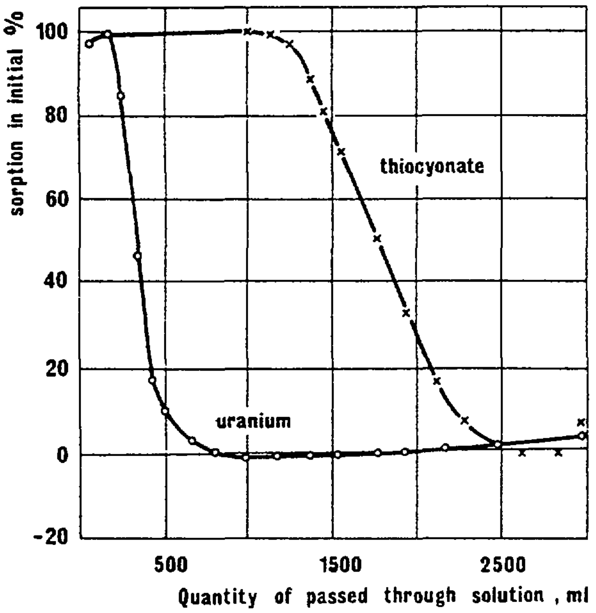


Fig. 10. Sorption of uranium and thiocyanate on ion-exchange resin of Deacidit FF type.

disadvantages of the following deleterious effects are much greater and cover up the previous advantage:

1. Strong-base anion-exchangers show greater affinity for rhodanide complexes than for uranyl trisulfate complex, therefore because of sorption of the previous ones the capacity of resin for uranium decreases.
2. Uranyl rhodanide anion-complexes are sorbed on anion-exchangers more strongly than uranyl sulfate anion complexes, therefore the latter cannot be removed from resin by the usual elution, so it makes the useful capacity of resin decrease.
3. Rhodanide salts are sorbed very strongly on strong-base anion-exchangers, therefore after the total elution of the uranium (uranyl trisulfate and uranyl rhodanide ions) there will be some salts on the resin decreasing its useful capacity.

As the rhodanide ions in practice cannot be totally removed from anion-exchangers even by elution using nitrate, they will accumulate dangerously in ion-exchange cycle. In nitrate-containing medium of elution the rhodanide ions can be decomposed and as a consequnce of this elementary sulfur can be separated.

In order to avoid poisoning effect of rhodanides it is advisable to wash out the ore with water thoroughly and to apply acid concentration as high as possible in the first stage of the leaching to decompose cyanides to a great extent.

The resin, already poisoned by rhodanide ions (and by elementary sulfur) must be given a special regeneration.

The silicon dioxide poisons the resin in a physical manner. Sulfuric acid leaching solutions always contain silicium in different forms and quantities. In sulfuric acid solution the solved silicium occurs in mono- or dimer i.e. low polymer form (AMP form - reacting with ammonium molybdate) which is soluble, or in colloidal polysilicic acid of higher polymerization degree. If concentration of soluble silicon dioxide of AMP form is above 2 g/l, then - one part of it - relatively quickly changes into silicon dioxide of colloidal form - about to the value of 1 g/l SiO_2. This means that in practice, during the sorption, the increase of SiO_2 content of the resin is in direct relation with the SiO_2 content of AMP form of the solution and not with total SiO_2 content (see Fig. 11). Silicium is sorbed from the solution on the resin in mono- and dimer, and low polymer form, respectively.

On strong-base resin the silicium is not sorbed in ionic form. This is proved even by the fact that at sorption of silicon dioxide counter ion should not appear in the solution /e.g. Cl^- or NO_3^-/. According to our

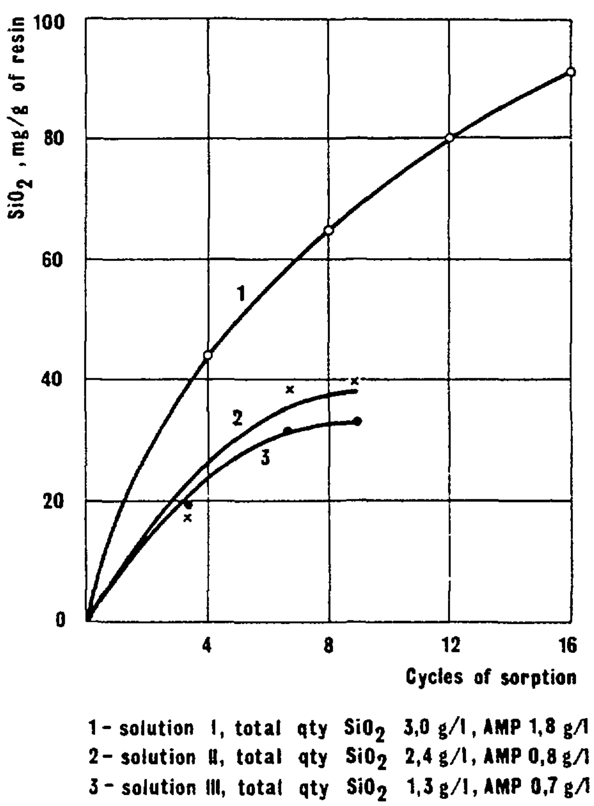


Fig. 11. Sorption of silica on ion-exchangers of Deacidit FF type from leaching solutions.

present knowledge the sorption of silicium on anion-exchangers takes place similarly to the mechanism of water diffusion. The explanation is that silicic acid should not dissociate in practice under the circumstances of the sorption (high salt content, pH = 1.5-1.8). Then silicium, getting into resin by diffusion, quickly polymerizes which is promoted by water washing of the resin, i.e. by increase of pH of surrounding solution.

Non-polymerized quartz is removed from strong-base resin by normal elution; but the polymerized one does not leave, it fills up the pores of the resin, makes the kinetics of sorption and elution slow down and reduces the capacity due to filling up the pore volume. Only alkaline treatment can be effectively applied for removal of such poisons. In such a case the poisoned resin is regenerated either in its original place (from elution) or by a separate regenerating process.

Poisoning of ion-exchangers by elemental sulfur takes place as a secondary process of sorption of rhodanide and polythionate ions, discussed previously. In contrast with poisoning effect of chemical character of these two processes, the elementary sulfur is a poison of resin of physical nature. Fine aggregated sulfur, arising as a result of decomposition of polythionates and rhodanide ions, mechanically closes the free channels and the active groups of ion-exchangers, by hindering or preventing diffusion and consequently the ion-exchange. Such elemental sulfur can be removed from the resin only by NaOH solution. By an alkaline treatment the sulfur being on the resin can be transformed into sulfide- and polysulfide sulfur respectively which can then be easily removed from the resin by common salt. Applying this method the sulfur can be totally removed from the anion-exchangers.

Molybdenum and some other elements can also play the role as a poison of resin for extracting uranium. If the ore contains molybdenite, it can be dissolved during leaching by using sulfuric acid. In the solution the molybdenite cations /MoO_2^{2+}/, being present because of amphoteric characteristics of molybdenum, form anionic complexes which are similar to uranyl sulfate anions and they are sorbed on strong-base anion-exchangers.

Molybdenum does not cause decrease of resin capacity even after several cycles when elution of resin by nitrate is employed but it does when elution is by chloride. This may be explained by the fact that in nitrate-containing medium the molybdenum should be polymerized and leave the resin. Molybdenum can be easily removed from the resin by lye.

In sulfate-containing solution titanium also forms an anionic-complex. But it can easily precipitate if the pH of the solution increases. Titanium precipitation may occur on anion-exchange resin for example during washing which causes physical poisoning of resin. The separated titanium precipitate can be dissolved by sulfuric acid containing ammonium bifluoride solution.

Zirconium also forms sulfate complexes, but in the presence of phosphorus it can be sorbed on the resin in $ZrOHPO_4$ form as well. It can be eluted from the resin by strong sulfuric acid.

Thorium also can be accumulated in a small quantity on the anion-exchangers at sorption of sulfuric acid containing solution. It can be removed by elution using sulfuric acid.

Different groups of organic materials being solved from the ores may behave as poisons of resin: for example, humic acids, some sulfonic acids, etc. Organic molecules can be sorbed on anion-exchange resin either by sorption or by ion-exchange. First of all the resins of gel-type are susceptible for poisoning. The poisoned ion-exchanger can be regenerated by sodium hydroxide solution.

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CHAPTER 4

ION-EXCHANGE SYSTEMS AND ION-EXCHANGE MATERIALS IN NUCLEAR POWER PLANTS

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Abstract

Specific technological solutions for ion-exchange plants used in NPP are explained: Water treatment (make up) plants;Ion-exchange water treatment plants in NPP with PWRs (Condensate polishing systems in secondary circuit;Plants for clean-up of blowdown water from steam generators); Ion-exchange systems in the reactor circuit of PWRs (Chemical and Volume Control Systems-bypas instalation for reactor water purification;Ion-exchange systems for control of H_3BO_3 concentration in reactor water); Ion-exchange water treatment plants in NPP with BWRs reactor clean-up systems and turbine condensate(feed water) polishing systems.

The ion-exchange units in typical radioactive liquid waste systems and the cleaning up of fuel storage pools in NPP are also explained.

An attempt to evaluate the efficiency of technological behaiviour of the ion-exchange systems cited above was made. The evaluation is based on the data of units running in NPP in UK,Bulgaria,Japan,Belgium,Soviet Union,Sweden,India,USA,Canada etc.

4.1 ION-EXCHANGE UNITS IN NUCLEAR POWER PLANTS.WATER TREATMENT PLANTS

In the NPP with BWRs and PWRs the necessary desalinated water to make up the unavoidable water losses is usually produced by ion-exchange demineralization of fresh water (from rivers,lakes,reservoirs,underground sources etc).In most cases the demineralized water must meet the following requirements:

- chlorides content: max 20* (100) μg/l;
- silicates content: max 20* (50) μg/l;
- specific electrical conductivity:below 0.5 (1.0) μS.cm^{-1}

In order that the desalinated water meets these requirements it is necessary to resort in all cases to ion-exchange processes.

Depending on the quality of the raw water,the ion-exchange part of the water treatment plants comprises units for:

1. H-removal with strongly acidic cation exchangers.(In the case of high alkalinity units for H-removal with weakly-acidic cation exchangers can be preconnected):

2. OH-removal with weakly anion exchangers.(Usually,macroporous weakly basic anion exchangers are used thus quaranteeing the effective protection of the postconnected strongly basic anion exchangers threatend by contamination with organic matter contained in the water (1,3).

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* These data are characteristic of the water treatment plant at Kozlodui NPP (1).

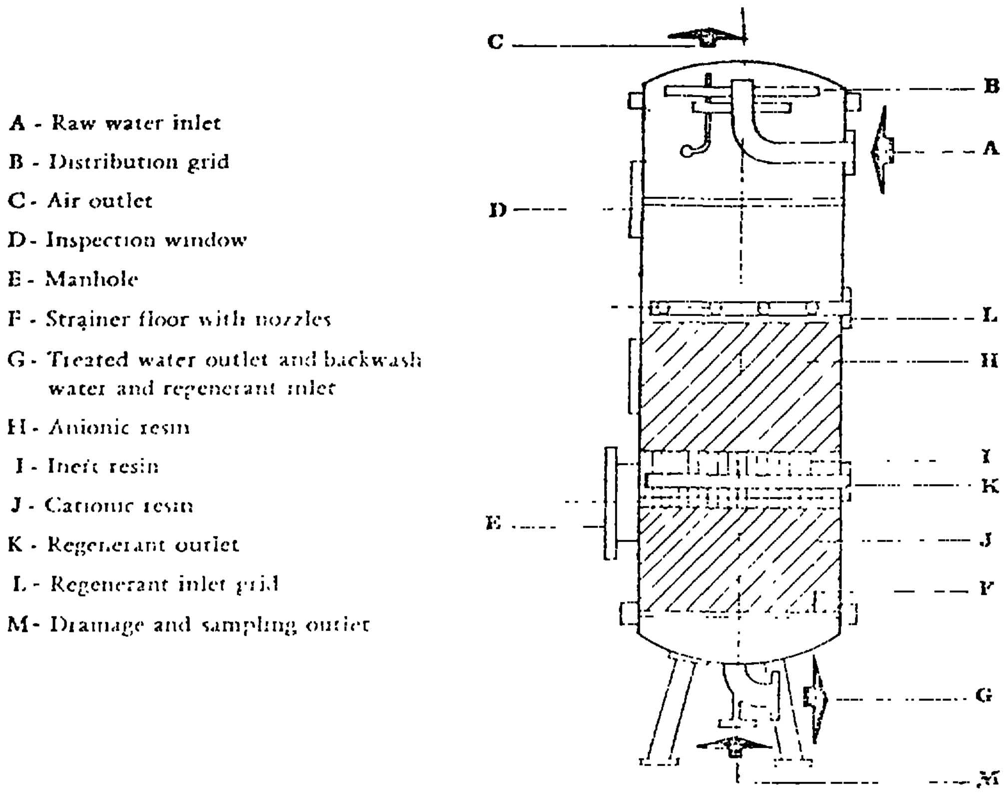

Fig. 1 Type of equipment used for triobed system (2).

3. OH-removal with strongly basic anion exchangers. (Usually strongly basic anion exchangers type I with gel structure. When treating surface waters, strongly contaminated with organic substances, macroporous or isoporous strongly basic anion exchangers are recommended):

4. Demineralization through mixed bed (with internal or external regeneration) loaded with strongly acidic cation exchanger and strongly basic anion exchanger usually in a 1:2 ratio by volume.

In order to achieve a higher degree of water demineralization and to use more effectively the reagents for regeneration mixed beds of the "trio-bed" type have also been recommended in recent years (2). Fig. 1.

In order to limit to the possible minimum the chloride ions concentration in high purity water the regeneration of the strongly acidic cation exchangers in mixed bed is done usually with sulfuric acid instead of hydrochloric acid.

The introducing of systems for counter-current regeneration (for the H-cation exchanger units) and of conjugated regeneration for the units loaded with strongly basic and weakly basic anion exchangers makes possible a 30-40% cut of the costs for acids and respectively 20-30% cut of the costs for the hydroxides as compared with the ordinary (once-through) ion-exchange method (3).

At normal service cycle of the individual ion-exchange units (over 18-20 hours) the annual losses of ion-exchange resines do not exceed.

1% for the cation exchangers and

2% for the anion exchangers (1% in the case of macroporous anion exchangers).

The usual total life of the ion exchangers is over 10 years. This life is also valid for the gel type strongly basic anion exchangers if the ion exchangers units, loaded with this type of ion exchanger, are preceeded by units with macroporous weakly basic anion exchangers.

(Any irreversable contamination of the anion exchangers with organic substances or ions of heavy metals might result in shortening this life to 1 or 2 years.)

Some authors (4) recommend to avoid water from survace sources in the water treatment plants of NPP because this water contains organic substances some of which pass directly through the water treatment plant, its ion exchange units included.

The eventual degradation of these organic substances at elevated temperatures may cause an increase of water corrosion of the steam produced from it (5).

Practice at Kozlodui NPP shows (6) that if macroporous weakly basic anion exchangers are used in the water treatment plant and the post-connected strongly basic anion exchangers are macroporous or isoporous and if they are followed by MBF loaded with strongly acidic cation exchanger and strongly basic anion exchanger type I with a gel structure then the highly demineralized water is practically free from organic substances, irrespective of the fact that water from the Danube,considerably contaminated with organic substances,is desalinated.

In conclusion it can be pointed out that the methods and ion-exchange resins used for water treatment in the conventional thermal power plants can be applied in the ion-exchange water demineralization units in NPP,certainly under consideration of the qualities of the respective water sourse.The right choice of the reagents for ion exchangers regeneration might help meet the stringent requirement that demineralized water in NPP has an exceptionally low concentration of chlorides(1).

4.1.1.ION-EXCHANGE WATER TREATMENT PLANTS IN NPP WITH PWRs

4.1.1.1.ION-EXCHANGE PLANTS IN THE SECONDARY CIRCUIT.CONDENSATE POLISHING SYSTEMS

Irrespective of the initial view that condensate polishing is not a typical technological solution in a NPP with PWR, practice shows that the clean-up of the whole amount of condensate in the secondary circuit of NPP with PWR is necessary not only in the cases of high salt content in turbine condensers cooling water (7,8) but also of medium salt content of this water (9,10) and especially so when the steam generators tubes are made of stainless steel (7,11,12). The clean-up of the whole amount of condensate in the condensate polishing system (CPS) makes possible a considerable reducing of blowdown water amount of the steam generators. Thus, heat losses are reduced and in the case of NPP with VVER-400 conditions are created to increase unit's capacity by about 20% (11).

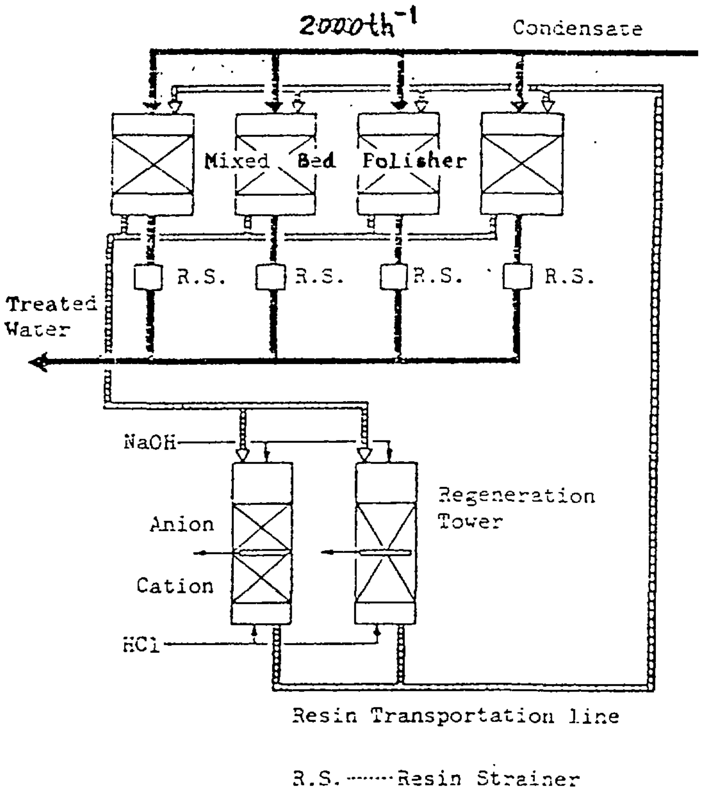

Fig. 2 Condensate polishing system for PWR (8).

The ion-exchange units are indispensable from CPS in the secondary circuits of NPP with PWR. CPS in the Japanese NPP of this type are as those presented in Fig. 2 (8), ie CPS consists only of MBF loaded with strongly basic anion exchanger and strongly-acidic cation exchanger in OH- and H- form, respectively. The effectiveness of this system is evident from data presented in Fig. 3 (8).

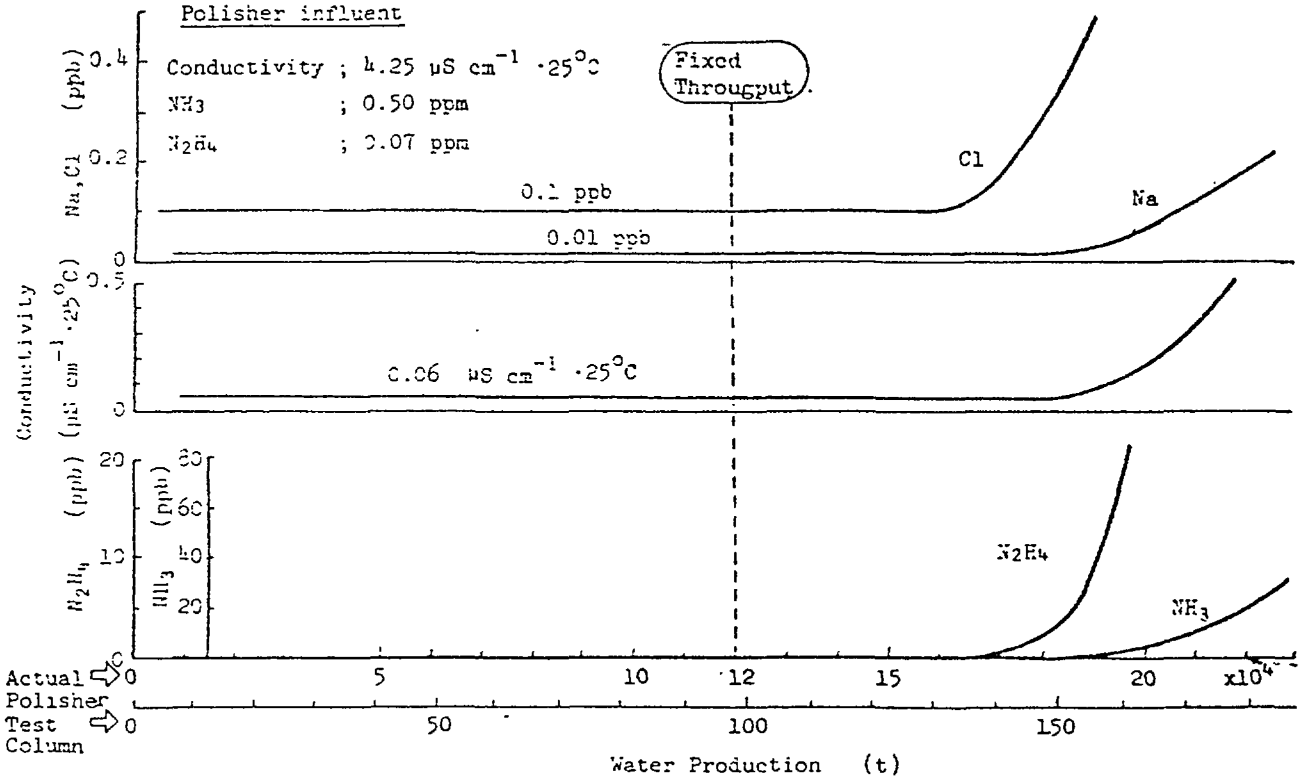

Fig. 3 Over-production test of a codensate polisher exceeding the fixed throughput (8).

The technology of CPS in the secondary circuit of Bruno Leuschner NPP, GDR (VVER-400) is similar (7). This CPS consists of 5 MBF dia 2 000 mm with external regeneration. Each mixed bed contains 4.5 m^3 ion-exchange mixture: 3 m^3 Wofatit SBW-MB and 1.5 m^3 Wofatit KPS-MB. Each mixed bed is designed for flowrate 180-250 m^3/h at filtration rate 60-80 m/h. The ion-exchange resins are regenerated with 5% NaOH, respectively 5% H_2SO_4. The polished condensate has always a specific electrical conductivity below 0,1 μS.cm^{-1}. Rest content of chlorides in the polished condensate is below 20 ppb (even when, due to leakages in the condensers, chlorides content in the turbine condensate is 1 ppm) (7).

Alkalyzing reagents are not added into the water in the secondary circuit for which reason each MBF treats about 900 000 m^3 condensate between two regenerations. However, under such conditions the degree of corrosion products removal from the turbine condensate is comparatively low-30% of the iron and 60% of the copper corrosion products are removed (7).

Unlike Bruno Leuschner NPP, in PWR Doel, Belgium (9,10) volatile alkalyzing reagents (ammonia and hydrazine) are added in the water of the secondary circuit (in the turbine condensate). This is reflected in the CPS scheme adopted, Fig.4 (10).

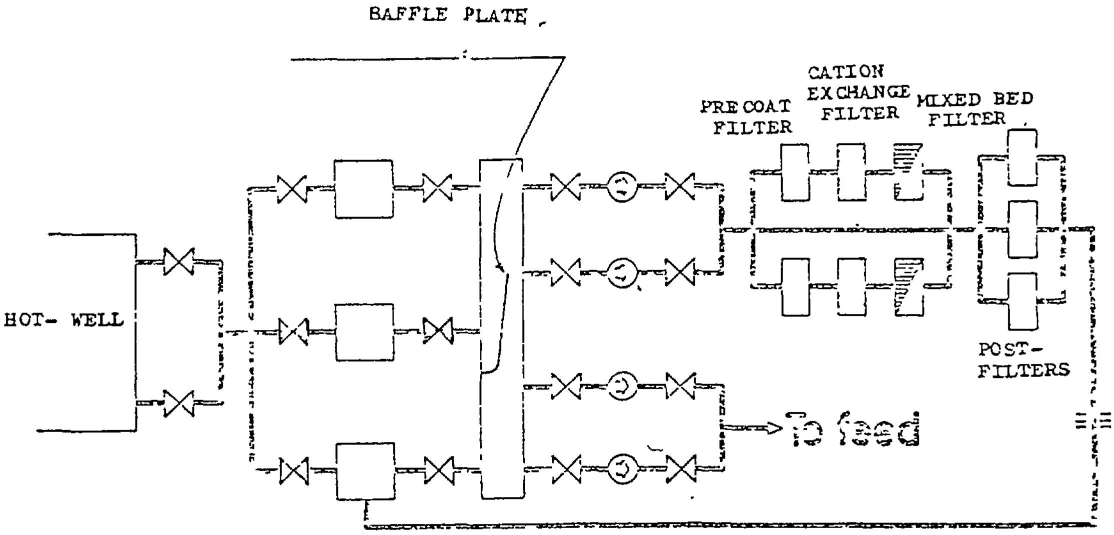

Fig. 4 Doel full flow condensate polishing system (10).

The condensate polishing system consists of:

a) precoat filter of inert material (removes the suspended corrosion products from the turbine condensate);

b) filter with strongly-acidic cation exchanger in H-form-Duolite C26C (removes the ammonia from the condensate);

c) MBF loaded with strongly-acidic cation exchanger in H-form (Duolite C26C and strongly-basic anion exchanger in OH-form-Duolite A161C).

The cation bed filter operates at a rate of 90 m/h, and MBF at 100 m/h.Each MBF is followed by a precoat filter of powdered ion exchangers (Powdex filter).This filter reduces sodium ions concentration in the condensate after MBF.(However, the main reason is the insufficient elution of the ion exchangers in MBF after regeneration.The ion exchangers in MBF are regenerated in the filter).Later,MBF were reconstructed in triobed filters, Fig. 1.To this end,inert material - Duolite S3-TR (bed height 20 cm),is insertd between the cation exchanger Duolite C26C and the anion exchanger Duolite A161C.The triobed filters consist of 6000 l Duolite A161C, 1000 l Duolite S3-TR and 4800 l Duolite C26C.Regeneration is done with H_2SO_4 and NaOH.

According to (2),sodium ions concentration in the polished condensate has been about 1 ppb when using MBF but has dropped about 20 times - up to 50 ppm - after implementing the triobed filters.The specific electrical conductivity of the polished condensate is $0.08-0.10 \mu S.cm^{-1}$.

In CPS of Kozlodui NPP,Bulgaria (12),(reactor type VVER-440) are envisaged 5 MBF with external regeneration loaded with macroporous strongly-acidic cation exchangers and strongly-basic anion exchanger of the macroporous type.The reasons for the selection of this type of ion-exchange resins are:

a) to prevent the irreversable contamination of the ion-exchange resins (anion exchanger) with organic matter (leaked in the turbine condensate through the turbine condensers).

b) to limit the mechanical degradation of the ion exchangers in view of the greater mechanical loading during the transportation operations of the external regeneration of MBF and at the high filtration rates, 80-100 m/h.

In conclusion it can be summarized that the ion-exchange resins in CPS in the secondary circuits of NPP with PWR does not have to be "nuclear grade" but a class C is recommended (for condensate-polishing systems) particularly when external regeneration of MBF is applied. Usually, these are macroporous resins, characterized by a higher chemomechanic and mechanic stability.

The triobed filters are to be preferred, especially in the cases when the ion exchangers are regenerated in MBF and the possibility of good separation of the cation and anion exchangers is limited.

4.1.1.2. PLANTS FOR CLEAN-UP OF BLOWDOWN WATER FROM THE STEAM GENERATORS

All plants for the clean-up of blowdown water from the steam generators comprise ion-exchange demineralization units strongly-acidic cation exchanger in H-form and strongly-basic anion exchanger in OH-form, put in different filters or mixed in MBF.

In the absence of condensate polishing in the secondary circuit the amount of blowdown water from the steam generators can reach up to 2% of feedwater consumption. (This is necessary so that the clean-up of blowdown water from the steam generators could affect more actively the eventual increase of admixtures in the feedwater as the result, in the majority of cases, of leakages in the turbine condensers).

In Stade NPP (PWR), FRG the plant for clean-up of blowdown water from the steam generators comprises MBF preceded by an electromagnetic filter which retains the main portion of the suspended cruds. This filter prevents the mechanical contamination of the ion-exchange beads with crud contained in the blowdown water.

In Kozlodui NPP, Bulgaria the plant for clean-up of blowdown water from the steam generators comprises an electromagnetic filter (13), but the strongly-acidic cation and the strongly-basic anion exchangers are in separate filters. (The ion exchangers used are Wofatit RH and Wofatit RO - nuclear). The ion exchangers are subjected periodically to regeneration with potassium hydroxide and nitric acid.

In some NPP with VVER-440 the systems for clean-up of blowdown water consist only of ion-exchange filters, the one with strongly-acidic cation exchanger also taking up the functions of the mechanical filter.

In the last case, regeneration and upwards rinse in order to remove the crude from the strongly-acidic cation exchanger is neede more often in comparisson to the case when using an electromagnetic filter. The advantages of the pre-connected electromagnetic filter are apparent, taking into consideration the saving of water for upwards rinse and regeneration: as known, this water cannot be released before being treated in special water purification installations.

Bayer (14) markets the macroporous ion-exchangers Lewatit SP112MB (strongly-acidic cation exchanger) and Lewatit MP500MB (strongly-basic anion exchanger) for MBF in the plants for clean-up of blowdown water from the steam generators. These ion-exchangers are not only more stable to osmotic shock and mechanical wear-out but are characterized by the easier elution (during regeneration and washing)due to their real porosity which quarantees better conditions for the diffusion processes.

4.1.1.3. ION-EXCHANGE SYSTEMS IN THE REACTOR CIRCUIT.

4.1.1.3.1. SYSTEMS FOR PURIFICATION AND CONTROL OF REACTOR COOLANT COMPOSITION.

Two main types of light water PWRs are currently used in NPP.

a) light water PWRs (type VVER-440) designed in the USSR, already installed in many NPP in the Soviet Union,Finland,GDR, Bulgaria,CSSR and Hungary;

b) light water PWRs designed by Westinghouse Co.Babckock & Wilcox Co,Kraftwerkunion etc.,delivered to NPP in the USA,FRG, France,Italy,Brasil,Sweden,Japan,Spain,etc.

The main differences between them are as follows (15):

-the VVER-440 reactors are equipped with horizontal steam generators with stainless-steel straight tubes while the other reactors have vertical steam generators with U-shaped tubes made of Inconel-600 and mainly Incaloy-800;

- the sheating of the fuel elements in VVER-440 consists of zirkonium-niobium alloy H-1 containing 1% niobium while that in the other reactors consists mainly of Zircaloy-4;

- operating temperature and pressure as well as thermal loading in VVER-440 are lower;

- the by-pass systems for reactor coolant purification and composition control in VVER-440 operate at the pressure of the primary circuit (12.5 MPa) while pressure in the other reactor is lower (1.5 - 2.5 MPa).

A characteristic feature of water chemistry in PWRs is that boric acid* is added to the coolant water. Physical aspects (operation and degree of fuel burn-up in the core) determine the range of boron concentration changes from 0 to 2500 ppm, Boric acid reduces the pH of the pure water for which reason alkalyzing agents to correct pH are needed.

According to the concept of the Moscow Institute for Atomic Energy (16) on water chemistry of reactors, the best solution of the problem of reactor water alkalyzation is the use of potassium hydroxide and ammonia as alkalyzing agents. Currently, all reactors of the VVER-440 type use KOH and NH_3 to alkalyze the reactor water (15). The other types of PWRs use lithium base (LiOH) as alkalyzing agent.

One of the basic problems of water chemistry in reactors is the determination of the optimum range of pH values in reactor water at the operating temperatures (260-320 °C) because corrosion rate of the construction materials, crude solubility, respectively crude transportation in the reactor circuit depend on pH at operating temperatures (17-19).

The concept of the Moscow Institute for Atomic Energy (16) allows for rather small changes of reactor water pH, viz. pH_{260°= 7.1 to 7.3 which corresponds to pH_{25°= 9.9 to 10.1

Water chemistry of PWRs of Westinghouse Co (17) allows for pH changes in the reactor water in a wider range, viz. pH_{25° = 4.2-9.5 or pH_{300° = 5.4 to 7.6.

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* H_3BO_3 is added as moderator to control reactivity of the nuclear reactors.

The above-mentioned differences in the concepts of VVER-440 and the Westinghouse-type reactors are reflected in the technologies adopted in their systems for reactor water purification and control of its composition.

In PWRs of the Westinghouse type the basic units in the by-pass system for reactor water purification, called chemical and volumetric control system (CVCS), include: mechanical filter, cation-exchange filter and mixed bed filter, Fig. 5 (17).

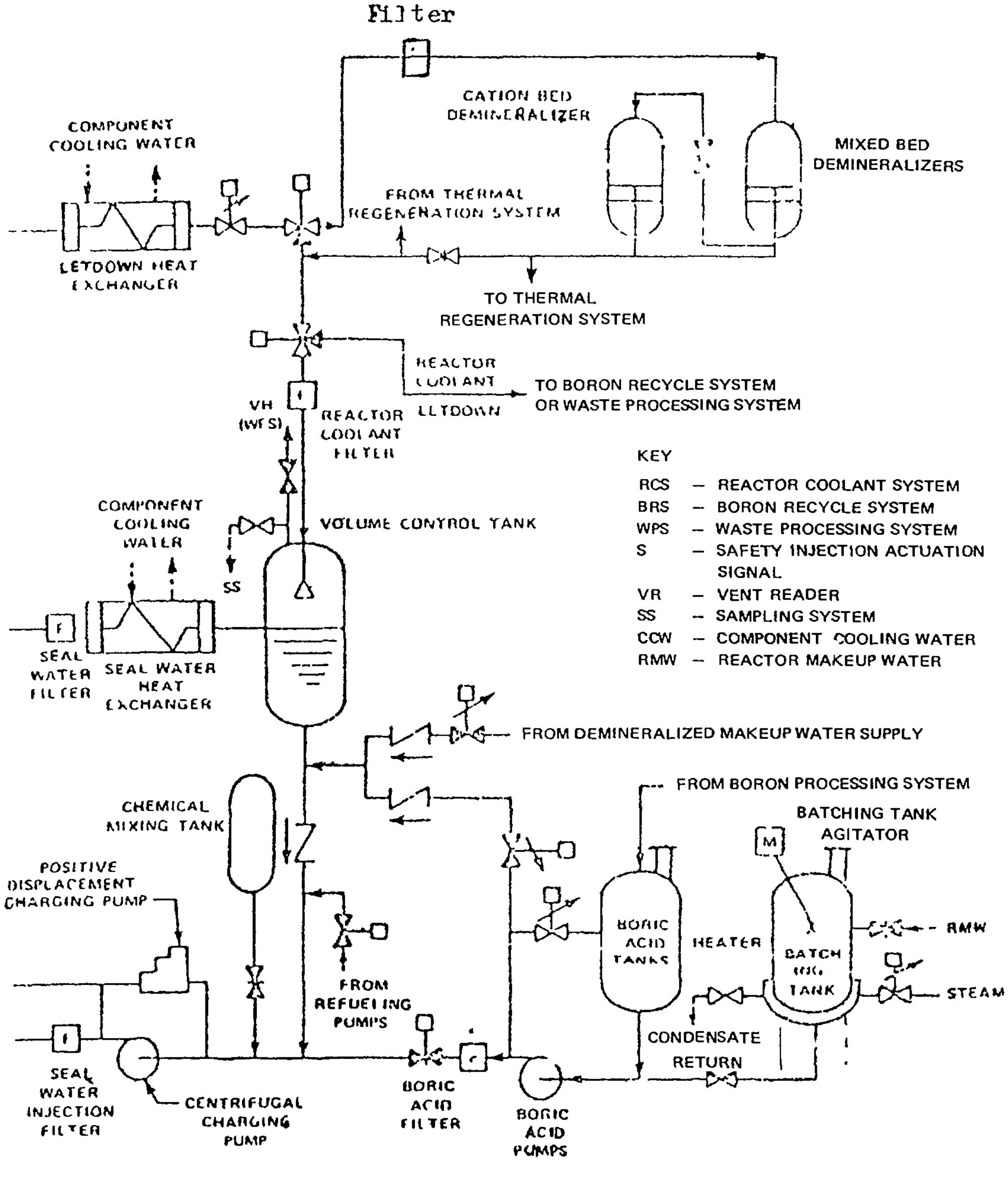

Fig. 5. Chemical and Volume Control System (17).

The coolant by-pass purification systemsin Biblis NPP (18) comprise two MBFs only.(Usually,one is operated on-line while the other is operated periodically in order to reduce lithium ion concentration in the reactor water)[*].

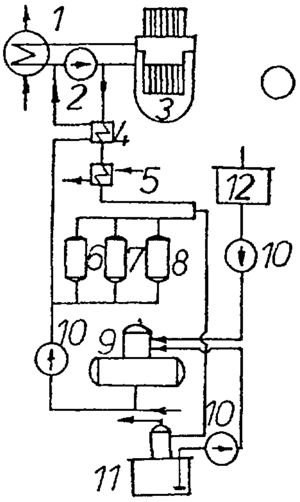

Fig. 6. Scheme of the bypass installation for reactor water purification in a VVER-440 unit in Kozlodui NPP (19).
1 - Steam generator; 2 - Main circulation pump ;
3 - Reactor; 4 - Regenerative heat exchanger;
5 - Heat exchanger - cooler; 6 - Cation exchanger filter in H-form; 8 - Mixed bed filter;
9 - Deaerator; 10 - Pump; 11 - Drainage tank.

The coolant by-pass purification system in Kozlodui NPP (type VVER-440) (19) consists of 3 ion-exchange filters,Fig.6 operated under a pressure of 12.5 MPa,viz.

a) filter with cation exchanger in H-form (item 6);

b) filter with anion exchanger in OH-form (item 7);

c) mixed bed filter with cation exchanger in K-NH_4 form and anion exchanger in BO_3 form (item 8).

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[*] The cation exchanger in the first filter is in Li-form and in the second filter is in H - form.

Normally, the mixed bed filter only is operating continually.

The anion filter is operated periodically in order to

a) reduce chloride ions concentration in the reactor water (if necessary), and

b) reduce boric acid concentration in the reactor water when H_3BO_3 content in the reactor water is below 1.0-1.2 g/l.

Upon exhaustion the ion exchanger is regenerated with KOH.

The cation filter is operated periodically in order to

a) reduce potassium, lithium and eventually ammonium ions in the reactor water to prevent pH increase above the permissible limits, and

b) reduce the concentration of all cations in the reactor water before it enters the anion filter in the cases when the latter is used to reduce chloride concentration in the reactor water.

Upon exhaustion the cation exchanger filter is regenerated with nitric acid.

In some NPPs with VVER-440 the cation exchanger filter in CVCS is substituted by a mixed bed filter (20).

According to available information, irrespective of the type of CVCS they have practically the same effectiveness.

The decontamination factor in relation to the total activity is in the range 50-100 (it depends on the total activity of reactor water), (17-19).

The unique technology for reactor water clean-up and control, adopted in the Soviet PWR type VVER-1000 (20) deserves mentioning. Two parallel plants for reactor water treatment are provided:

a) Plant 1 - It consists of 3 MBFs operated at the water pressure in the reactor circuit. These filters contain the strongly-acidic cation exchanger KY-2-8 and the strongly-basic anion exchanger AB-17-8 (volumetric ratio 1:1).(This plant is run at stationary operating conditions of the reactor).

b) Plant 2 - Consists of 2 lines,each one comprising 3 filters dia 1000 mm.(One of the lines is in operation while the other is a stand-by or is being regenerated).Operating pressure is 2 MPa.

Two of the filters in each line are with the strongly acidic cation exchanger KY-2-8 ,one in H-form and the other in NH_4^+ (K^+-NH_4^+) - form.The third filter is with the strongly-basic anion exchanger AB-17-8 in OH-form.

The ion-exchange resins in plant 1 are not regenerated.

The ion-exchange resins in plant 2 will be regenerated. Their life is between 2 and 3 years.

Considering the insufficient thermal stability of the anion exchange resins the treated water temperature is limited to a maximum 50 (60)°C in all ion-exchange plants for reactor water clean-up.

The ion-exchange resins in MBF are normally not regenerated. After one year,when their total γ-activity becomes 500-1000Ci/m^3 resin,they are replaced with fresh ion-exchange resins.

4.1.1.3.2 ION-EXCHANGE SYSTEMS FOR CONTROL OF BORIC ACID CONCENTRATION IN REACTOR WATER

There are technologies which make possible H_3BO_3 concentration in the reactor water to be controlled using ion-exchange

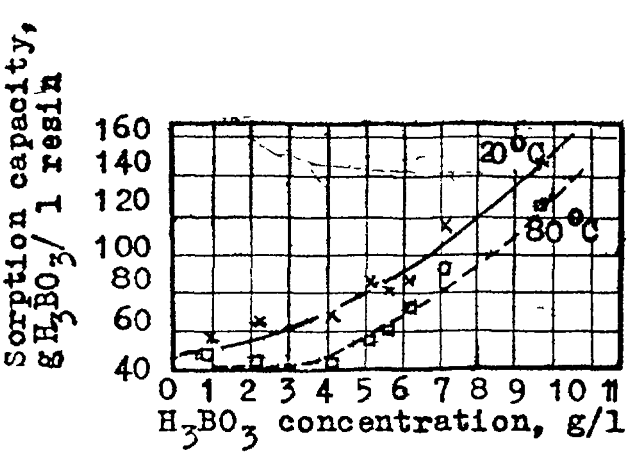


Fig. 7 Boric acid sorbtion capacity of strongly basic anion exchanger at 20°C and 80°C (25).

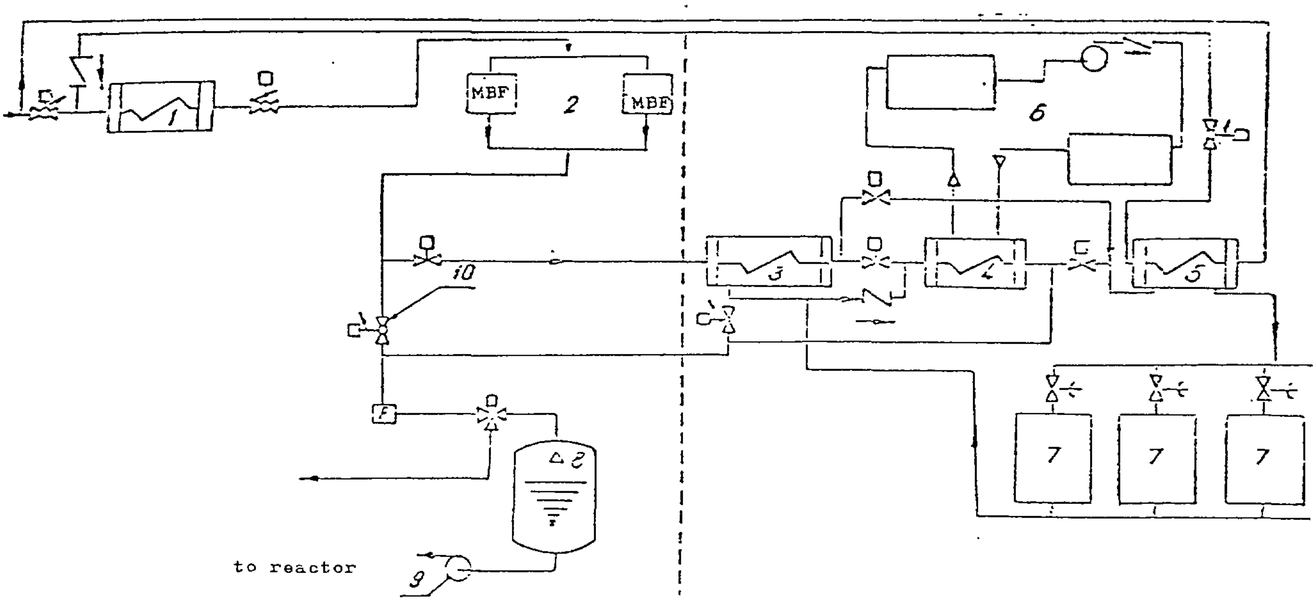
filters with strongly-basic anion exchanger in BO_3 form been found out that the strongly basic anion exchangers have different sorption capacities toward H_3BO_3 at different temperatures (21-24).

At higher temperatures (60-80°C) sorption capacity is lower than at 20°(10°)C, Fig. 7,(25).

This makes possible,by changing the temperature of the water stream in the ion-exchange filter,to reduce H_3BO_3 concentration in the water flow by sorption of H_3BO_3 by the ion-exchanger (when lowering the temperature to 10-20°C),or to effect desorption of H_3BO_3 by the ion-exchange filter,respectively to increase H_3BO_3 concentration in the water flow (when raising water flow temperature to 60-80°C).

A scheme of such ion-exchange plant for H_3BO_3 concentration control in the reactor water,using the so-called thermal regeneration process is shown in Fig.8.A plant of this type is already in operation in Ringhals NPP,Sweden.

The technological potentialities of this process can be judged from the data about the sorption-desorption capacity to



1-Regenerative heat exchanger, 2-Mixed bed filters, 3,4,5-Heat exchangers
6- Cooling circuite, 7-Anion exchange filters for HBO_3 sorbtion/desorbtion
8- Volume control tank, 9-Feed pump

Fig. 8 Flow Diagram of System for ion-exchange Thermal Regulation of Boric acid concentration (type Westinghouse Co.) (21).

H_3BO_3 of the strongly-basic anion exchangers used to this end at different temperatures,Fig.7.

The data in Fig.7 (25) reveal that the amount of H_3BO_3 which can absorb 1.0 l of the strongly-basic anion exchanger type I Wofatit RO at 80°C is by about 20 g less than the amount of H_3BO_3 which this anion exchanger can absorb at 20°C. It is evident also that this difference in the anion exchanger's absorption capacity,depending on temperature,remains practically constant at H_3BO_3 concentrations in the water in contact with the anion exchanger in the range 2-10g/l H_3BO_3.Evidently, without using reagents,only by changing the reactor water temperature through a filter with strongly-basic anion exchanger type I, each 1.0 l of this ion exchanger can desorb 20g H_3BO_3

(at 80°C) and sorb 20 g H_3BO_3 during the next temperature decrease to 20°C.

It is noteworthy that the strongly-basic anion exchanger Wofatit RO in BO_3-form is stable at 80°C and that the anion exchanger retains its capability to desorb-sorb reversely H_3BO_3 even after 20 cycles of thermal desorption-sorption. This stability has been confirmed by the treatment of the reactor water in the VVER-440 unit in Kozlodui NPP (25).

In Ringhals NPP whose system for ion-exchange control of H_3BO_3 concentration has been designed by Westinghouse Co the operating temperatures are

60°C (desorption of H_3BO_3), and
10°C (sorption of H_3BO_3), respectively.

4.1.2. ION-EXCHANGE SYSTEMS IN NPP WITH BWRs

4.1.2.1. ION-EXCHANGE SYSTEMS FOR REACTOR WATER CLEAN-UP AND TURBINE CONDENSATE (FEEDWATER) POLISHING

Normally, two systems for water streams clean-up are needed in order to meet the requirements for a high degree of purity of feedwater and reactor water in NPP with BWRs, Table 1, Fig. 9, viz:

a) System for feedwater (turbine condensate) purification);

b) System for reactor water clean-up.

In the Winfrith SGHWR (26) the same system (Powdex-filters) is used to clean up both the feedwater and the reactor water, Fig. 10. (Interesting in this case is that the turbine condensate after the LP heaters is being treated only).

TABLE 1. BWR WATER CHEMISTRY (27).

	Concentrations - Parts per Billion (ppb)				Conductivity	
	Iron	Copper	Chloride	Oxigen	μmho/cm at 25°C	pH at 25°C
Condensate	15 to 30	3 to 5	⩽ 20	⩽ 20	~0.1	~7
Condensate Treatment						
Effluent	5 to 15	< 1	~ 0.2	20 to 50	< 0.1	~7
Feedwater	5 to 15	< 1	~ 0.2	20 to 50	< 0.1	~7
Reactor water						
1. Normal Operation	10 to 50	< 20	< 20	100 to 300	0.2 to 0.5	~7
2. Shutdown	-	-	< 20		< 1	~7
3. Hot Standby	-	-	< 20		< 1	~7
4. Depressurized	-	-	< 20	8,000	< 2	6 to 6.5
Steam	0	0	0	10,000 to 30,000	~0.1	-
Control Rod Drive						
Cooling Water	50 to 500	-	< 20	⩽ 8,000	~ 1	~ 6

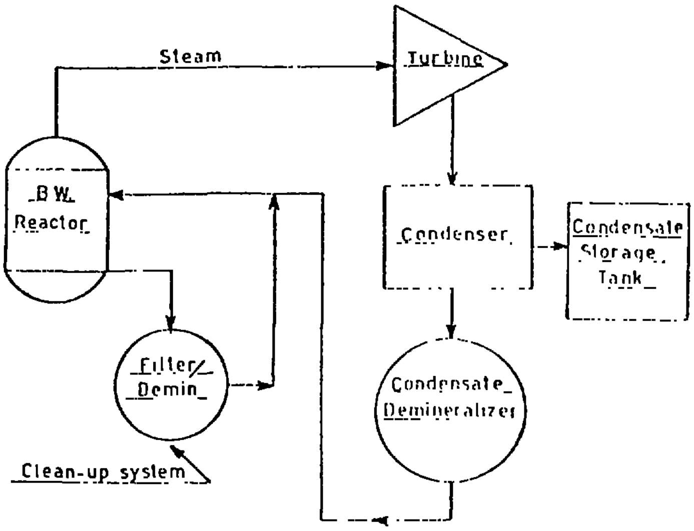


Fig. 9 BWR water cycle (26).

Although it poses operating limitations, the experience with this unique system is of undouted interest:

... "The SGHWR feedwater and coolant clean-up plant (26) consists of two Powdex filters (type Graver) operating at 110-116°C coated with powdered ion-exchange resins. (Cation /anion exchangers ratio is 2:1).

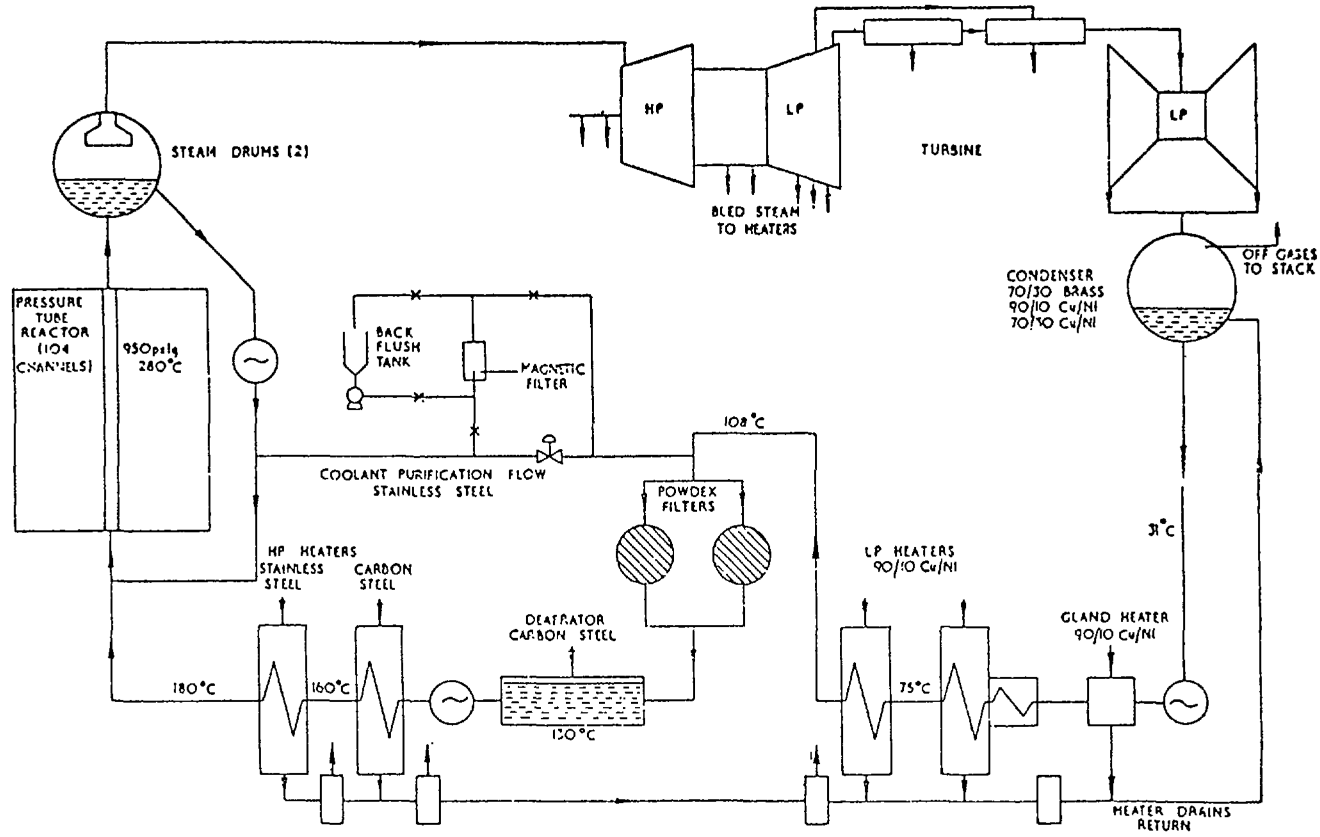


Fig.10 Simplified Feedwater / Coolant Cycle for WSCHWR (26).

The system deals with the full feedwater flow 550 m^3/h plus 20-25 m^3/h reactor coolant which is mixed with the feedwater.Operating period of each filter is about 2 weeks and normally one unit is recoated every 7 days.Weight of resin per recoat cycle is 81 kg dry resin.Therefore,one unit treates about 96 000 m^3 water between recoats,i.e. resin consumption is 0.85 g per 1 m^3 of water treated." ...

..."Total activity removal efficiency is about 85% for a total activity of water before the Powdex filter 0.05 Ci/l. (It deserves mentioning that coolant activity has been reduced 25 times because this water has been diluted in 25 times larger amount of feedwater)." ...

..."That comparatively high removal efficiency is due to the fact that at total activity of water up to 0.05 Ci/l the activity is caused mainly by the cations of the Fe,Cr,Zn,Mg isotopes etc" ...

..."When total activity of treated water is about 1 Ci/l, i.e. when the main nuclides are predominantly in anionic form (iodides or iodates of ^{131}I;^{133}I etc),plant's efficiency is lower. In the begining of the cycle removal efficiency is up to 75% and at the end it is barely 30%. (This is due to the thermal degradation of the anion exchanger in the Powdex filter.With time, at a temperature of 110°C,the anion exchanger looses its strongly-basic active groups)." ...

..."At 110°C the plant cannot remove the silica from the water treated.(If necessary,the temperature should be reduced to 55°C)..."(26).

The individual systems for coolant clean-up are usually designed to treat the coolant taken from the bypasses.The normal clean-up flow (m^3/h)is 2% of the feedwater flow at 100% reactor power.(However,in some NPP with BWR the amount of bypass treated coolant is larger, e.g. in Tsuruga the plant for coolant clean-up has a capacity 6,7% of the feedwater stream (28).

The coolant clean-up plants operate at pressures 20-30% higher than in the core.Treated water temperature is reduced to 30-60°C.The demineralization units are loaded with a mix of cation-exchange resin in H-form and anion-exchange resin in OH-form in a ration 1:1 to 2:1.

Removal efficiency of impurities from treated coolant is about 90% when the plant comprises only ion-exchange demineralizers of the mixed-bed filter type (29).

Hakala and Hinttala report that coolant clean-up in Finland's NPP TVO-I/II (34),using a radial flow MBF,is highly effective toward the radioactive impurities (99%).Silvennoinen (39) adds that this system is very effective also for corrosion products removal:Fe content in condensate is 50 ppb before MBF and 1 ppb after it.

Data are available (29) that the mechanical filters (Precoat type),installed before MBF,remove between 96 and 99% of the corrosion products,above 0.45 μm in size,from the coolant.

An idea about the demineralization potentialities of the ion-exchange demineralizers,type MBF (installed after the mechanical filters in the coolant clean-up system)give data in Table 2 referring to Tarapur NPP (29).

TABLE 2. Decontamination factors in the ion-exchange units of the coolant clean-up plant at Tarapur (29).

Nuclides	Initial phase of operating cycle	End of cycle*
^{131}I	8 000	16
^{132}I	3.1×10^4	2.6×10^3
^{133}I	5.2×10^3	1.3×10^3
^{239}NP	7.1×10^4	670
^{99}Tc	-	6.5×10^3
^{137}Cs	5.8×10^3	1.2×10^2
^{134}Cs	5.3×10^3	1.4×10^2
^{60}Co	over 1.5×10^2	1.7
^{103}Ru	-	5.9
^{95}Zr	-	1.52

* This cycle ranges between 8 and 12 months.

TABLE 3. Effect of Tsuruga NPP coolant clean-up plants (28).

Impurities, nuclides	Unit	Inlet mechanical filter	Outlet mixed bed demineralizer	Removal efficiency $\frac{\text{inlet concentr.}}{\text{outlet concentr.}}$
Conductivity at 25°C	μS/cm	0.10-0.16	0.05	
Chlorides	ppb	20	20	
Iron: a/ > 0.45 μm	ppb	6.3	0.02	315
b/ < 0.45 μm	ppb	0.04	0.01	4
Copper: a/ > 0.45 μm	ppb	0.1	0.001	10
b/ < 0.45 μm	ppb	0.32	0.005	64
Nickel: a/ > 0.45 μm	ppb	0.02	0.005	4
b/ < 0.45 μm	ppb	0.05	0.007	7
Cobalt: a/ > 0.45 μm	ppb	1.0	0.1	10
b/ < 0.45 μm	ppb	8.3	1.0	8.3
I-131	μCi/ml	2.5×10^{-4}	2.7×10^{-8}	9360 = DF
I-133	"	3.5×10^{-3}	5.2×10^{-7}	6730 = DF
Cs-137	"	9.0×10^{-7}	1.1×10^{-7}	8.2 = DF
Co-60	"	3.6×10^{-5}	4.6×10^{-6}	9 = DF

For comparison purposes, Table 3 illustrates the overall effect of clean-up at Tsuruga NPP (28) whose coolant clean-up consists of:

- Unit for mechanical filtration: precoated filter with Solcafloc;

- Unit for ion-exchange demineralization, type MBF.

The system for coolant clean-up in the Leningrad NPP is similar, Fig. 11 (30).

The coolant bypass purification system consists of precoat filters with Perlite powder as filter aid and mixed-bed filters with nuclear-grade cation exchanger KY-2-8 and anion exchanger AB-17-8 (Cat : An = 1:1).

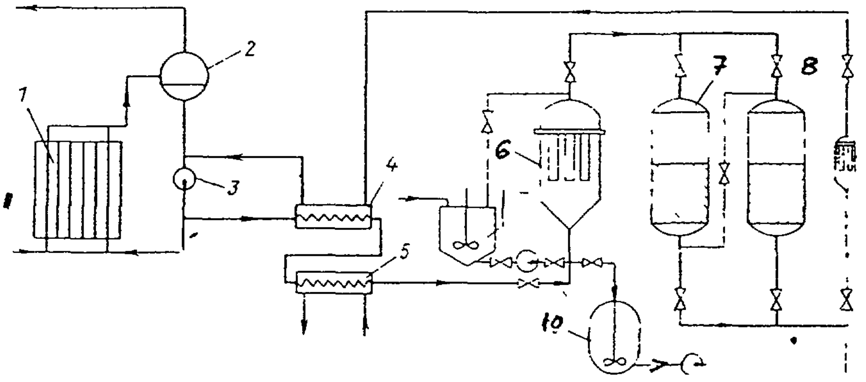


Fig. 11. Flow diagram of bypass reactor water purification system in RBMK* (30).
1 - Reactor; 2 - Steam generator; 3 - Main circulation ppump; 4 - Regenerative heat exchanger; 5 - Post-cooler; 6 - Precoat filter; 7,8 - Mixed-bed ion-exchange filters; 9 - Filter trap; 10 - Pulp vessel.

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* Reactor type RBMK-1000: Boiling-water channel-type uranium graphite reactor.

The protection against any drain system failure is provided by a mesh filter trap installed after the ion-exchange filters. The water for purification (200 m^3/h is taken from the pressure header of the main circulation pumps of both reactor circuits and is cooled down to 180°C in the regenerative heat exchanger and then to 50°C in the post-cooler. The purified water is returned through the regenerative heat exchanger to the reactor circulation circuit. The equipment operates under the pressure of the circuit; when the main circulation pumps are out of operation the purification water is delivered by shut-down circuit pumps. Heat exchangers/post-coolers are used in the shut-down reactor cooling system as well.

Down the ion-exchange filters the impurity concentrations were as follows: hardness salts - not detected, chlorides - less than 5 ppb, iron - 5-10 ppb, copper - less than 10 ppb. The pH value was 6.8 - 7.0.

The blow-down water DF equal to 100 (i.e log DF = 2) is reached by passing 800 000 m^3 water per 5 m^3 ion-exchange resin charge, i.e the coolant specific rate equals 160 000 m^3 of water per 1 m^3 of ion exchange resin, Fig. 12.

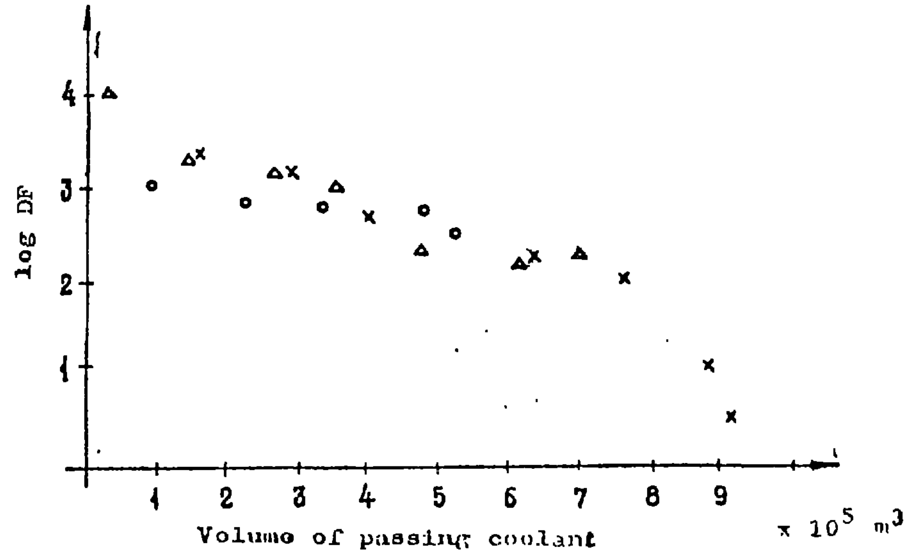

Fig. 12. Change of Decontamination Factor (DF) of mixed bed purification system (30).
x - first, △ - second, o - third charge of ion exchangers

The ion-exchange resins in coolant clean-up systems are not regenerated. Instead, fresh resin is loaded.

The efficiency of the coolant clean-up systems consisting of Powdex filters only is usually higher than that with MBF. Normally, life of the Powdex filters is about a month.

Normally, the powdered ion-exchange resins used to clean up the coolant are changed in the following cases:

a) hydraulic resistance of the filtering layer ion-exchange resin abnormally high;

b) increased silica concentration in the filtrate;

c) specific electrical conductivity of filtrate above 0.2 μS/cm.

Usually, total γ-activity of the exhausted powdered ion-exchange resin is about 50 Ci/m^3.

In the condensate polishing systems of NPP with BWR, ion-exchange demineralization and removal of corrosion products from the turbine condensate (dissolved or suspended in it) is done with:

a) Mixed bed filters of strongly-acidic cation exchanger in H-form and strongly-basic anion exchanger in OH-form. (For example the condensate polishing system of the Leningrad NPP, USSR (30), Tsuruga NPP, Japan (28), Dresden NPP, USA (31).

b) Powdex filters - pre-coated with a mixture of powdered strongly-acidic cation exchanger in H-form and strongly-basic anion exchanger in OH-form. (For example the condensate polishing systems in Würgassen NPP, FRG (32), Mühleberg NPP, Switzerland (33), TVO-I/II NPP, Finland (34), Vermont Yankee NPP, USA (35). Comparatively rare is the case of the BWR in Ringhals NPP, Sweden with its two possibilities for condensate polishing:

- ion-exchange filters pre-coated with powdered ion-exchange resins (Powdex filters),
- ion-exchange filters type MBF.

Under normal operating conditions, only the first Powdex plant is in operation while MBF is operated only in case of considerable leakages from the turbine condensers (increased electrical conductivity of turbine condensate).

Schröder (36) points out that the main advantage of the condensate-polishing systems with Powdex filters is that they remove over 90% of the corrosion products contained in the condensate treated, the respective figure in the case of MBF being about 60%.

However, as evidenced from data in Table 4, (28) about the condensate-polishing system of Tsuruga NPP*, the efficiency of corrosion products removal using MBF is also around 90%.

TABLE 4. Effect of condensate polishing system in Tsuruga NPP (28).

Indicator	Unit	Inlet	Outlet	Removal efficiency: $\frac{\text{inlet concentr.}}{\text{outlet concentr.}}$
		Condensate polishing system		
Conductivity at 25°C	μS/cm	0.07	0.06	-
Iron (> 0.45 μm	ppb	26.6	1.6	17
< 0.45 μm)	ppb	0.7	0.4	1.8
Copper (> 0.45 μm	ppb	1.56	0.03	52
< 0.45 μm)	ppb	0.50	0.03	17
Nickel (> 0.45 μm	ppb	0.03	0.004	7.5
< 0.45 μm)	ppb	0.05	0.007	7.1
Chromium (> 0.45 μm	ppb	0.05	0.004	13
< 0.45 μm)	ppb	0.004	0.002	2
Cobalt (> 0.45 μm	ppb	2.6	0.3	8.7
< 0.45 μm)	ppb	12.1	0.9	13
I-131	μCi/ml	8.1×10^{-6}	1.1×10^{-8}	736 = DF
I-133	μCi/ml	8.5×10^{-5}	1.3×10^{-7}	654 = DF
Co-60	μCi/ml	1.1×10^{-8}	1.3×10^{-10}	85 = DF

It should be also mentioned that the ion-exchange resins in the condensate-polishing systems with MBF are often strongly contaminated with corrosion products which results in shorter life of the filters, increased consumption of water and chemicals for regeneration and increase of radioactive waters volume.

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* The system comprises 5 MBS each holding 5.1 m^3 mixture of strongly-acidic cation exchanger and strongly-basic anion exchanger (ratio by volume 1.7:1). Filtration rate of condensate through MBF is 90 m/h, (28).

As practice in Dresden 2 and 3 NPP shows (37) the negative phenomena in the operation of condensate polishing systems with MBF can be considerably avoided if adopting ultrasonic cleaning of resins for condensate purification mixed bed filters (38), Fig. 13.

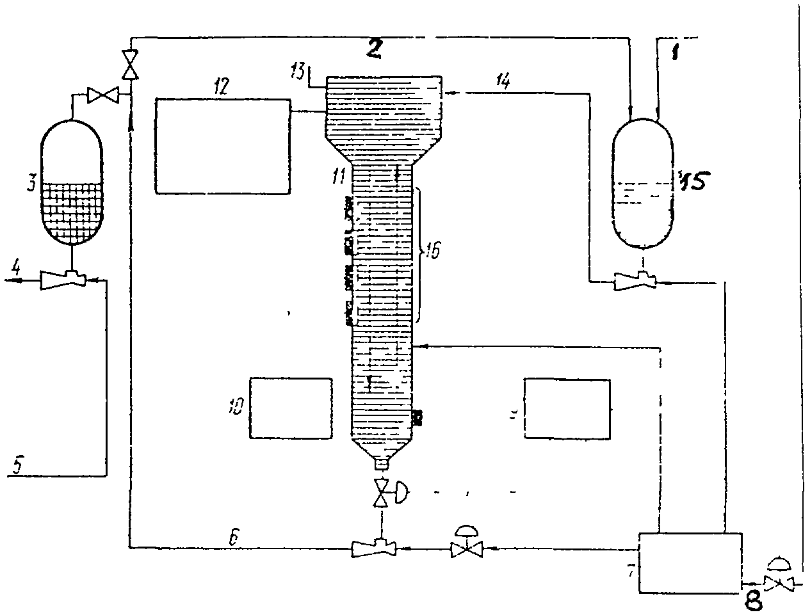

Fig.13. Ultrasonic cleaning system of deep-bed resins for condensate demineralization systems (38).

1 - Input of deep-bed ion-exchange resins; 2 - Recirculation line; 3 - Cleaned ion-exchange resin; 4 - To the filters of the condensate-polishing system; 5,8 - Deionized water; 6 - Line for transportation of the ion-exchange resin cleaned ultrasonically; 7,9 - Control board; 10 - Power supply board; 11 - Column for ultrasonic clean-up; 12 - Pulp and waste water vessel; 13 - Air breader; 14 - Transportation line for the water ion-exchange resin mixture transportation; 15 - Ion-exchange resin vessel; 16. Clean-up region.

Ultrasonic treatment (0.5 W/cm^2) makes possible to remove over 80% of the corrosion products stuck to the ion-exchange without causing any mechanical destruction of the resin beads. It has been established that when using periodically (once per 10-20 days) ultrasonic cleaning of the ion-exchange resins of

MBF in Dresden 2 and 3 NPP the ion-exchange resins must be chemically regenerated once per 120 days. As a result, MBF regeneration costs have been cut five-fold (38).

The turbine condensate in the Leningrad NPP is polished by running it consecutively through a H-cation exchanger filter (serving as a pre-filter) and MBF. In the latter filters external regeneration in special vessels is provided (Items 4 and 5 in Fig. 14).

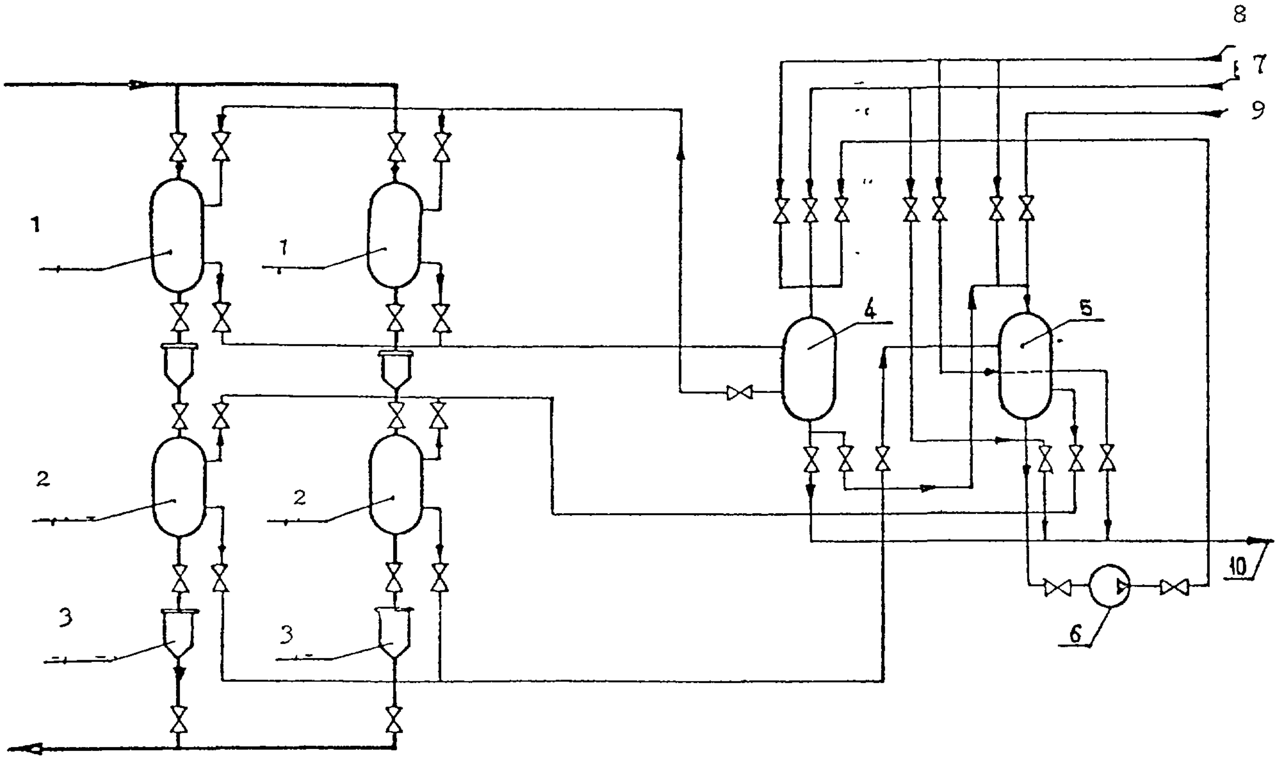

Fig. 14. Turbine condensate purification system (30).

1 - cation exchange prefilter, 2 - mixed bed filter, 3 - filter-trap, 4 - cation exchanger regeneration tank, 5 - mixed bed resins regenerationen tank, 6 - rinse water pump, 7 - 5% HNO_3, 8 - return water, 9 - 4% KOH, 10 - discharge for reprocessing.

Filtration rate of turbine condensate through the ion-exchange filters is 80 m/h. When pressure loss in the H-filters reaches 0.25 MPa they are shut down and the ion-exchange resin is washed with demineralized water. Usually, this operation takes place once per 10 days.

In MBF the cation exchanger and the anion exchanger are in a ratio of 1:2. The increase of sodium ions leakage leads to MBF shutdown.

Operating time of MBF is about 4 months. The anion exchanger is regenerated with 4% NaOH, and the cation exchanger with 5% HNO_3.

The qualities of the polished condensate are as follows:

pH	-	6.9-7.1	6.8-7.2
conductivity	μS/cm	0.4	0.4
total hardness	g-eg/kg	1	1
chloride	ppb	1	1
oxygen	ppb	10-30	5-40
iron	ppb	1-4	1-4
copper	ppb	0.2	0.2

According to Ryan (37), the condensate polishing systems with Powdex filters in NPP with BWR have certain advantages as compared to MBF:

... " ...Fig. 15 presents a comparison of total operating costs for one full power year for the three systems. The costs include installed capital costs converted to an annual cost by use of a 13% factor. The comparison shown on Fig. 15 demonstrates several intersting points.

For the range of service periods for each alternate, the radwaste costs are a significant part of the total for the two systems utilizing deep beds of bead ion-exchange resins. The powdered ion-exchange system costs are affected to a similar degree by radwaste considerations. For powdered resins the radwasteassociated costs represent only 6.8% of the total costs at a 20-day run length and 10% at a 10-day run length.

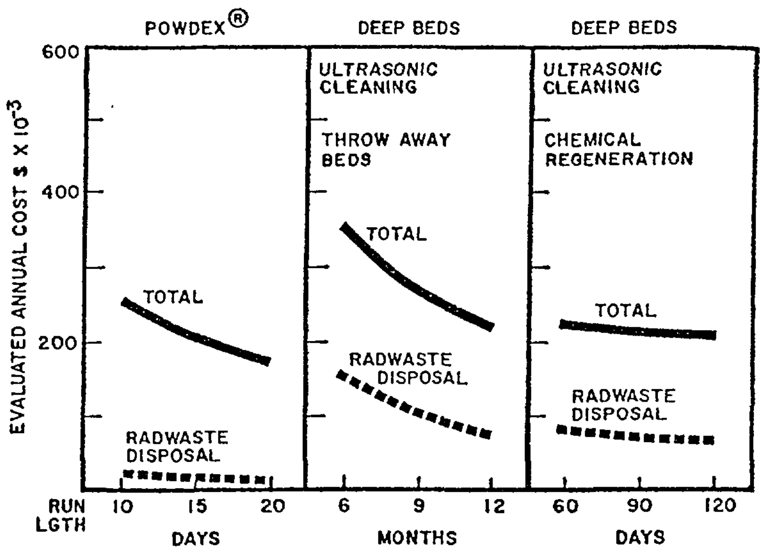

Fig. 15. Comparison of total operating costs for one full power year (37).

For the deep-bed system,using ultrasonic cleaning and periodic regenerations,there is little additional total cost reduction achieved by extending periods between regeneration beyond 60 days.At 60 days,the cost of regenerants and their disposal have been reduced to about 15% of the total cost.

By using the narrow range in cost for the ultrasonic cleaning plus regeneration system as a base the run length for the powdered ion-exchange resin system must be in the range of 12 to 15 days to be equivalent.For the throwaway bed system, the beds must last at least 12 months to be equivalent.Thus, even allowing for the approximate nature of the cost estimates, an order-of-magnitude comparison is available comparing actual or anticipated performanes."(37)

Experience in NPPs with BWR shows the technological effectiveness of the powdered resins (32,34):In Würgassen NPP (32) by using of the powdered resins the quality of the condensate polishing unit effluent is as follows:

total iron	not detectable
total copper	1 ppb
chloride	not detectable
SiO_2	4 ppb
conductivity (at 20°C)	0.05 μS/cm

The similar results have been obtained in TVO I/II NPP, Finland (34) where the condensate polishing is processed in the full flow pre-coat filter (filter-demineralizer) system designed by ASEA-ATOM. The system consists of 7 filters with vertical rod-shaped filter elements coated with powdered ion-exchange resin. One of the filters is in stand-by. The filter area is 73 m^2.

The operating temperature of the filter is 65°C. The ion-exchange resin is a mixture of anion-exchange and cation-exchange resins.

As a characteristic information about the powdered ion-exchange resins consumption for condensate polishing by Powdex filters in NPP with BWR can be used data for Mühleberg NPP, Switzerland(33). The run length of the powdered ion-exchange resins are about 1 month while powdered ion-exchange resin consumption is 0.25 g per 1 m^3 polished condensate. Usually, the exhausted powdered ion-exchange resin from condensate polishing units in NPP with BWR has total γ-activity 1-5 Ci/m^3.

4.1.3 ION-EXCHANGE UNITS IN TYPICAL RADIOACTIVE LIQUID WASTE SYSTEM AND IN CLEAN-UP OF FUEL STORAGE POOLS IN PWR AND BWR STATIONS

Ion-exchange processes find application in liquid (aqueous) radwaste treatment in nuclear power plants.

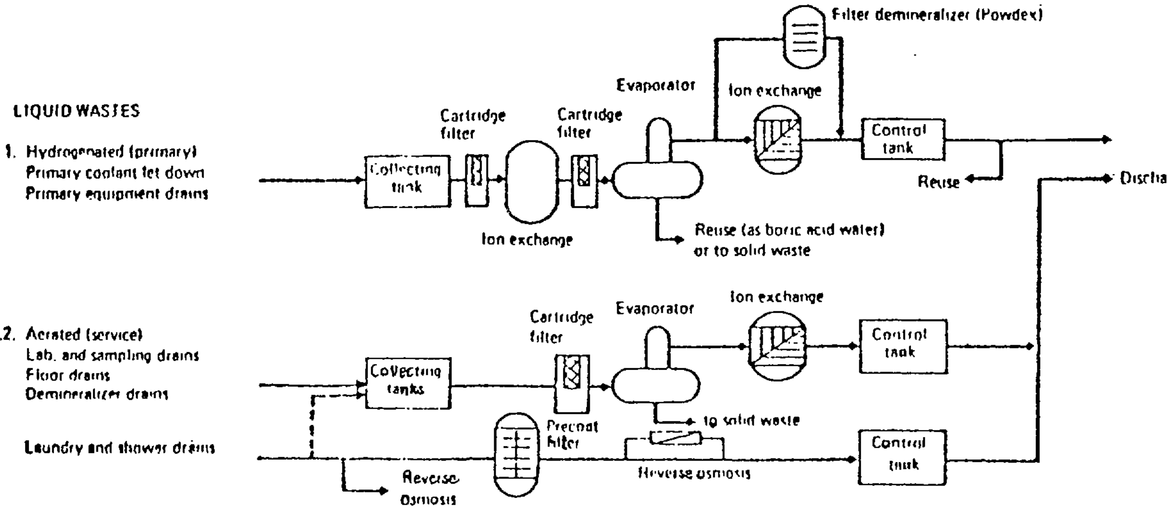

Fig.16 Typical radioactive liquid waste systems for a pressurized water reactor (PWR) (40).

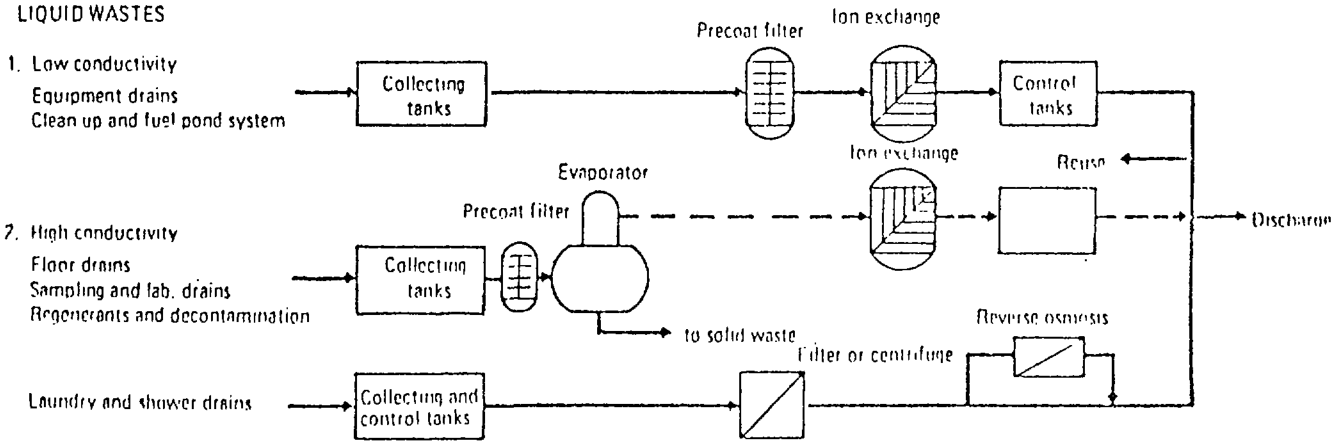

Fig.17 Typical radioactive liquid waste systems for a boiling water reactor (BWR) (40).

Usually, they are used for decontamination of water flows with total dissolved solids content of less than 500 (1000) mg/kg.

For that reason, as evident from Fig. 16 and Fig. 17 (40) the ion-exchange processes are used mainly to decontaminate water flows with limited salt content and condensates produced in evaporators when treating liquid radwaste with considerable concentrations of dissolved and suspended matter.

The ion-exchange units used in these cases are either individual cation-exchange and anion exchange filters or mixed bed filters. (In more rare cases precoat filters are used).

Most frequently, strongly-acidic resins and strongly-basic resins of the macroreticular type are used.

The normally exhausted ion-exchange resins are regenerated, i.e. they are used many times.

The decontamination factors found with the ion-exchange units with respect to the various nuclides depend on the type of the treated water and the ion-exchange system used. This is best illustrated in Table 5.

TABLE 5. Decontamination factors for BWR and PWR liquid waste treatment systems (Ion-exchange units) (40).

Treatment system	Decontamination factor		
Demineralizers	Anion	Cs.Rb	Other nuclides
<u>B W R</u>			
High purity waste (mixed bed)	$10^2(10)^6$	10(10)	$10^2(10)$
Low purity waste			
mixed bed	$10^2(10)$	2(10)	$10^2(10)$
cation exchanger bed	1(1)	10(10)	$10^2(10)$
anion exchanger bed	$10^2(10)$	1 (1)	1 (1)
<u>P W R</u>			
Radwaste (H^+/OH^--ion exchanger filters	$10^2(10)$	2(10)	$10^2(10)$
Evaporator condensate polishing	10	10	10
Boron recycle system feed (H_3BO_3)	10	2	10

The ion-exchange systems for fuel storage basins (pools) are designed for decontamination and clarification of the pool water.In view of the fact that pool water* contains both soluble and insoluble impurities it is often filtered (Precoat-filter) followed by mixed-bed ion-exchange unit.

In some cases,when Cs isotopes prevail in the pool water, inorganic ion-exchangers are preferred because of their higher selectivity toward these ions.

Lin (42) describes such a system for pool water clean-up. The system consists of a filter containing Zeolon-900 (inorganic ion-exchanger).For Cs content in pool water 4×10^{-2} Ci/ml this filter treats approximately 40 000 bed volumes of pool water before breakthrough of ^{137}Cs.The ion-exchanger used is regenerated with ammonium sulfate solution (42).

As evident from the above text,the operation of nuclear power plants is accompanied by the producing of some amounts of ion-exchange resins,mostly containing nuclides, Table 6 (41). The problems of their storage pose a separate technological problem which will not be discussed here because recently IAEA published a detailed account on this subject (41) which reflects the experience,the state of the art and the future trends in this field.

We will point out here only a recently studied perspective possibility to lower the total activity of spent resins with electrodialysis partial decontamination of spent ion-exchange resins(43).It concerns spent ion-exchange resins decontamination

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* Fuel storage basins of NPP provide storage facilities before irradiated fuel elements are sent for reprocessing.

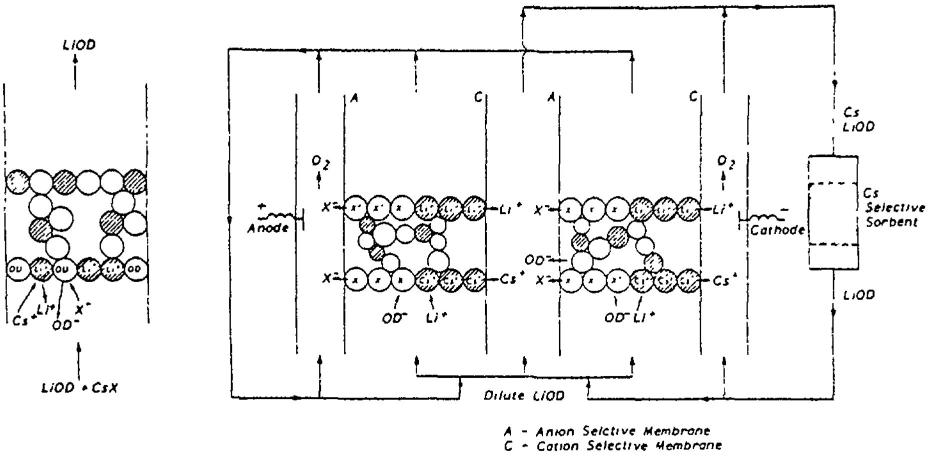
TABLE 6. Spent ion-exchange resin waste arising from operating nuclear power plants (41).

Country	Reactor Type	Power output MW(e)	Type of ion-exchange resins	Quantity m^3/yr	Specific Activity Ci/m^3	Remarks
Germany, Fed. Rep. of,	PWR	1300	bead resins	3	$10^2 - 5.10^2$	General date (average)
	BWR	1300	powdered resins	115	$2.10^{-2} - 10^{-1}$	condensate cleaning
			" "	10	1-10	reactor water cleaning
	BWR (Lingen)	240	" "	35 ⓐ	10-20	ⓐ Cumulative for 9 years
	BWR (Gundremmingen)	237	" "	4.5	400	reactor coolant
			" "	2	70	liquid effluents
			" "	0.5	10	fuel storage pond
	BWR (Würgassen)	640	" "	10	1	condensate cleaning
			" "	1	50	reactor coolant
			bead resins	4	2	liquid effluents
	PWR (Stade)	622	" "	0.4		reactor coolant cleaning
				0.65	100-200	reactor coolant treatment
				0.5		fuel storage pond
	PWR (Biblis)	1200	" "	~2		

TABLE 6. (continued).

Country	Reactor Type	Power output MW(e)	Type of ion-exchange resins	Quantity ft^3/yr	Specific Activity Ci/ft^3	Remarks
USA	BWR (Nine Mile Point)	620	bead resins	500 ft^3	0.1-1 Ci/ft^3	- condensate demineralizes - fuel storage pond - waste collector - Rx cleanup
			powdex and/or solka floc	1,582 ft^3		
	BWR (Oyster Creek)	670	bead resins	500 ft^3	0.2-3 Ci/ft^3	" " " "
			powdex and/or solka floc	2,625 ft^3		

from CANDU-PHT purification columns (mixed bed ion-exchange resins in Li^+/OD^- forms). The principle of the process-termed EDRD (Electro-Dialysis Resin Decontamination) is illustrated in Fig. 18.



1(a) 1(b)

Fig.18 Principle of the Electro-Dialytic Resin Decontamination (EDRD) Process (43).

..."The process involves passage of a dc electric current through a bed of the spent ion-exchange resin in a specially designed electro-dialytic- cell consisting of alternate cation and anion selective ion exchange membranes.Fig.18(a) shows the service run of a fresh Li^+/OD^- form mixed bed resin during which radioactive Cs^+(fission product) in the PHT fluid is exchanged for Li^+ on the cation resin component.Fig. 18 (b) shows the decontamination process.Under the influence of an applied dc electric potential,electric current passes through the Cs^+ form resin,in preference to the Li^+ form resin,thus preferentially removing Cs^+ ions from the resin bed and transporting them through the cation selective membrane.Dilute LiOD ($\sim$0.01 M) solution is circulated through the cell as shown in the figure.Any exchange sites vacated by Cs^+ ions will be occupied by Li^+ ions provided by the solution thus improving further passage of electric current through the Cs^+ sites on the resin.A dilute LiOD effluent stream from the cell,containing small amounts of Cs^+ is passed through a Cs selective sorbent which selectively removes Cs^+ from the stream,and the LiOD solution exiting the sorbent column is returned to the electrodialytic cell.

The EDRD process appears to be economically attractive. Annual cost saving of about 110 000 Canadian dollars are estimated for EDRD processing of Ontario Hydro's spent PHT resins. Although the EDRD process was developed primary for decontamination volume reduction of spent PHT resins,the process can be effectively applied to in-line purification in the PHT circuits of CANDU reactors to directly minimize the volume of ion exchange resin usage." ... (43)

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CHAPTER 5

ION EXCHANGE TECHNOLOGY IN SPENT FUEL REPROCESSING

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Abstract

Solvent extraction is the major unit operation employed in spent nuclear fuel reprocessing. The operation yields three streams: fission product waste, uranium product and plutonium product. Ion exchange is primarily used in reprocessing as a tail-end method to concentrate and isolate the plutonium product stream. This chapter will describe the details of plutonium recovery and purification by both cation and anion exchange processing. A brief overview of miscellaneous uses of ion exchange employed in reprocessing will also be given.

INTRODUCTION

Irradiated or spent fuel discharged from nuclear reactors contains fission products, uranium and plutonium. Reprocessing technology is used to recover fissile values for reuse as nuclear fuel. The major reprocessing steps are outlined in Figure 1.

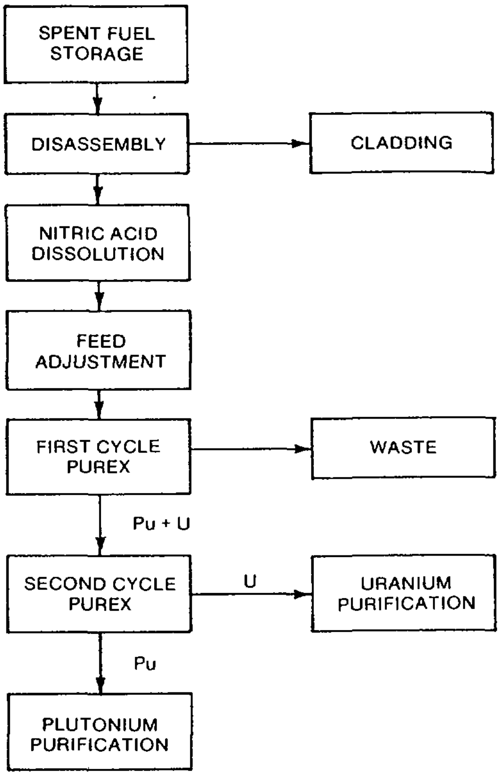

FIGURE 1. Simplified flowsheet for spent fuel reprocessing.

After storage and disassembly, the spent fuel is dissolved in nitric acid. The nitric acid concentration of the dissolver solution is then adjusted and the plutonium(IV) oxidation state is stabilized by addition of sodium nitrite prior to tri-n-butyl phosphate (TBP) extraction (designated Purex solvent extraction process). The process is used to separate uranium and plutonium from fission products[1-5].

The first extraction cycle of the Purex process co-extracts both plutonium and uranium into TBP leaving the fission products, the actinides (neptunium, americium and curium), and small amounts of plutonium and uranium in the raffinate or waste stream. The second cycle is used to partition or separate the uranium from the plutonium; this is done by scrubbing the loaded TBP with dilute nitric acid containing a reducing agent to reduce plutonium to the non-extractable III oxidation state. The uranium is then stripped from the TBP with water. The separate uranium and plutonium streams are purified further by another cycle of the Purex process. Final purification of the uranium stream is accomplished by either another cycle of the Purex process or more commonly by silica-gel adsorption. Purex, cation exchange and anion exchange have been used as the tail-end plutonium purification step for plutonium.

This chapter will discuss in detail both the cation and anion exchange processes for the concentration and isolation of plutonium. Furthermore, a brief overview of the recovery and purification of uranium and other actinides and isotopes will be given.

PLUTONIUM RECOVERY AND PURIFICATION

All nuclear fuel reprocessing operations include recovery and purification of plutonium, free of uranium, fission products and other impurities. Methods such as evaporation, precipitation, solvent extraction and ion exchange have been proposed to accomplish the concentration and isolation of plutonium. Evaporation does not provide any decontamination whatsoever, and even concentrates impurities. Precipitation yields high losses of plutonium and poor decontamination. Both solvent extraction and ion exchange have been used successfully, but the latter method has advantages of less equipment, simpler operation and less waste generation.

Both cation-exchange[6] and anion exchange[7] can be used to separate plutonium from fission products, uranium and other impurities. However, anion exchange is more efficient and provides pure product solution readily handled in subsequent processing steps. A combination of cation and anion exchange processing has also been used[6].

History

In the early days of the Manhattan Project, ion exchange was considered as an alternative to the bismuth phosphate precipitation process used at Hanford for fuel reprocessing. In 1943 a flowsheet was developed using deep beds of newly developed organic cation exchange resins containing sulfonic acid groups[3]. The process consisted of loading plutonium(IV) from a nitric acid solution onto the resin while uranyl nitrate and fission products passed through the column. The column was then washed free of residual uranium and fission products with dilute sulfuric acid and oxalic acid, respectively. Thereafter, the plutonium was eluted with 0.4

M oxalic acid or 1.25 M sodium hydrogen sulfate. The newly developed organic cation exchangers were not adopted for primary fuel reprocessing because of low decontamination factors for fission products and satisfactory operation of the bismuth phosphate process. Later the bismuth phosphate precipitation process was replaced by solvent extraction, and improved cation exchange resins with higher capacities did provide an alternative process for concentration and isolation of plutonium from dilute product streams in solvent extraction processes.

In 1953, Durham and Mills[8] showed that plutonium(IV) could be sorbed on Dowex 1 anion exchange resins from 7-8 M nitric acid. Based on this work, Ryan and Wheelwright[7] evaluated process variables and various resins which provided operating conditions for subsequent utilization of anion exchange at Hanford and other sites[2,9].

Cation Exchange

Cation exchange has been applied for the concentration and recovery of plutonium from the dilute product stream of the Purex process[3,6]. In the process (Figure 2), sulfamic acid is usually added to the dilute nitric acid solution containing plutonium to prevent the oxidation of plutonium(III) to (IV); such oxidation can cause gas bubbles of nitrogen oxides to form in the ion exchange column and create

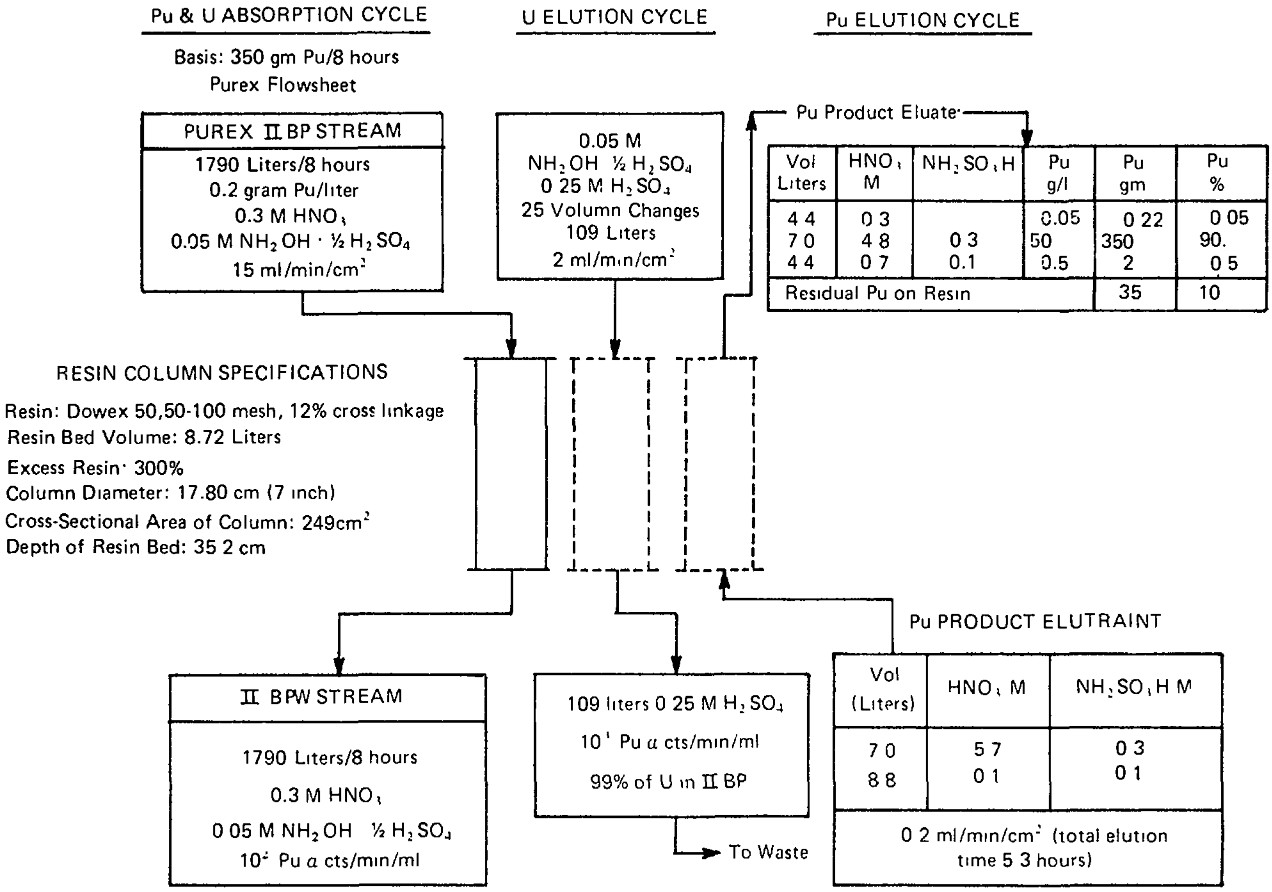

FIGURE 2. Flowsheet for concentration of plutonium nitrate solution by cation exchange. From ref. 5.

channeling of the solution and resultant inefficient elution. The distribution coefficients (g Pu/g resin per g Pu/g solution) for plutonium(IV) and plutonium (III) are 3 x 10^4 and 4 x 10^3, respectively. Although plutonium(IV) has higher distribution coefficients, loading plutonium(III) takes less resin and complexes less with sulfate ion, thus lowering plutonium losses during uranium elution.

The feed solution is passed through the column and plutonium(III) sorbs onto the resin. Anionic and most of the monovalent and divalent cationic impurities report to the effluent stream. Uranium is washed from the resin with dilute sulfuric acid.

The plutonium is eluted from the resin with strong nitric acid yielding a plutonium concentration of 40-60 g/l in 5-6 M nitric acid. As mentioned above, cation exchange does not yield good decontamination of some elements[5], and fission product decontamination factors are low. During loading, about 40 percent of the rutherium reports to the effluent. The wash solution removes only small amounts of ruthenium and rare earths along with the uranium. Beta and gamma decontamination of plutonium have been reported as 3 and 6, respectively.

The primary benefit of cation exchange is product concentration. However, the high nitric acid concentration requires lowering to provide feed adaptable to liquid-to-solid conversion processes, such as peroxide, trifluoride, or oxalate precipitation. The eluate solution is readily acceptable as feed to anion exchange and thus a combination process using both cation and anion exchange is advantageous.

Dowex 50-X12, 50-100 mesh resins have been utilized in most cases. Dowex 50 is a microreticular or gel type resin with 12 percent crosslinkage. Recently new macroreticular or macroporous (porous gel resins) cation exchange resins (20-50 mesh) have been evaluated for plutonium loading and elution kinetics[10]. Dowex MSC-1 was found to have much faster plutonium elution kinetics and better decontamination properties than Dowex 50.

In the United States, cation exchange is used routinely at Savannah River for concentration of the plutonium[11]. Since anion exchange provides better product decontamination than cation exchange, it has been more commonly used since introduced in 1959[2].

Anion Exchange

In the anion exchange process, plutonium is sorbed on anion exchange resin from a strong nitric solution. Strong and very dilute nitric acid is used to wash impurities from the resin and to elute the plutonium, respectively. Details of the process chemistry follow.

In strong nitric acid solutions, plutonium forms a hexanitrato anionic complex which sorbs on the resin according to the following equation:

$$Pu(NO_3)_6^{2-} + 2(\text{resin})NO_3 \rightleftarrows (\text{resin})_2Pu(NO_3)_6 + 2NO_3^- \qquad (1)$$

The maximum distribution coefficient for plutonium is obtained at about 7 M nitric acid (Figure 3). As the nitric acid concentration increases between 6 and 10M, acid species of the

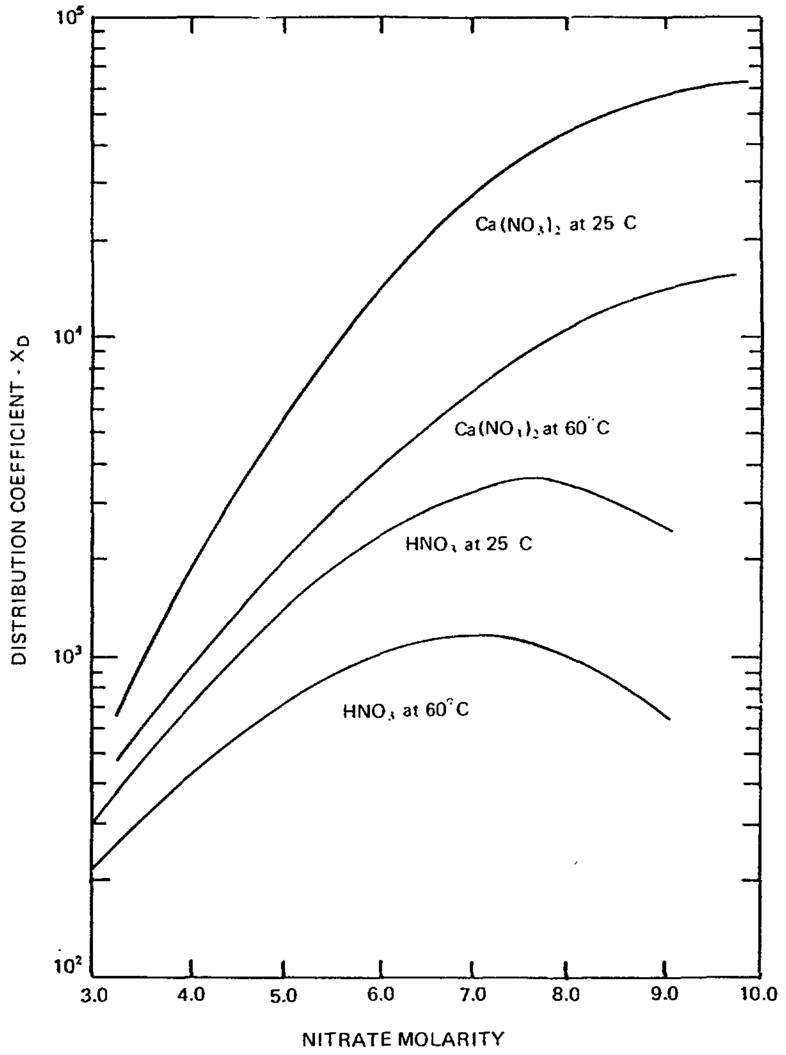

FIGURE 3. Plutonium(IV) distribution coefficient as a function of nitrate molarity.
From ref. 7.

plutonium complex are formed

$$Pu(NO_3)_6^{2-} + H^+ \rightleftarrows H\ Pu(NO_3)_6^- \qquad (2)$$

$$H\ Pu(NO_3)_6^- + H^+ \rightleftarrows H_2Pu(NO_3)_6 \qquad (3)$$

which are not sorbed as strongly as the $Pu(NO_3)_6^{2-}$ species. Furthermore, nitrate ions also compete with the plutonium complexes for resin sites. Both of these effects decrease the plutonium distribution ratios at high acidities. Adding metal nitrates, such as calcium nitrate to low nitric acid feeds overcomes these effects and significantly increases the distribution coefficient for plutonium (Figure 3).

Plutonium sorption is more strongly influenced by kinetics (which demands higher temperatures) than by equilibrium (which demands lower temperatures). The large size of the plutonium hexanitrato complex presumably causes the ion exchange process to be slow. The loading kinetics can be increased by adjusting the temperature of the feed solutions to 60-70° C. (Figure 4)

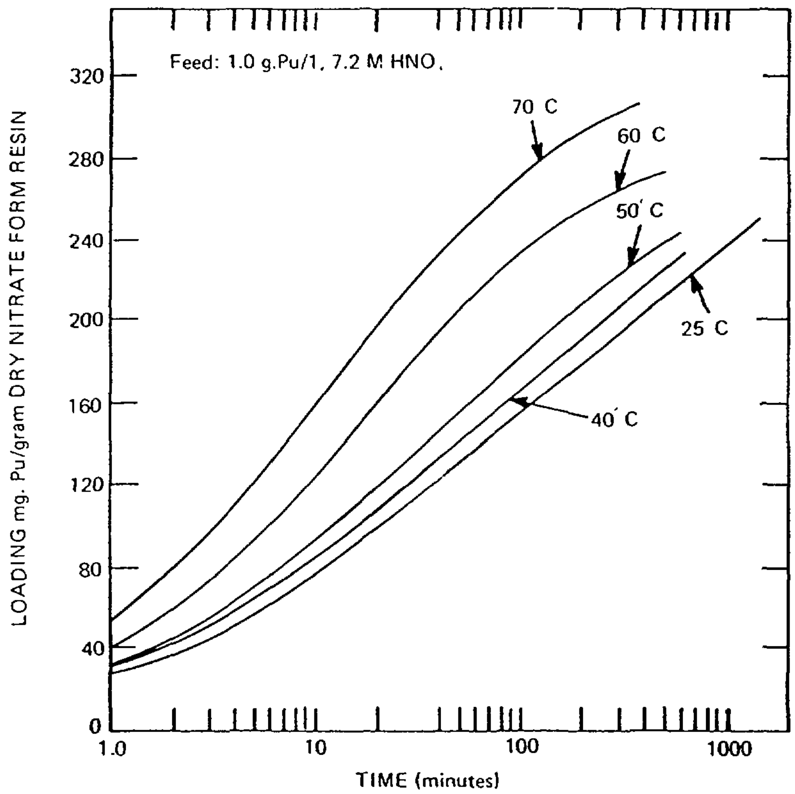

FIGURE 4. Plutonium(IV) sorption kinetics versus feed temperature. From ref. 7.

Typically gel or microreticular anion exchange resins such as Dowex 1-x4 or Permutit SK have been used. However, new macroreticular or macroporous resins have shown to have better loading and elution kinetics (Table 1). Notwithstanding, the large bead (20-50 mesh) macroporous resins still do not outperform small bead (50-100 mesh) Dowex 1-x4.

TABLE 1. The effect of resin properties on plutonium breakthrough capacity and elution. From J. D. Navratil and L. L. Martella, Nucl. Technol., 46, 106 (1979).

Resin (20 to 50 mesh)	Resin Properties[a]	Breakthrough Capacity[b]		Elution Volume[c]
		500 mg/ℓ Feed (3.5 ml/min·cm²)	10 mg/ℓ Feed (29 ml/min·cm²)	
Amberlite IRA-938	M-S-P	20	0.5	4
Dowex MSA-1	M-S-P	9	0.4	6
Amberlite IRA-900	M-S-P	7	0.3	14
Amberlite IRA-910	M-S-P	5	0.2	6
Amberlite XE-299	M-W-P	10	0.4	4
Amberlite IRA-93	M-W-P	4	0.3	5
Duolite ES-561	M-W-Ph	<1	---	23
Dowex 11 (A)	G-S-P	12	0.5	29
Ionac ASB-1	G-S-P	10	0.2	33
Dowex 11 (B)	G-S-P	9	0.4	60
Dowex 1-X4	G-S-P	8	0.5	72
Amberlite IRA-402	G-S-P	7	0.4	68
Duolite A-101D	G-S-P	6	---	30
Amberlite IRA-410	G-S-P[d]	4	0.2	15
Amberlite IRA-458	G-S-A	7	0.2	7
Ionac A-581	G-S-Pd	<1	---	4
Amberlite IRA-68	G-W-A	<1	---	13
Duolite A-30B	G-W-E	<1	---	27

*All values have an estimated accuracy of ±10%. Based on triplicate runs with four different resins.

[a] G = gel or M = macroreticular resin; S = strong or W = weak base; P = polystyrene-divinylbenzene, Ph = phenolic, A = acrylic, Pd = pyridinium, or E = epoxy-amine.

[b] Breakthrough capacity is the milligrams of plutonium passed per millilitre of resin when the ratio of plutonium concentration in the effluent to the plutonium concentration in feed reached 0.1.

[c] Millilitres of 0.35 *M* HNO_3 to elute 90% of the plutonium from 1.0 ml of resin. Flow rate = 3.5 ml/min·cm².

[d] Amberlite IRA-410 is a Type II resin $\left[\begin{matrix}-\overset{+}{N}-(CH_3)_2\\ CH_2CH_2OH\end{matrix}\right]$; all other strong-base resins are Type I $[+N_-(CH_3)_3]$.

The plutonium can be eluted from the resin with dilute nitric acid because the anionic plutonium nitrate complex is destroyed. Usually 0.35 M nitric acid is used; lower acid concentrations are avoided to prevent hydrolysis and plutonium polymer formation. Eluent solutions containing reducing agents can improve elution kinetics by forming plutonium(III). Some reducing agents can add impurities, such as iron and sulfate, but the use of hydroxylamine nitrate sometimes coupled with hydrazine will not add impurities. The use of ascorbic acid can cause precipitate formation from the products of the reductant. Reducing agents can cause gassing problems in the column resulting in channeling of solution and resultant inefficient elution.

Plutonium product concentrations of 50-60 g/l can be attained in 2-3 M nitric acid, readily adaptable for liquid-to-solid conversion processes such as oxalate precipitation.

The anion exchange process offers excellent product decontamination since few metal ions form anions in 7 M nitric acid. Neptunium(IV) also forms a hexanitrato complex which can load on the resin. The nitrato complexes of the tetravalent actinides have stability constants much higher than the hexavalent actinides. The stability constants for trivalent and pentavalent actinide nitrate complexes are very small. Fission products do not form anionic complexes in nitric acid (except for some sorption of Ce(IV), technetium and certain ruthenium complexes).

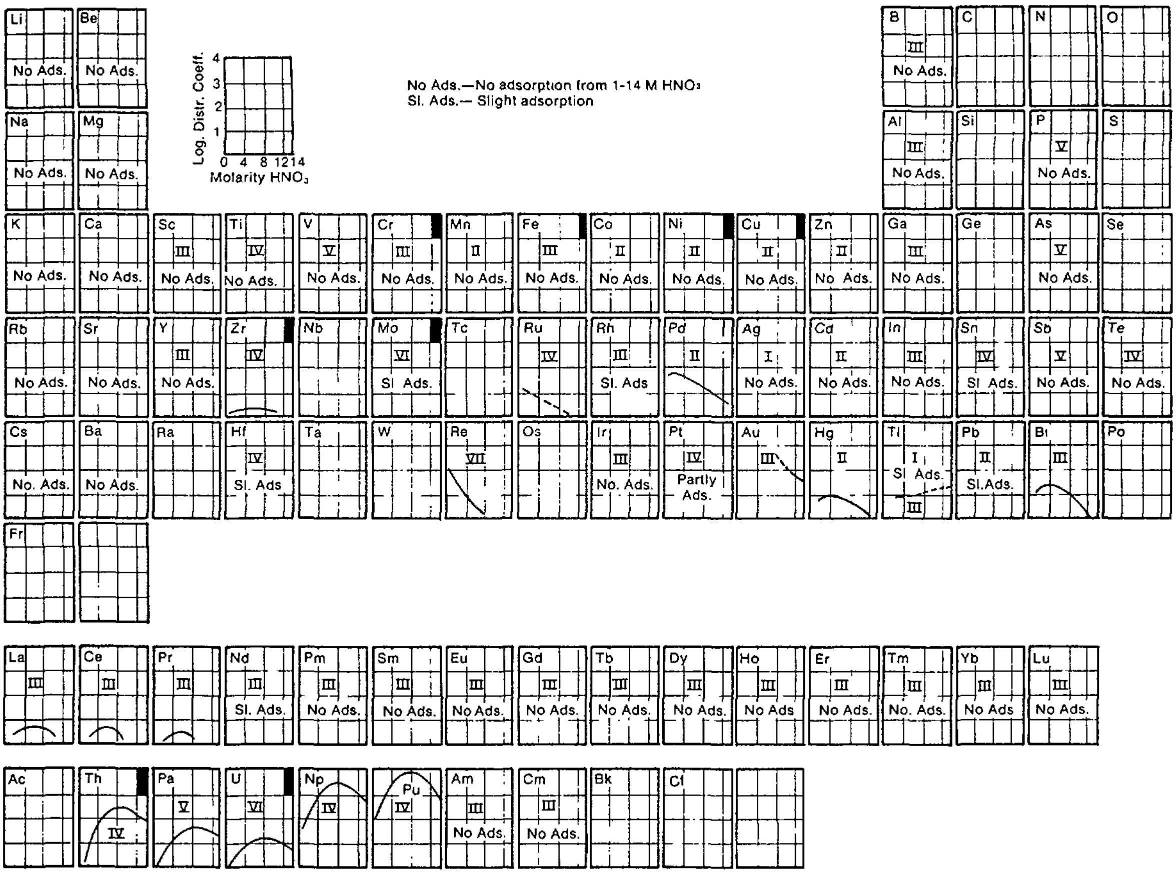

FIGURE 5. Removal of elements from solution in 1-14 M nitric acid with strongly basic anion exchange resin.
From R. F. Buchanan and J. P. Faris, in Radioisotopes in the Physical Sciences and Industry, IAEA, Vienna, 1960.

Figure 5 shows the distribution ratio of most elements sorbed onto anion exchange resin from 1-14 M nitric acid. Table 2 lists the classification of elements by degree of sorption on Dowex 1-x4 resin from a nitrate media. The elements that show no sorption can be easily washed from the resin with only one or two column volumes of 7 M nitric acid. Most of the weekly sorbed elements are removed with several more column volumes of wash solution. Elements such as Hg^{2+}, Ce^{3+}, UO_2^{2+} and Bi^{3+} require much more wash, even as much as 20 column volumes. The strongly sorbed platinum metals can be separated from plutonium

TABLE 2. Classification of elements by degree of sorption on Dowex 1 x 4 resin from nitrate media.
From E. L. Christenson and W. J. Maraman, U.S. A.E.C. Rept. LA-3542, Los Alamos National Laboratory, 1969.

ELEMENTS		
NO SORPTION Distribution Coefficient ~0	WEAK SORPTION Distribution Coefficient <4	STRONG SORPTION Distribution Coefficent >5
Mg	Sc	Pd
Al	As	Ir
Ti	Se	Pt
V	Zr	Au
Cr	Nb	Th
Mn	Mo	
Fe	Ru	
Co	Ag	
Ni	Cd	
Cu	La	
Zn	Hf	
Ga	W	
Ge	Re	
Y	Os	
In	Hg	
Sn	Pb	
Sb	Bi	
Ta	Ce	
Tl	Rare Earths	
	U	
	Am	
	Rh	

because they will not elute with dilute nitric acid. Thus, under the proper conditions, plutonium can be separated from all elements except thorium and neptunium by anion exchange.

From a safety standpoint, the most important consideration in the ion-exchange process is the prevention of over-pressurization and elevated temperatures in the columns. Anion exchange resins loaded with the plutonium nitrate complex contain up to three nitrate ions per exchange site compared to nitrate form resin with only one nitrate ion per site. If the column is not vented and elevated temperatures are attained, an exothermic and autocatalytic reaction can be initiated and a rapid chemical excursion can take place. Furthermore, if the resin loaded with plutonium is permitted to dry out, the situation is aggravated. To insure that this circumstance never occurs, precautions are taken. Whenever the anion exchange is shut down for any period of time exceeding 8 hours, the resin bed is left saturated with dilute nitric acid. As an additional safety measure, the resin bed is never left loaded with plutonium for more than 8 hours at one time. Further, the columns should be fitted with rupture disks to prevent overpressurization.

Anion exchange has been used routinely for the third cycle of plutonium purification following Purex solvent extraction[12]. Furthermore, plutonium has been concentrated and purified effectively from irradiated fuel solutions. Gamma decontamination factors for plutonium were 2×10^4 in a single cycle and 4×10^7 in two cycles; niobium was the limiting activity. The same process is used for recovery of ^{238}Pu and ^{237}Np in the production of ^{238}Pu for isotopic heat sources[13].

One-cycle of Purex was eliminated at Hanford by utilizing anion exchange purification of plutonium[5,6]. The process was operated continuously using a Higgins contactor (Figure 6). The loading and elution sec-

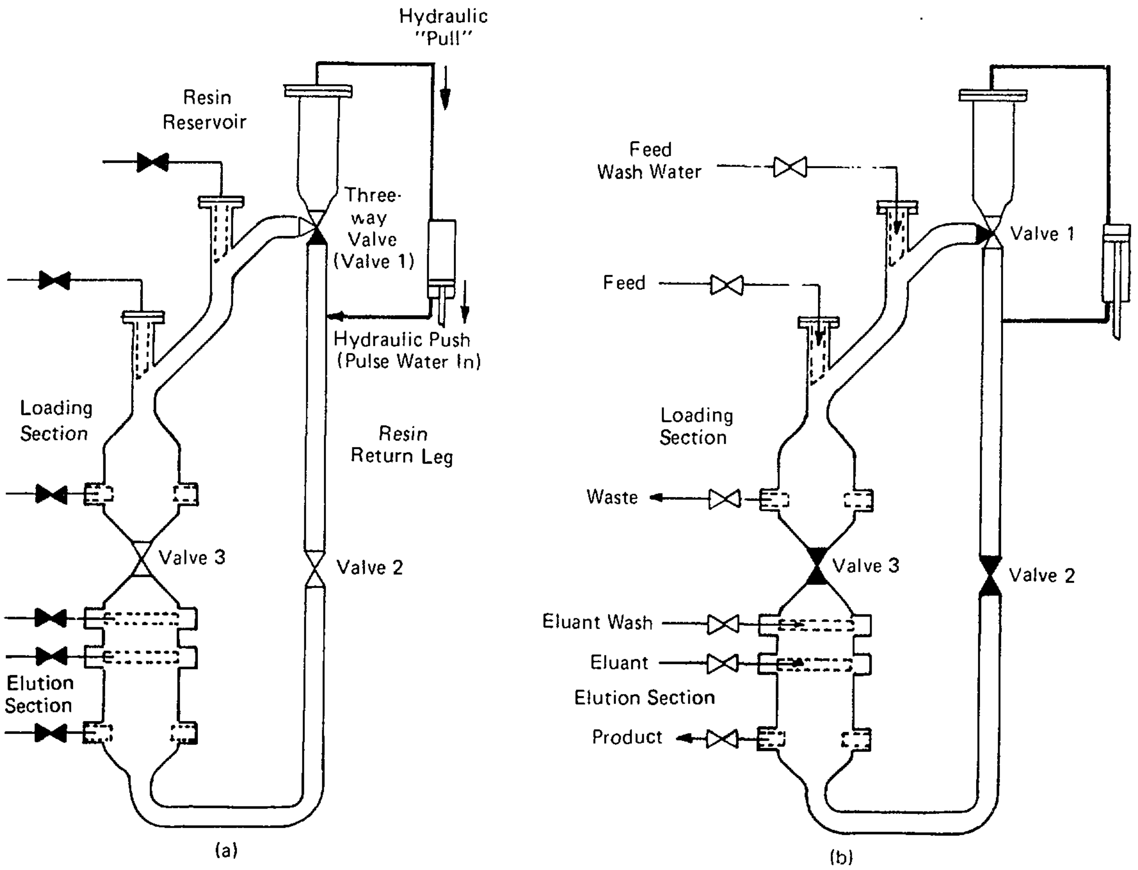

FIGURE 6. Mode of operation of a Higgins quasi-continuous ion-exchange contactor. From J. T. Roberts, U.S. A.E.C. Rept. ORNL-2504, Oak Ridge National Laboratory, 1958.

tions are both 13 cm in diameter and 2.1 m high. The resin is loaded to a plutonium concentration of 30-50 g Pu/l resin. The effluent contained 0.5 percent of the plutonium feed, but this stream is recycled to prevent any loss. The process was operated for more than two years with an efficiency of about 95 percent. It provided good decontamination of uranium (10^5 - 10^6), fission product impurities (10^4 for ruthenium and 10^5 for zirconium-niobium), and other impurities.

Anion exchange has been used for recovery of plutonium from oxalate solutions[4], however nitric acid concentration of 9 M is needed to prevent interference from oxalate. Interference of fluoride ion in anion exchange processing can be overcome by adding aluminum nitrate to complex the fluoride ion.

MISCELLANEOUS USES OF ION EXCHANGE

Although the most important use of ion exchange in fuel reprocessing is the tail-end purification and concentration of plutonium following Purex processing, ion exchange has been utilized for uranium purification, separation and recovery of individual actinide elements and isotopes, and treatment of low-level wastes.

Excellent reviews of ion exchange in the Atomic Energy Industry have been written by Jenkins[14-16]; he has summarized ion exchange studies dealing with the following topics: thorium, protactinium and uranium; neptunium and plutonium; americium, curium and actinide-lanthanide separations; the higher actinides, Cm, Bk, Cf, Es, and Fm; and fission product separation (mainly cesium and strontium). Also, recent books contain various chapters on actinide separation, recovery and purification[17,18].

Uranium

Although the most common tail-end process for uranium purification is silica-gel adsorption[4], where the uranium nitrate solution is passed through the silica-gel column which removes gamma-emitting impurities by a factor of approximately 20, ion exchange has been utilized somewhat.

Uranium has been decontaminated of ruthenium by a factor of 10 or greater by ion exchange[4]. Uranyl nitrate solution is first heated at 90° C for 1/2 hr. after adding 2 g thiourea/l solution. This solution is then passed through a bed of carboxylic acid resin which sorbs the ruthenium. The ruthenium can be stripped from the resin with 6 M nitric acid.

Uranium has also been concentrated from dilute solution by sorption on sulfonic type cation exchange resins[4].

Neptunium

Neptunium(IV) can be separated from uranium, plutonium and other common metallic impurities by sorption on anion exchangers from a 6 M nitric acid solution containing a reducing agent such as ferrous sulfamate to maintain Pu(III) and Np(IV)[13]. The impurities are washed from the column with 6 M nitric acid. The sorption and elution behavior of neptunium is similar to plutonium.

Other Elements

Cation exchange, usually in conjunction with other separation processes, has been used to separate and purify cesium, strontium, promethium and other rare earth fission product elements, and americium and higher actinides[2-5,19]. Technetium has been recovered by anion exchange processing[4]. Applications of ion exchange in nuclear fuel reprocessing, including low-level waste treatment, continue to grow[14-16,20].

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CHAPTER 6

MISCELLANEOUS USES OF ION EXCHANGE IN THE NUCLEAR FUEL CYCLE

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Abstract

Miscellaneous uses of ion exchange technology are described for isotope separation of light elements (lithium, boron and nitrogen), separaton of uranium isotopes and other actinide elements, and for the recovery of uranium from phosphoric acid solutions. Application of ion exchange membrane is also indicated for the electrolytic reduction of uranium and for the decomposition of ammonium ion in the alpha-bearing liquid wastes.

6-1. ISOTOPE SEPARATION OF LIGHT ELEMENTS

6-1-1. LITHIUM ISOTOPES

The first experiments on the lithium isotope separation were carried out by T.I. Taylor and H.C. Urey using a zeolite inorganic ion exchanger contained in a stainless steel pipe (35 ft long and 3/4 inch diameter).[1]. The experiments initially aimed to separate lithium isotopes by extraction. Lithium bromide was extracted with methylamyl alcohol from an aqueous solution reducing the concentration finally 1000 to 1. The residue showed no difference in the isotopic composition of lithium isotopes. During the experimental work, however, they found the fact that the commercial lithium compounds have different isotopic ratios. It appered that somewhere in the process of the manufacture, an appreciable separation of lithium isotopes had occurred. They set up the column packed with zeolite which had been used in the manufacturing process to extract lithium from aluminum silicate ores, and obtained successful results from the experiments.

D.A. Lee, G.M. Begun and J.S. Drury studied the isotope effects in ion exchange processes of lithium ion using synthetic organic ion exchangers of Dowex 50.[2-5]. They determined the single stage separation factors for the systems consisting of ion exchange resins and aqueous solutions. The single stage isotope separation factor is defined as,

$$\alpha = (^6\overline{\mathrm{Li}})(^7\mathrm{Li}) \;/\; (^7\overline{\mathrm{Li}})(^6\mathrm{Li}) \qquad (1)$$

where "¯" denotes isotopes in resin phase. In their experiments the single stage separation factor was found to depend on the structure of resins, compositions of the outer solution, and experimental temperatures. Some results from the work are shown in Fig. 1.

The isotope effects in this process are attributed to the difference in the hydration of lithium ion between two phases. Lithium ion is fully hydrated with around seven water molecules in a diluted aqueous solution. Dehydration occurs when lithium ions enter into ion exchange resins. The lighter isotope ^{6}Li gathers in the dehydrated state, i.e. lithium ions in resin, and the heavier ^{7}Li is fractionated in the hydrated state in the aqueous solution. The degree of hydration of cations in ion exchange resins decreases with increase of the crosslinking of the resins. Larger isotope separation factors are expected in the systems using higher crosslinking resins accordingly.

Ion exchange resin is theoretically regarded as a kind of a highly concentrated aqueous solution. The ion exchange selectivity depends on the concentration of the outer solution, as a general rule. When concentrated solutions are used as eluents, the chemical states of both phases (resin and solution) become close each other, which results in the small selectivities of the resin for the ionic species involved. Since isotope separation factors depend also on the ion exchange selectivity, It is reasonable that the lithium isotope separation factors were observed to decrease with increase of the concentration of eluents.

As predicted from theoretical treatments, isotope effects based on the molecular vibration depend on temperature[6]. The net isotope effect, separation factor - 1, is expected to be linearly proportional to (1/T) as a first approximation, where T indicates absolute temperature.

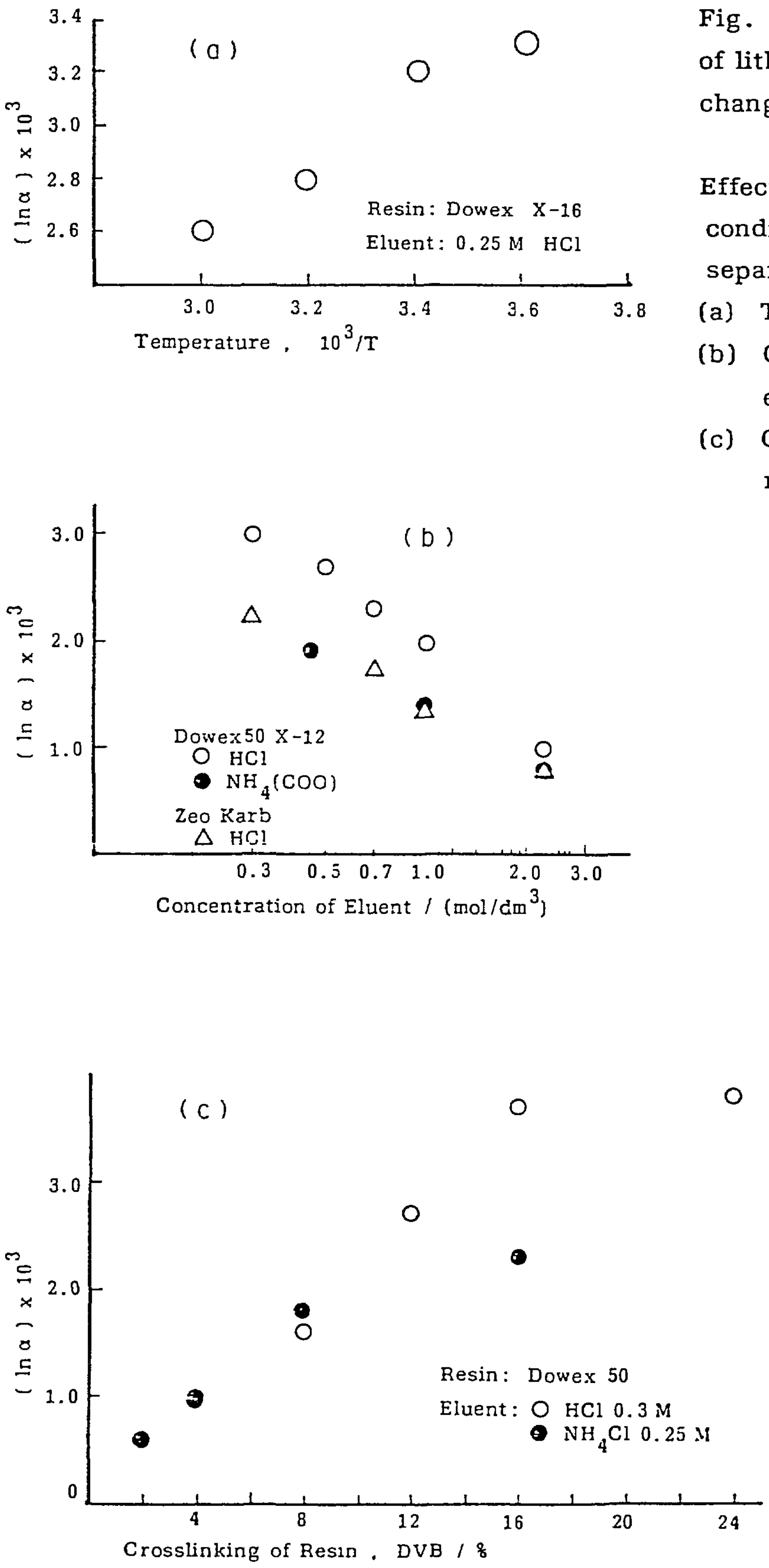


Fig. 1. Isotope effects of lithium in cation exchange chromatography.

Effects of experimental conditions on the isotope separation factor α .

(a) Temperature.

(b) Concentration of eluent.

(c) Crosslinking of resin.

6-1-2. BORON ISOTOPES

In the era of the Manhattan Project, boron isotope separation was also investigated. Adduct compounds of Lewis acids, e.g. $BF_3O(CH_3)$, were discovered to have large isotope effects in the evaporation processes. Anisole complex -$COCH_3BF_3$ shows an isotope separation factor of 1.039 at 2 °C.

On the other hand ion exchange processes have relatively smaller isotope separation factors of 1.01 - 1.03. S. Makishima et al.[7] first applied ion exchange chromatography to the separation of boron isotopes. They used strong base anion exchange resin Amberlite CG-400-I, 100 - 200 mesh. The anion exchange resin packed in a column (120 cm long) was initially converted to the OH^- form. Then a boric acid solution or a boric acid plus glycerol solution was fed into the column, resulting in a strong adsorption of boric acid ions in the anion exchange resin. The chromatographic operations were conducted in a displacement break-through manner. The effluent fractions of the boric acid solution

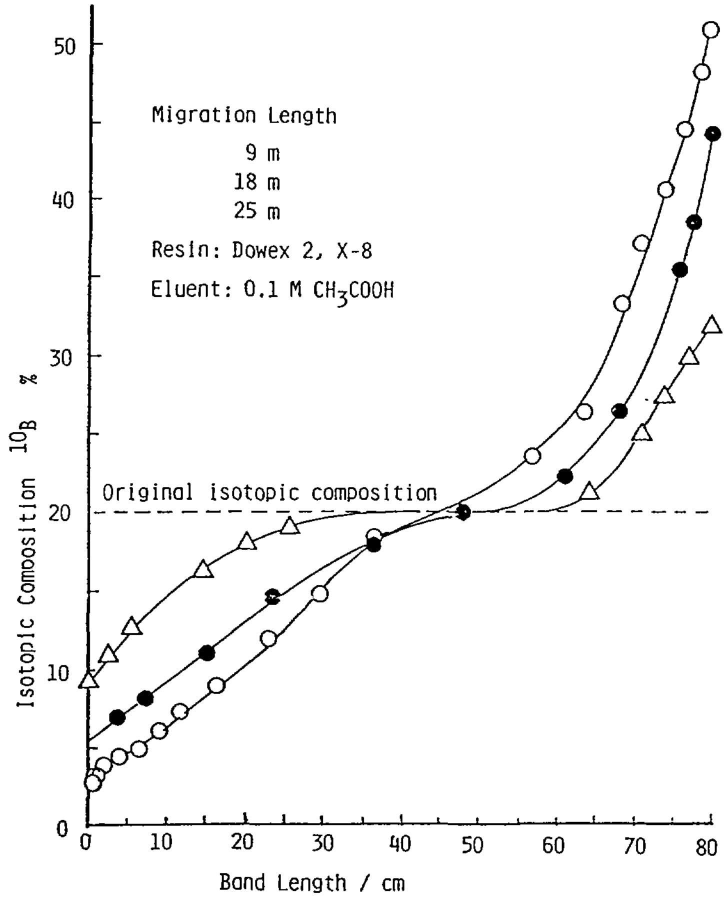


Fig. 2. Boron isotope separation by anion exchange Chromatography. Ref.(8)

were analysed and it was found that the heavier isotope ^{11}B was enriched at the front boundary of the boric acid zone. The observed isotopic separation factors were 1.011 and 1.016 for the system of a boric acid solution and for the system of a boric acid plus glycerol solution, respectively.

M.M. Urgell et al.[8] extended this system using Dowex 1x8 and Dowex 2x8, 200 - 400 mesh. In their experiments the adsorption bands of boric acid were displaced by acetic acid solutions, and boron 10 was enriched at the rear boundary. The profile of isotope distribution in a boric acid band is shown in Fig. 2. The resin used in this process is regenerated by alkali solutions which usually contain CO_3^{2-}. When the resin is treated with acids in elution, the adsorbed CO_3^{2-} ions cause a problem of evolution of carbon dioxide gas.

H. Kakihana et al.[9] developed a weak anion exchange resin system for the boron isotope separation . They found a weak base anion exchange resin, Diaion WA 21, absorbs boric acid ions when charged with a pure boric acid solution, and releases the boric acid ions when treated with pure water. No gas evolution was observed in long migration experiments up to 256 m.

6-1-3. NITROGEN ISOTOPES

F.H. Spedding et al.[10] conducted the experimental studies on nitrogen isotopes using a cation exchange resin Dowex 50W X12. The cation exchange resin packed in a column was first converted to H^+ ion form, then ammonium ions were loaded on the resin bed. The ammonium band was finnaly eluted in a displacement manner by a 0.1 M (mol/dm^3) NaOH solution. After the chromatographic operation it was found that the heavier isotope ^{15}N was enriched in the resin phase and accumulated at the rear boundary of the ammonium adsorption band. The single stage isotope separation factor was determined as 1.025. The isotope separation factor corresponds to the equilibrium constant of the following isotope exchange reaction,

$$^{14}NH_4\text{-}R \;+\; ^{15}NH_4OH \;=\; ^{15}NH_4\text{-}R \;+\; ^{14}NH_4OH \;. \qquad (2)$$

Since NH_4^+ ions are in the resin phase and NH_4OH molecules are in the solution phase, the experimental results indicate that ^{15}N isotope is preferentially fractionated in NH_4^+ ions and the lighter ^{14}N is in NH_4OH molecules which are partially dissociating into NH_3 and H_2O molecules in an aqueous solution. The isotope effect between NH_4^+ and NH_3 is theoretically calculated as 1.035 at 25 °C as indicated in Table I. Such a large isotope effect for the NH_3 - NH_4^+ system is attributed to the structual difference between these molecules: the ammonia molecule takes a triangle pyramidal structure, while ammonium ion forms a tetrahedral structure.

TABLE I. THE STANDARD ELECTRODE POTENTIALS OF REDOX REACTIONS.

Redox Reactions	S. E. P. (V)
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000
$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$	0.099
$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}$	0.108
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.15
$Cu^{2+} + e^- \rightleftharpoons Cu^-$	0.155
$AgCl + e^- \rightleftharpoons Ag + Cl^-$	0.222
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	0.330
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	0.359
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.36
$MnO_4^{2-} + 2H_2O + 2e^- \rightleftharpoons MnO_2 + 4OH^-$	0.60
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.771
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1.33

The ammonium adsorption band migrates through the column displacing the preceding hydrogen ions, simultaneously being displaced by the following sodium ions. At the band boundaries, front and rear, the ion exchange reactions proceed to completion, owing to the large equilibrium constants of the reactions: at the front boundary,

$$H^+\text{-}R + NH_4OH \rightleftharpoons NH_4^+\text{-}R + H_2O \quad (K = 10^9) \qquad (3)$$

and at the rear boundary,

$$NH_4^+\text{-}R + NaOH \rightleftharpoons Na^+\text{-}R + NH_4OH \quad (K = 10^5). \qquad (4)$$

The nitrogen isotope enrichment obtained by M. Urgell et al. [8] using the above-mentioned system is shown in Fig. 3.

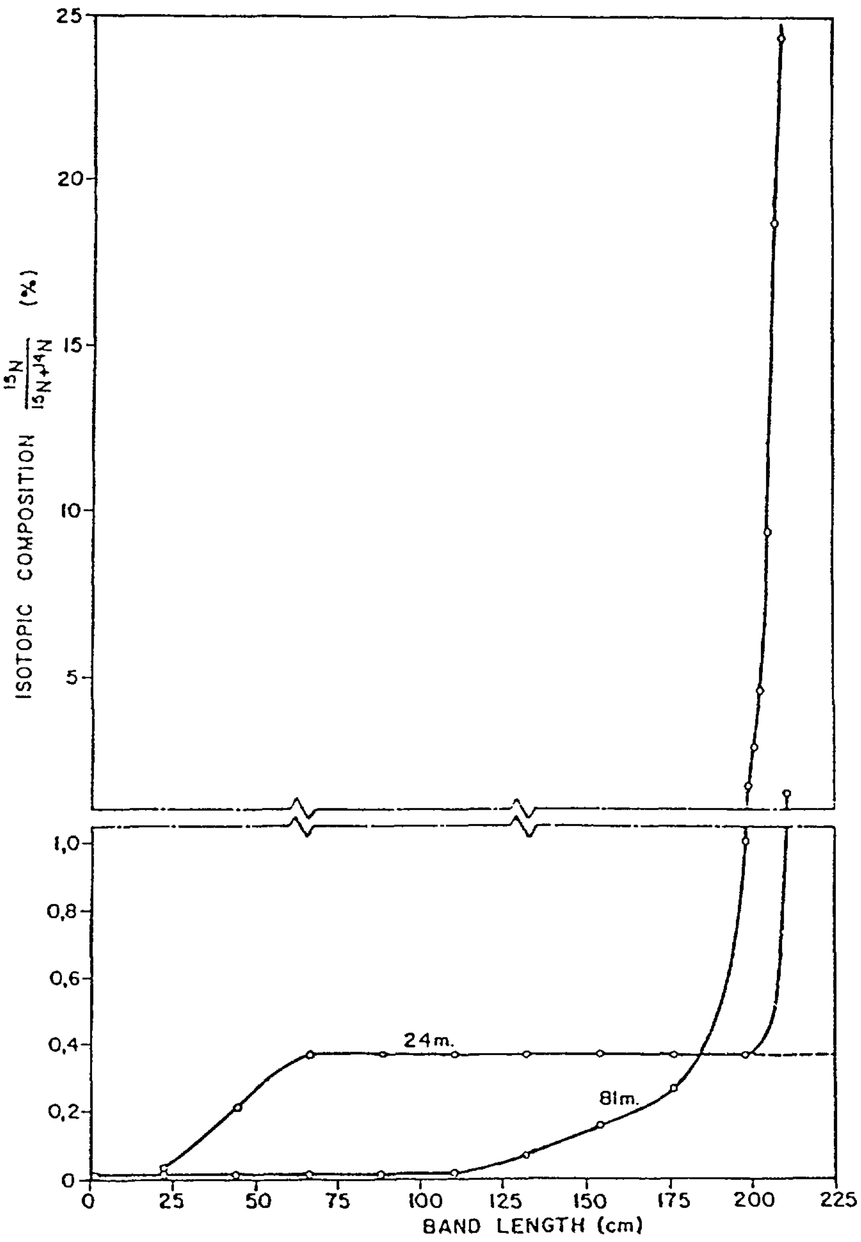


Fig. 3. ISOTOPIC COMPOSITION OF A NH_4^+ BAND AFTER A DISPLACEMENT OF 24 AND 81 m.
Ref. (8)

6-2. SEPARATION OF URANIUM ISOTOPES

6-2-1. CHEMICAL SYSTEMS

For many years research and development work has been conducted on the uranium enrichment process for peaceful use of nuclear power. The chemical exchange process is regarded as one of the promising methods. A number of chemical systems studied for the uranium enrichment by chemical exchange are classified into two chief chategories: 1. ligand exchange systems, and 2. electron exchange systems.

The ligand exchange systems involve complex formation of uranium ions with organic and inorganic ligands, e.g. F^- ion, organic acids with carboxyl groups. The observed separation coefficients (= single stage separation factor) for uranyl complex formation systems are in the range of approx. 1.0001 - 1.0002. The observed separation coefficients for uranous complex systems are smaller than those for uranyl complexes. In spite of the relatively smaller values of the separation coefficients, the ligand exchange systems have the feature of the simple experimental procedure. The investigations on the ligand exchange systems have been still actively continued to elucidae the mechanism of the isotope separation processes employing ion exchange chromatography.

The electron exchange systems include two possible processes of the U(III) - U(IV) exchange system and the U(IV) - U(VI) exchange system. The former was developed by French CEA and quoted as giving a comparatively large isotope separation coefficient of approx. 1.003. The enrichment process based on this system has been realized by employing solvent extraction [16]. The latter, U(IV) - U(VI) system, has been studied by several groups of investigators [11-15]: a test plant has been constructed by Asahi Chem. Co. in Japan. The experimentally observed separation coefficients for this process are in the range of 1.0007 - 1.0014. The feasibility of the enrichment process largely depends on the magunitude of the separation coefficient, and the efficiency of multiplication stages. The U(III) - U(IV) exchange system is characterized as having a large separation coefficient, and the U(IV) - U(VI) system has the advantage of the small HETP (height equvalent to a theoretical plate) accomplished by implementation of ion exchange chromatography. The following sub-sections briefly describe major technological points which should be considered in the development of the enrichment process based on the U(IV) - U(VI) exchange system.

6-2-2. REDOX REAGENTS

Table I lists the standard electrode potentials of several redox reactions. The U(IV) - U(VI) system has the standard potential of 0.33 V. This indicates the fact that U(VI) ion is reduced by Cu(I), Sn(II), Ti(III) ions etc., while U(IV) is oxidized by Mn(VI), Fe(III).

The standard potentials of the reductants are required to be lower enough than that of uranium so that the reduction can proceed to completion, but not so low as the potential of H^+/H_2 system to avoid the generation of H_2 gas. Titanium (III), Ti^{3+} ions, is chosen as the most appropriate reductant for this purpose. In a similar manner, ferric ion, Fe(III), is chosen as the oxidant: its standard potential is high enough to oxidize U(IV) ion, but not so high as to oxidize the organic materials of the medium. More detailed considerations on the concentrations of ions involved in the redox reaction are given by the Nernst's equation,

$$E = E_{M,o} + (RT/nF)\ln(M_{ox})/(M_{red}), \qquad (5)$$

where E is the potential of a solution, $E_{M,o}$ the standard electrode potential of M, R the gas constant, T temperature, n the number of electrons transferred in the reaction, F the Faraday constant, (M_{ox}) and (M_{red}) are concentrations of ions in the oxidized and reduced state, respectively. When n of the oxidant or reductant is unity, the concentration ratio of U(IV) and U(VI) is given as,

$$[U(VI)]/[U(IV)] = ([M_{ox}]/[M_{red}])^2 \exp[2F(E_{M,o} - E_{U,o})/RT]. \qquad (6)$$

6-2-3. ION EXCHANGE SELECTIVITY

Uranium displacement chromatography is achieved by using either cation exchange resins or anion exchange resins. Uranium ion is adsorbed on cation exchange resins and on anion exchange resins as well due to its complex formation with anion ligands. In either case of exchangers Ti(III) and Fe(III) are used as a reductant and an oxidant, respectively.

Cation Exchange Chromatography. The form of U(IV) is U^{4+} in aqueous solutions and the form of U(VI) is UO_2^{2+}. U(IV) ion has a actually higher valency, and therefore shows a stronger adsorption selectivity on cation exchange resins than U(VI) does. A similar tendency is found in the system of a pair of ions of Ti(III) and Ti(IV). Ti(IV) forms TiO^{2+} in aqueous solutions and has lower selectivity on a cation exchange resins than Ti(III) does. The selectivities of a cation exchange resin for some relating cations are listed in Table II.

Based on the selectivities shown in Table III, that is, Fe(III) $\gg$ Fe(II), U(IV) $\gg$ U(VI) & Fe(II), and Ti(III) $\gg$ Ti(IV) & Fe(II), the redox cation exchange system is set up for uranium displacement chromatography. The cation exchange resins packed in a column

TABLE II. DISTRIBUTION COEFFICIENTS, K_d, OF SELECTED IONS FOR CATION EXCHANGE RESIN.

	Concentration of HCl	
	0.2 mol/dm^3	1 mol/dm^3
U^{4+}	2.x10^4	800
UO_2^{2+}	860	19.2
Ti(IV)	297	11.9
Fe^{3+}	3400	35.4
Fe^{2+}	370	19.8
Ti^{3+}	ca. 10^4	ca. 10^2

$K_d = [\underline{M}] / [M]$,

TABLE III. TYPICAL DESIGN CHARACTERISTICS FOR ENRICHMENT PLANT WITH THE CAPACITY OF 500 te 3% (U-235) URANIUM/YEAR.

Plant capacity	P	500 t/y
Product enrichment	Rp	0.03
Feed isotope abundance	R_o	0.0072
Uranium adsorption capacity	q	0.23 t/m^3
Separation coefficient	ε	0.001
Cycles of operation	N	500 cycle/y
Reain bed efficiency	Φ	0.33
Required resin volume	V	4.2x10^4 m^3
Unit production capacity	P/V	12 kg/m^{3}y (3% U-235)

are first completely converted to the form of Ti(III), then U(VI) is introduced to make an appropriate width of a uranium adsorption band. The U(VI) ions are reduced to U(IV) and adsorbed on the cation exchange resins replacing titanium ions. In order to elute uranium ions, a Fe(III) solution is fed into the column. The adsorbed U(IV) ions are oxidized to U(VI) by Fe(III) ions and released from the resin. The released U(VI) ions pass through the column repeating isotope exchange reactions with adsorbed U(VI) ions, and reach at the frontal boundary of the uranium band. The U(VI) ions at the front boundary are reduced by Ti(III) and re-adsorbed on the resins as previously mentioned.

The redox reactions involved in this system are:
at the front boundary, $2\mathrm{Ti(III)}_R + \mathrm{U(VI)}_S \longrightarrow \mathrm{U(IV)}_R + 2\mathrm{Ti(IV)}_S$,
at the rear boundary, $\mathrm{U(IV)}_R + 2\mathrm{Fe(III)}_S \longrightarrow 2\mathrm{Fe(II)}_R + \mathrm{U(VI)}_S$,
where subscripts R and S refer to the phases of resin and solution, respectively. The Fe(II) ions adsorbed on the resin are easily eluted out by the succeeding Fe(III) ions, and flow down in the column without adsorption, according to the selectivities shown above.

Anion Exchange Chromatography. Chloride ions makes complexes with a number of cations, including uranium ions. The adsorption of concerned uranium, titanium, iron ions from hydrochloric acid solutions on an ion exchange resin is presented in Fig. 4 [18]. Figure 4 shows that the sorption depends on the concentration of chloride ions. If suitable concentration of HCl is chosen, the following sequences of ion exchange selectivities can be acieved.

$\mathrm{Fe(III)} \gg \mathrm{Fe(II)}, \quad \mathrm{U(VI)} \gg \mathrm{U(IV)}$ & $\mathrm{Ti(III)}$.

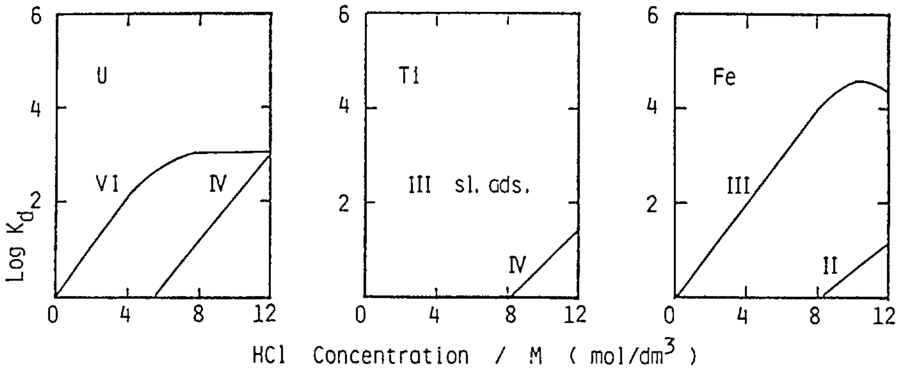


Fig. 4. Anion exchange selectivities of complex cations.
$K_d = [\underline{M}] / [M]_{sol}$, at very low concentration of M ions.
Ref. (17).

Based on these selectivities, anion exchange redox chromatography is realized by using concentrated HCl solutions as the medium for the moving phase. Apparently the tendency of the selectivities for U(IV) and U(VI) in the anion exchange system is reverse to that of the cation exchange system. The redox reagents are arranged in the reverse sequence in anion exchange system against the cation exchange system.

Anion exchange resins packed in a column is first conditioned to the form of Fe(III)-Cl complex. Then U(IV) is introduced, and oxidized to U(VI) by Fe(III). The generated U(VI) is adsorbed on the resin, making chloride complexes. The U(VI) in resin is reduced to U(IV) by Ti(III) in the eluent. The redox reactions in anion exchange chromatography are as follows.

At the front boundary,

$$2\mathrm{Fe(III)}_R + \mathrm{U(IV)}_S \longrightarrow \mathrm{U(VI)}_R + \mathrm{Fe(II)}_S,$$

at the rear boundary,

$$\mathrm{U(VI)}_R + 2\mathrm{Ti(III)}_S + n\mathrm{Cl}^- \longrightarrow n\mathrm{Cl}^-_R + \mathrm{U(IV)}_S + 2\mathrm{Ti(IV)}_S.$$

U(IV) and Ti(IV) ions in the latter reaction have very small adsorbabilities toward the anion exchange resins. The vacant sites caused by the release of uranium ions are filled with Cl ions, instead of Ti(IV) ions.

The models of chromatography are shematically shown for both cation and anion exchange systems in Fig. 5.

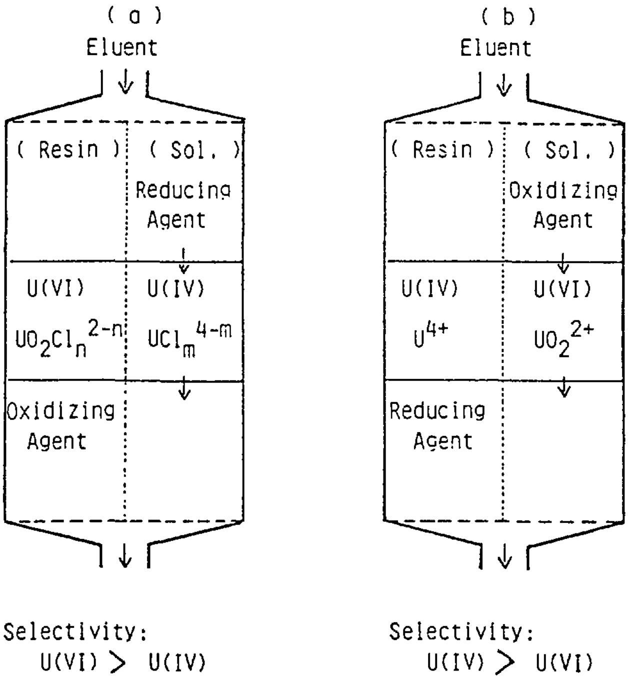


Fig. 5. Chromatographic systems for uranium isotope separation based on U(IV)-U(VI) exchange reaction.
(a) a system using anion exchange resin,
(b) a system using cation exchange resin.

<u>Electron Exchange Reactions.</u> The isotope exchange reaction between U(IV) and U(VI) ions gives the most fundamental base for the isotope separation system.

$$^{235}\mathrm{U(IV)} + {}^{238}\mathrm{U(VI)} \rightleftharpoons {}^{238}\mathrm{U(IV)} + {}^{235}\mathrm{U(VI)} \qquad (7)$$

The rate of this reaction is governed by the electron exchange between U(IV) and U(VI). The rate equation is expressed by using a second order rate constant.

$$\mathrm{Rate} = k_{ex}[\mathrm{U(IV)}][\mathrm{U(VI)}] \qquad (8)$$

The constant k_{ex} depends on the concentration of H^+ ions in the medium. E. Rona [18] observed that the k_{ex} values decrease with increase of H^+ concentration in the pH region. K. Gonda et al. [19-20] found that the rate constant in a HCl solution increases again with increase of the H^+ concentration above 4 M, giving the minimum values at ca. 3 M. They reported also that the exchange reaction has a large activation energy of 25 kcal/mol. From the view point of kinetics, both high pH regions and high HCl concentration regions are preferable conditions for chromatographic operations. Due to the large activation energy the operation temperature should be elevated as high as possible, and the employment of a catalyst would be of great use for production of enriched uranium. H. Tomiyasu [21] found that U(IV) - U(VI) electron exchange reaction is catalyzed by Fe(II)/Fe(III) ions.

Ion Exchange Reactions. To attain the isotopic equilibrium at any cross-section in the uranium adsorption band, the ions U(IV) and U(VI) must be exchanged at sufficiently fast rate between the two phases of resin and solution. This process is governed by ion exchange properties. Both U(IV) and U(VI) ions are contained in both phases of resin and solution as either a major component or a minor component. The exchange reactions take place among all these ions in two phases. These reactions are depicted in Fig. 6 . Figure 6 indicates that three of the four steps must be fast to attain the equilibrium in a short time, while one step is allowed to be slow. It means that at least one of two ion exchange processes of U(IV) and U(VI) should be fast.

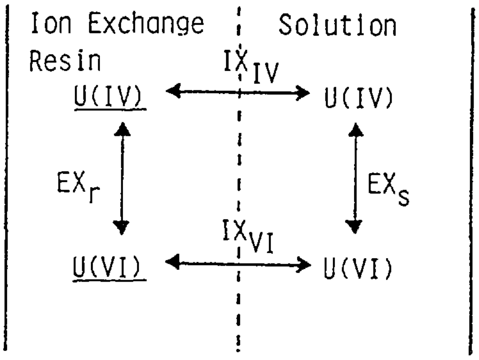


Fig. 6 . Kinetic processes in uranium ion exchange chromatography:
IX_{IV}, IX_{VI} : ion exchange of U(IV) , U(VI),
EX_r, EX_s : electron exchange in resin and solution phase, respectively.

6-2-4. REACTION RATES

In addition to above-mentioned factors on equilibrium, another important factor is the kinetics of the chemical reactions involved in the process. There are three different types of reactions of which reaction rates should be considered in the system of uranium enrichment by ion exchange chromatography.

- Uranium redox reactions at uranium band boundaries.
- U(IV) - U(VI) electron exchange reactions.
- U(IV), U(VI) ion exchange rates.

Uranium Redox Reactions. In the redox reaction of uranium ions, two electrons are transferred between the pair of ions of U(IV) and U(VI). Two-electron reactions have, as a rule, slow reaction rates compaired with one-electron reactions. For example the reduction of U(VI) by Sn(II) is possible in respect to the thermodynamic aspect, however the reaction rate of this redox system is so slow that the system is not applicable for the redox chromatography. In the cases of Fe(III) and Ti(III) used as redox reagents, on the other hand, the redox reactions show fairly rapid reaction rates. The reason for this would be given by the mechanism that U(IV), and U(VI) can be oxidized or reduced through the U(V) state in the redox reactions by Fe(III) or Ti(III) ions. In either case of cation or anion exchange chromatography, the redox reactions take place very rapidly. As far as the uranium redox reactions with Fe(III) and Ti(III) ions concerned, the reaction rates are sufficiently fast. This fact is confirmed from the development of very sharp boundaries at the ends of a uranium band. The solutions containing those ions of iron, titanium and uranium show different colors: Fe(II) light blue, Fe(III) light brown, Ti(III) purple, Ti(IV) transparent, U(IV) dark green, and U(VI) yellow. During the migration the formation of uranium band boundaries can be visibly checked through the glass wall of the column.

The rate of isotopic ion exchange processes are indicated in terms of the self-diffusion coefficients of given ions. As a rule polyvalent ions have small self-diffusion coefficients. Examples of self-diffusion coefficients are shown in Fig. 7 .(23)

It is well known that the rate of ion exchange is contralled by the diffusion processes, and two concepts are proposed for the determining step in the diffusion: the film diffusion and the particle diffusion. A simple criterion is given to identify

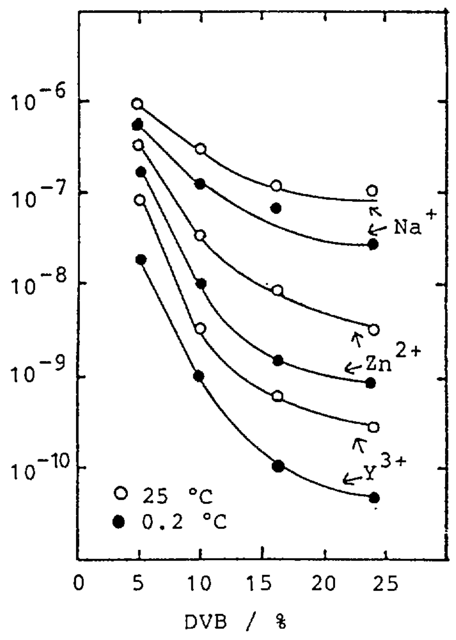


Fig. 7 . Self-diffusion constants in sulfonic acid cation exchange resin. Ref. (23).

the rate ditermining step: (22)

$$C_R D_R \delta / C_S D_S r_o = \left\{ \begin{array}{lll} 0.13 & \text{--} & \text{particle diffusion control,} \\ 0.13 & \text{--} & \text{film diffusion control,} \end{array} \right\} \quad (9)$$

where subscripts R and S refer to resin and solution, respectively, C is the concentration of concerned ion, D is the self-diffusion coefficient, δ is a film thickness, and r_o is a bead radius. For the cases of uranium ion exchange, the values of the terms in the criterion are estimated approximately as $(C_R/C_S) = 10$, $(D_R/D_S) = 10^{-2}$, $(\delta/r_o) = 10^{-1}$. Then the particle diffusion is estimated to be the rate determining step of the ion exchange. If the self-diffusion coefficients are improved by one order in the resin phase, and very fine resins are used, the rate determining step would be changed to the intermediate or the film diffusion.

From the view point of ion exchange kinetics, the low valent ions are preferable to be used in the chromatography. It is possible to reduce the actual valency of uranium ions by using appropriate complex ligands. In such case, however, the ion exchange selectivities for uranium ions decrease, because of the reduced valencies of ions, and the chromatography would not be realized with the low selectivities of ion exchange resins. The optimum conditions could be chosen considering all those factors above-mentioned in this paper.

6-2-5. CAPACITY OF PRODUCTION

In terms of the cascade theory the chromatographic process is regarded as the square cascade for the isotope separation. The design factors of an enrichment plant can be calculated by using the cascade theory, in principle. Here it is shown that a simple equation derived to determine the separation coefficient of chromatographic isotope separation processes can be used for the estimation of the separation power of the plant employing ion exchange chromatography.

$$P = \varepsilon qR_o(1 - R_o)VN\Phi/(R_p - R_o), \qquad (10)$$

where P = production capacity, ε = separation coefficient (= $\ln\alpha$),
q = isotope adsorption capacity per unit volume,
V = total volume of resin packed in the column,
Φ = ratio of uranium band length to total bed length for one cycle operation, N = cycle of operarion per unit time,e.g. year,
R_o = isotope abundance ratio of feed,
R_p = isotope abundance ratio of product

The capacity of the production for the uranium enrichment system is estimated by using this equation. The chromatographic operation conditions and resulting data are presented in Table III. The flow diagram of a uranium enrichment plant designed by Asahi Chemical Industry is shown in Fig. 8.

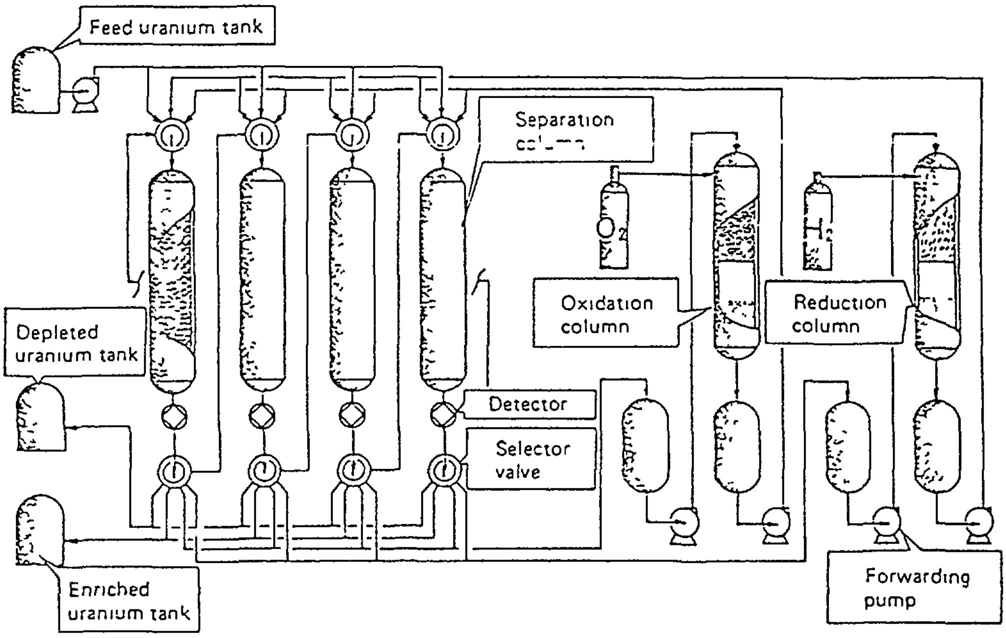


Fig. 8. Flow diagram of uranium enrichment plant. Ref. (13).

Experiments have been reported on U(IV) - U(VI) exchange systems using both cation and anion exchange chromatographies [11-18]. An example of the experimental work is shown in Fig.9 [24]. The experimental conditions of Fig. 9 may be far from the required conditions for industrial plants, however the results clearly shows the importance of the consideration given in this paper.

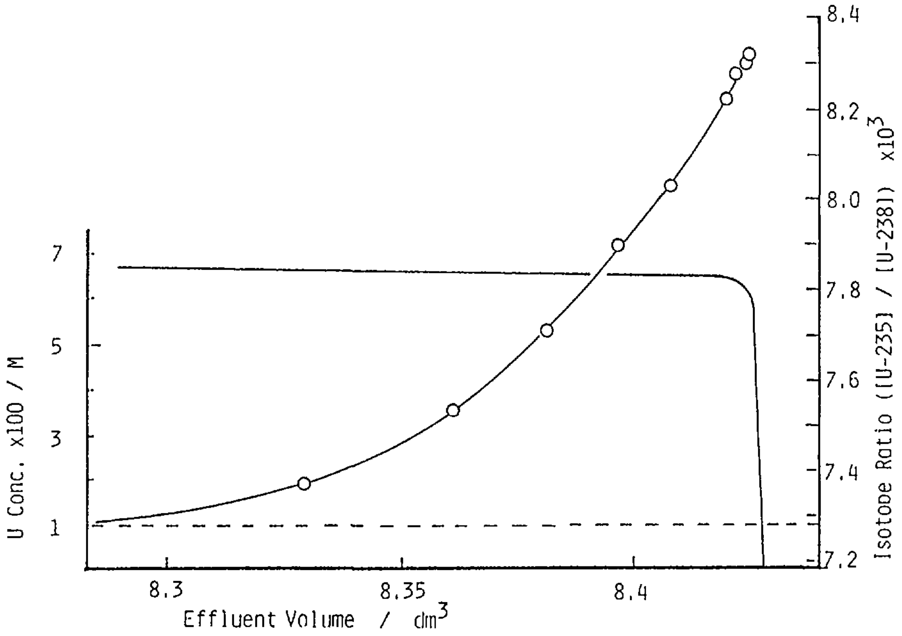


Fig. 9. Uranium isotope separation by using anion exchange resin Migration length 22 m, Experimental temperature 70 °C, Ref. (24).

6-3. SEPARATION OF ACTINIDE ELEMENTS

Since the actinide elements involve long-lived α-emitters, of which emission lasts over thousands years, the contamination with actinide elements raise serious problems in handling and storage of nuclear wastes. There have been continuing efforts to develop technical measures which ascertain the highly safe containments of the α-emitters in the waste during the long-term storage. The most direct and effective measure for this purpose is to decrease the level of the contamination of the actinide elements in the wastes, and this is accomplished by the implementation of separation and recovery of actinide elements from the wastes. So far the experiences in this subject field have been essentially in the laboratory work level. The potential meaning of the actinide separation, however, would be enormous to continue the expansion of the peaceful uses of nuclear energy. The followings are some basic experiments and laboratory experiences on the separation of actinide elements.

Group Separation. The lighter actinides of uranium, neptunium and plutonium are strongly adsorbed on strongly basic anion exchange resins from a concentrated HCl solution, whereas transplutonium elements show much smaller adsorbability at the concentrated HCl solutions. This tendency is essentially true in the system of the anion exchange resin and concentrated HNO_3 solutions.

In the work carried out at JAERI (Japan Atomic Energy Research Institute) [25] the irradiated fuel sample was solved in HCl solutions and adsorbed on the anion exchange resin Dowex 1X8. The groups of elements were eluted out from the resin by successively charging the different solutions in the operational mode as follows.

(i) At the first step fission products and heavier actinides Am and Cm were eluted by a 9M HCl - 0.1 M HNO_3 solution.

(ii) Zr was then eluted by a 9 M HCl - 0.1 M HNO_3 - 0.01 M HF solution.

(iii) Thirdly, Pu and Np was eluted by a 4 M HCl solution.

(iv) Finally U was eluted by a 0.1 M HCl solution.

Mutual Separation of Actinides. In the above-mentioned process Pu and Np coexist in the effluents of the third step. To separate Pu and Np these elements were loaded on the anion exchange resin, Dowex 1X8, then Pu was reduced from tetra-valent to tri-valent by adding NH_2OH. The Pu(III) in the resin was eluted by a 9 M HCl solition containing 0.1 M HI. The remaining Np was eluted by a low concentration HCl solution.

The mutual separation of transplutonium elements is achieved by cation exchange chromatography. By using this technique decigram quantities of transplutonium elements were separated at ORNL (Oak Ridge National Laboratory). In this work [26] cation exchange resin Dowex 50 W-X8 (28 - 70 m) was packed in stainless columns and converted to ammonium form by 0.3 M NH_4NO_3. The column system consisted of two columns: one short (14 mm I.D. and 0.2 m long, packed with 56 - 70 m resin) for loading, and the other long (13.4 mm I.D. and 1.2 m long packed with 28 - 56 m resin) for separation. The tri-valent actinides were loaded on the short column, and eluted with an eluent containing a complex forming reagent alpha-hydroxyisobutyrate (AHIB) 0.25 M, adjusted to pH 3.9. The effluent from the column was then charged to a longer column. The elution of the actinides adsorbed in the longer column was carried out by changing the pH values and the concentrations of AHIB in the eluents. Fermium, einsteinium and californium were eluted with the eluent 0.25 M AHIP pH 4.2, thereafter berkelium was eluted by 0.25 M AHIP pH 4.6, americium and curium were eluted by 0.5 M AHIB pH 4.8. The effluent of this separation was collected in fractions and subjected to alpha counting to detect the actinides.

The separated transplutonium elements by this process at ORNL were totally, 4.6 g of ^{252}Cf, 0.5 g of ^{249}Bk, 19 mg of ^{253}Es and 10 pg of ^{257}Fm (estimated). After the operation, the radiation damage to the ion exchange resin was found to be serious, especially, in the short loading column.

Plutonium Recovery. At the LASC (Los Alamos Scientific Laboratory) plutonium was recovered from plutonium-bearing residues created in the many research and development programmes [27]. The plutonium waste treatment at the facility comprises a number of process lines designed to recover and purify the plutonium in the residues. For example, the plutonium is removed from non-combustibles in pickling operation with an HNO_3 leach. The process rags are burned in an incinerator at a low temperature to produce an ash which is then dissolved in HNO_3-CaF_2. These HNO_3 solutions and various other types of processing solutions are transferred to an anion exchange system to remove plutonium. The flow of the waste treatment at the facility is illustrated in Fig. 10.

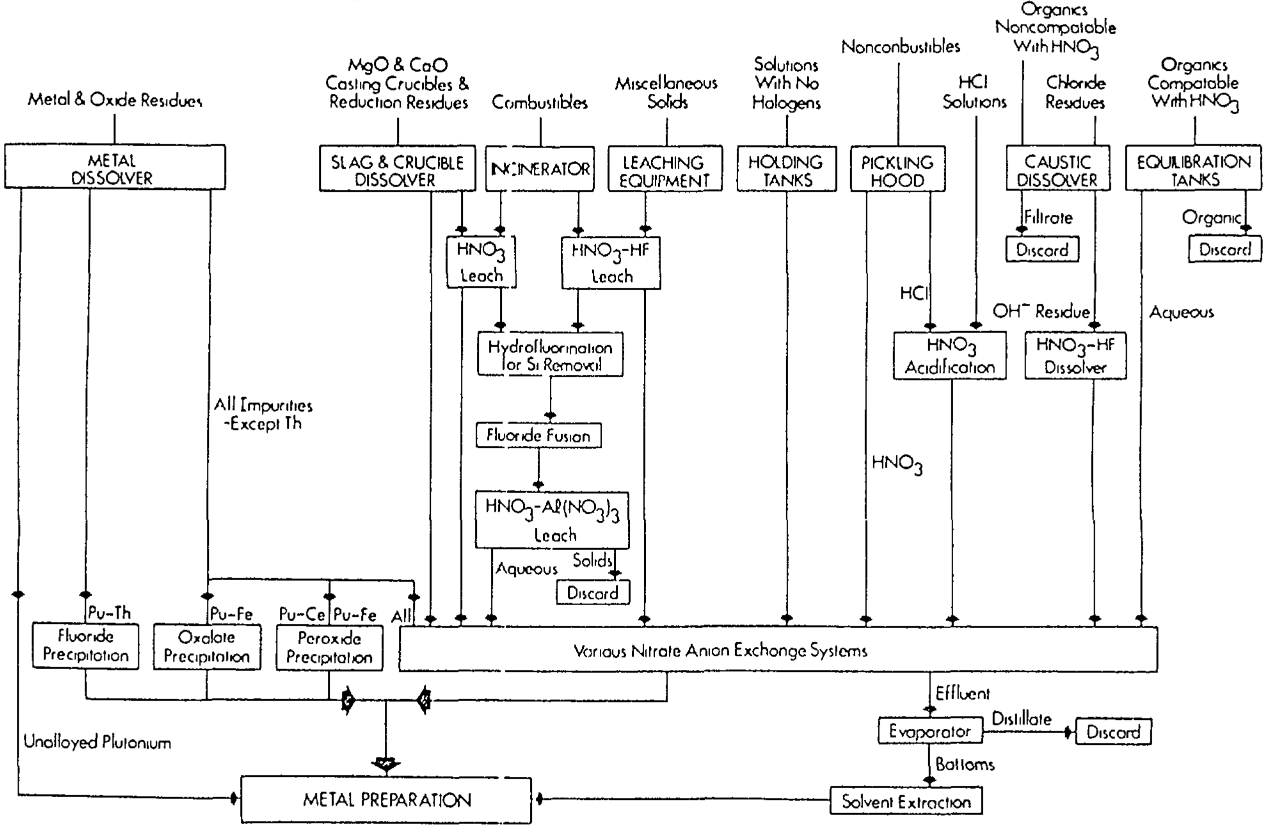


Fig. 10. Flow of material in the plutonium recovery plant in Los Alamos Scientific Laboratory. Re. 27.

In the anion exchange system, HNO_3 solutions containing Pu are charged into Dowex 1X4 resin columns. The adsorbed resin is washed with a 7 M HNO_3 solution, then conditioned with 1 M HNO_3. Thereafter plutonium is eluted with a 0.3 M HNO_3 solution containing the reducing agent NH_2OH. More detailed process conditions are presented in Fig. 11.

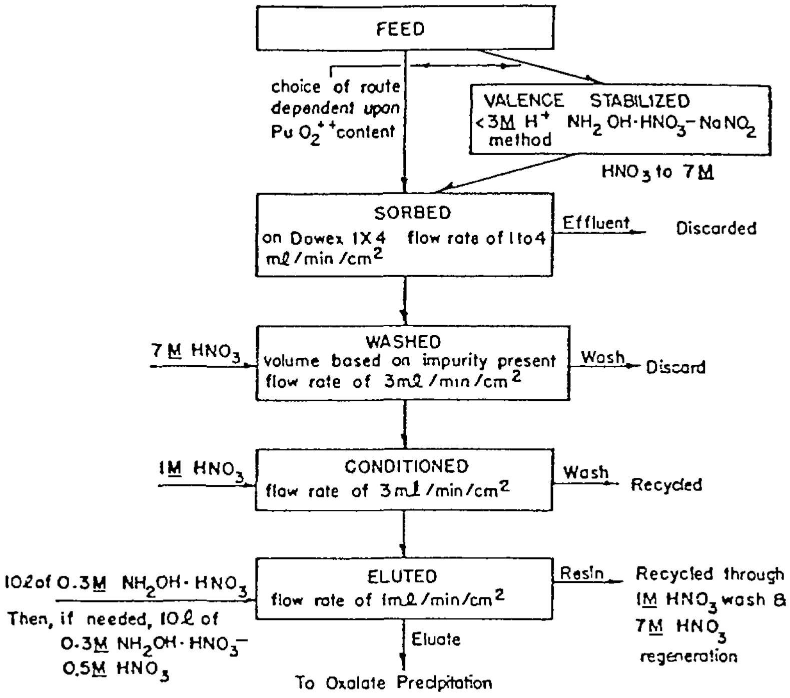


Fig. 11. The operation of the ion exchange system for plutonium recovery from waste stream.

6-4. RECOVERY OF URANIUM FROM PHOSPHORIC ACID SOLUTIONS

Uranium is found in phosphate rock (phosphorite) at the concentration ranging between 50 and 130 ppm U. Uranium reserves in phosphate rock in the world is estimated to amount to approximately 15 million tonnes [28]. The regional distribution of uranium reserves in phosphate rock is shown in Table IV. As is conceived, the large amount of uranium is carried in the products from the phosphate rock, mainely in the phosphoric acid ferilizer. The theoretical amounts of uranium contained in the pnosphoric acid products are presented in Table V.

Several plants have been constracted in the USA to produce uranium from phosphoric acid solutions. All of these plants are employing the solvent extraction process. In this case of uranium

TABLE IV. DISTRIBUTION OF URANIUM IN MARINE PHOSPATE DEPOSITS.

Area		Uranium/ million tonnes U
Africa		8.5
USA		3.0
Near East and Asia		1.6
Australia		0.8
Pacific Islands		0.015
	Total	15.0 (rounded)

Ref. 28 .

TABLE V. PHOSPHORIC ACID PRODUCTION CAPACITIES AND THEORETICAL URANIUM CONTENTS (1981).

Continent	tonnes P_2O_5/a	tonnes U
Western Europe	2,725,000	680
Eastern Europe	6,505,000	1,620
North America	9,197,000	2,290
Latain America	1,001,000	250
Africa	3,167,000	790
Near East	1,993,000	500
South East Asia	829,000	200
Total	25,417,000	6,330

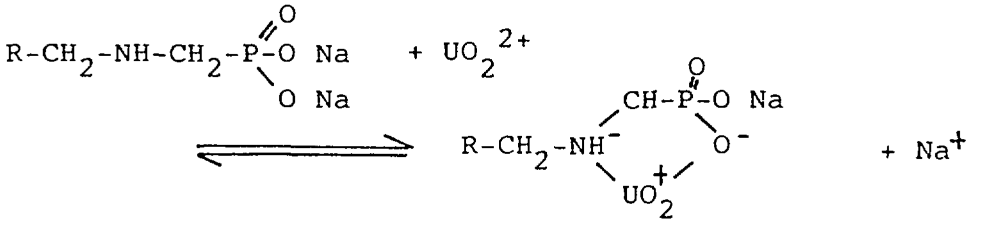
* For plants larger than 150,000 te P_2O_5 /a .

** Assuming 32.5 % P_2O_5 in the phosphate rock; 10 % wet-process losses; 0.009 % avarage grade of uranium in the rock.

Ref. 28 .

production ion exchange is a promissing alternative and the R and D work for this purpose has been conducted in various institutes.

S. Gonzalez-Luque and M. Streat [29] reported that the aminophosphonic group ion exchange resin Duolite ES 467 showed excellent adsorption of uranium from phosphoric acid in the concentration range 1 - 6 M. It was found in this work that impurities of Ca^{2+}, Fe^{3+} ions in the feed solutions did not seriously affect the adsorption of uranium on the resin from the phosporic acid feed solutions, while the presence of Fe^{2+} ions caused the reduced adsorption of the uranium. In phosporic acid solutions ferrous ions can reduce uranium (VI) to U(IV) which has less adsorbability toward the amino phosphonic type resin. The uranium adsorbed on the resin was eluted with 3 M H_3PO_4 containing 0.3 M Fe^{2+}, accordingly. An ammonium carbonate solution, also, was found as the excellent eluting agent, and the elution of the adsorbed uranium was carried out with 1 M $(NH_4)_2CO_3$. The adsorption of uranium



(11)

on the aminophosphric acid resin is expressed as Eq. 11

The research work on the uranium recovery from phosphoric acid has been conducted at Ben Gurion University [30]. In this work several special ion exchangers were developed. A synergistic mixture of two extractants, diethylhexyl phosphoric acid (DEHPA) and trioctylphosphine oxide (TOPO), was immobilized in a polymer matrix (stylene and methyl methacrylate, crosslinked by divinylbenzene); the crosslinkings of these resins are 15 % and 30 % DVB. It was found that the uranium capacity of the resin increases with increase in the contents of extractants DEHPA and TOPO in the resin. The column operation tests were carried out on the resins, which showed good performances in the preliminary tests, changing the coditions of solutions. The column operation of the best case in the experiments is as follows.

The resin containing the synergistic mixture of DEHPA and TOPO was packed in a column (bed height 125 cm, 2 cm I.D.). The column was fed with a 4.5 M technical grade phosphoric acid solution containing uranium at the concentration of 160 mg U/dm^3. The uranium adsorbed on the resin was eluted with 6 M phosphoric acid containing Fe^{2+} ($20 g/dm^3$). The average uranium concentration in the effluent was found as 17 g U/dm^3, and the capacity of uranium uptaken in the resin as 3.5 g U/ kg resin.

Phosphoric group is a well known ligand for uranyl ions. The phosphoric type ion exchange resins would be useful not only for the recovery of uranium from phosphoric acid solution but also for other types of uranium recovery from various solutions, such as mining waste water, mineral leaching solutions, liquid wastes in reprocessing facilities.

6-5. APPLICATION OF ION EXCHANGE MEMBRANE

The first successful application of the ion exchange membrane to the major process in the nuclear fuel cycle would be the electrolytic reduction of uranium in the uranium processing pilot plant at Ningyo-Toge. The Ningyo-Toge works comprises the test plants for the up-stream processes in the nuclear fuel cycle, specifically uranium mining, milling, leaching, refining, conversion and enrichment. The electrolytic reduction process,in which ion exchange membranes are used, is incorporated in the conversion stage to produce tetravalent uranium, U(IV), from refined uranium in the form of UO_2^{2+} ions. Thereafter U(IV) solutions are added with fluoride ions resuling in the precipitates of UF_4 [31]. This is a very efficient route to reach UF_4. By using ion exchange membrane as the barrier between the cathode and anode electrolytic compartments, the reduction of uranium was acieved: the reported data [31] are the reduction rate of 99.5 % and the average current efficiency of 82.3 %.

This technique was applied also to the decomposition of ammonium ion in the alpha-bearing liquid wastes discharged from the processes in the plutonium fuel facility [32]. The ammonium decomposition process consists of two steps: the electrolytic reduction of NH_4NO_3 to NH_4NO_2 and the thermal decomposition of NH_4NO_2 to N_2 and H_2O. By the implementation of the above-mentioned process, much effective volume reduction was achieved in the waste treatment of HNO_3 solutions by nutralizing with NH_4OH instead of conventional NaOH. The illustrates of the electrolyzer and the process flow are shown in Fig. 12 (a) and (b).

The cation exchange membrane used as the barrier in the electrolyzer plays a key role in this technology. The special cation exchange membrane of the fluorocarbon polymer type was developed for this purpose, and the membrane showed excellent durability and performance. The current efficiency of almost 80 % was achieved at the conditions of lower temperature than 40 °C and higher pH than 9 of the electrolyte solution in the cathode compartment.

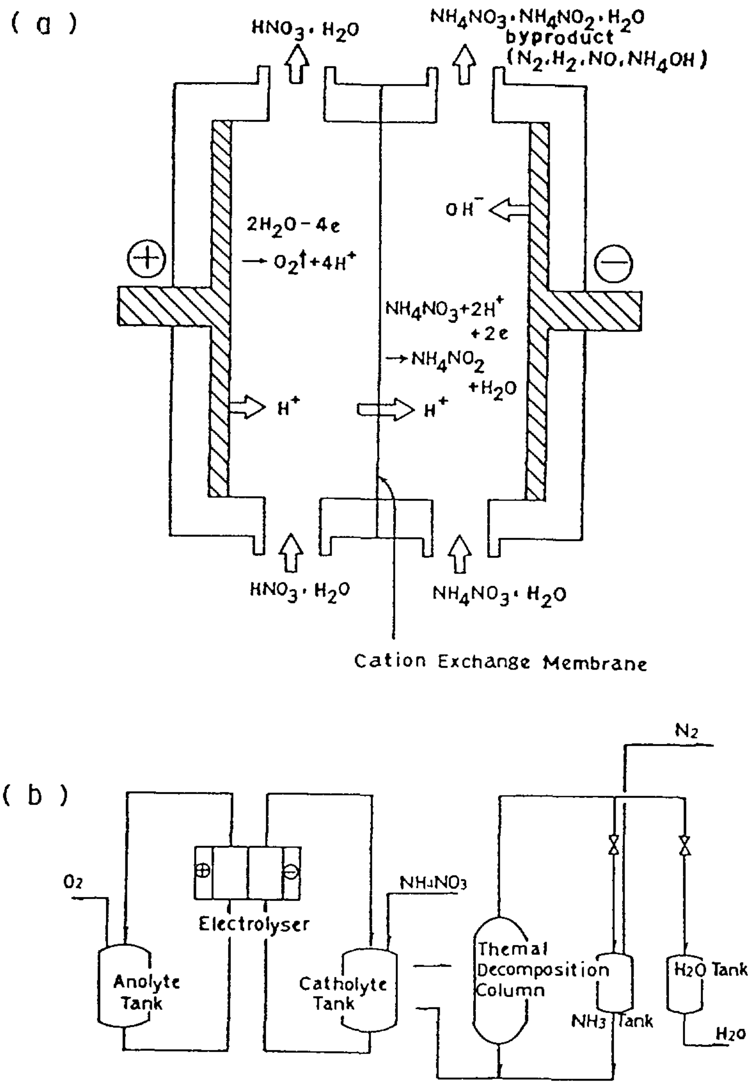


Fig. 12. Illustrates of ammonium decomposition process.
(a) Electrolyzer . (above)
(b) Process flow . (below)

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APPENDIX 1

GLOSSARY

(Drafted by J.D. Navratil and supplemented by A. Himsley and Y. Fujii)

Amine Type Resin: An anion exchange resin which involves amine as the fixed functional group.

Anion: A negatively charged ion.

Anion Exchange Resin: A synthetic ion exchanger which can adsorb and exchange anionic substances. Cationic functional groups are fixed in the resin.

Amphoteric Ion Exchange Resin: An ion exchange resin which has the properties of both acid and base. For example, the resin contains aminoacids (NH_2-R-COOH) as the fixed functional groups.

Adsorption: Adhesion of gaseous molecules or dissolving substances in liquids to the surface of solids. This term is used to specifically express the stoichiometric sorption of ionic species into ion exchangers in order to distinguish from the non-stoichiometric sorption of solvents.

Amine: A group of compounds derived from ammonia by substituting organic radicals for the hydrogens; primary amine is H_2NR, secondary HNR_2, tertiary NR_3, quarternary NR_4^+. The basicity increases in this sequence.

Attrition: The breakage and wear of resin particles.

Backwashing: Upward flow of solution through an ion-exchange resin bed to reduce compaction of the bed and cleanse it of foreign material.

Base Exchange: Exchange of cations between solution and a cation-exchange material.

Batch Operation: Method of using ion-exchange material in which the material and the solution are mixed in a vessel and, after equilibrium is attained, the liquid is decanted or filtered off.

Bed Depth: Depth of the ion-exchange material in a column.

Bed Expansion: Separation and rise of ion-exchange materials in a column during an upward fluidizing flow.

Bed Volume: The total volume of wet settled resin in an ion exchange column.

Breakthrough: The point where the concentration of the exchanging ion in the effluent begins to increase significantly.

Breakthrough Curve: The curve or isotherm which shows the effluent concentration of an operating ion exchanger with respect to the number of unit volumes (usually Bed Volumes) of liquid passed through the exchanger until the effluent concentration is 90% or more of the influent concentration.

Cation: A positively charged ion.

Cation Exchange Resin: A synthetic ion exchanger which can adsorb and exchange cationic substances. Anionic functional groups are fixed in the resin.

Carboxylic Acid Type Resin: A cation exchange resin of which fixed functional groups are carboxylic acid.

Channeling: Creation of isolated paths of less resistance in the ion-exchange material bed caused by the introduction of dirt, air pockets, and other factors which cause uneven pressure gradients in the bed. Channeling prevents the solution being processed from uniformly contacting the entire resin bed.

Chemical Stability: Ability of an ion-exchange material to resist changes in its properties when in contact with aggressive chemical solutions such as oxidizing agents or ionizing radiation.

Chelate Type Resin: Chelating reagents, capable of forming rings with metal ions by one or two coordinated bondings, are embeded in the ion exchange resin as the fixed functional groups.

Chromatography: A technique by which separation in a mixture is achieved by virtue of the differences in migration of the mixed components in a packed column or, more generally, in a separating medium.

Co-ion: Any ion, whether in the exchanger or in the solution being treated, which has the same sign as the exchanger framework.

Color Throw: The impartation of color from an ion-exchange material to a solution.

Column Operation: Most common method for employing ion exchange in which the solution to be treated passes through a bed of ion-exchange material.

Counter-ion: Any ion, whether in the exchanger or in the solution being treated, which has a charge sign opposite to that of the exchanger framework.

Crosslinkage: Binding of the linear polymer chains in the matrix of an ion-exchange material with a crosslinking agent which produces a three-dimensional, insoluble copolymer.

Decontaminaition Factor (DF): The ratio of the radioactivities in a solution prior to and following treatment.

Deionization: Removal of ionizable constituents from a solution by ion-exchange processing.

Distribution Coefficient: Referred to a counter ion, the distribution coefficient is the ratio of the concentrations of the counbter ion in the exchanger and in the solution.

Displacement: A chemical exchange in which one element, molecule or ionic species is replaced by another element, molecule or ionic species.

Divinylbenzene (DVB): Organic monomer containing two double bonds.

Effluent: The treated solution which emerges from an ion-exchange column.

Electrolyte: A substance which, when added to water, will provide a solution which will conduct electricity. Most inorganic acids, bases, and salts are electrolytes, whereas most organic compounds are not.

Eluant: The solution used to remove the sorbed ions from the resin.

Eluate: The concentrated solution of ions stripped from the resin by the eluant.

Elution: Stripping of sorbed ions from an ion-exchange material by passing through the material an eluant solution of such composition that it will change the distribution coefficient of the sorbed ion with respect to the ions in the eluant.

Elution Curve: The curve showing the concentration of the ion of interest in the eluate with respect to the number of bed volumes of eluant passed through the column until the concentration of the ion in the eluate is sufficiently low as to indicate the resin is almost completely stripped.

Exchange Capacity (Total): A constant which represents the number of inorganic groups per specific weight of exchanger when the material is completely converted to the H^+ or Cl^- form, as meq/g, or the number of inorganic groups in a specified volume of a fully water-swollen packed bed of exchanger usually when the material is completely converted to the H^+ or Cl^- form, in terms of meq/ml. The counter-ion content of an exchanger.

Exchanger: Ion exchange materials or resins which are insoluble acids or bases.

Exhaustion: The point in an ion-exchange cycle in which the ion exchanger can no longer remove the ions of interest from the solution being processed.

Fixed Bed Process: The solid phase (ion exchanger) is fixed in a separation column, forming a packed bed. Regeneration is made in a batchwise manner.

Fluidized Bed Process: The solid ion exchanger is handled, in many respects, like a fluid in an operational vessel under the up-stream of feed solution.

Freeboard: Space provided above the resin bed in the column to accommodate the expansion of the resin material during backwashing.

Head Loss: Loss in liquid pressure resulting from the passage of the solution through the bed of ion-exchange material.

Hydraulic Classification: Tendency of small resin particles to rise to the top of, and large resin particles to settle to the bottom of, the column during a backwash operation.

Hydrogen Cycle: Cation-exchange material operation in which the regenerated ionic form of the material is the hydrogen ion.

Influent: Solution entering an ion-exchange material bed.

Ion Exchange: A stoichiometric, reversible reaction in which mobile ions of a solid exchange with the mobile ions of a solution of an electrolyte when the solution contacts the solid.

Ion Exchange Zone: That space existing in a resin bed above which the resin is in equilibrium with the influent and below which it is in equilibrium with the eluant i.e. regenerated or unused. It is within this zone that the ion exchange is occurring.

Leakage: Appearance in the effluent from an ion-exchange column of ions which are desired to be removed from the liquid being processed.

Macroreticular Resins: Highly porous resins. (From "macro" meaning "large" and "reticular" meaning "netlike" or "sievelike".)

Mixed Bed: An ion exchange bed consisting of cation and anion exchange resins packed with 1:1 equivalent ratio.

Molecular Sieve: Materials with porous adsorbing properties which chemically lock molecules or ionic species into their pores.

Moving Bed Process: The ion exchange separation process in which the solution is continuously fed and the resin is continuously or semi-continuously recycled through the regeneration process.

Operating Capacity: Portion of the total exchange capacity of an ion-exchange material for the removal of a particular ion which is utilized in a practical ion-exchange operation. This is less than the total capacity due to the incompleteness of regeneration of the resin and competition of other ions in the influent.

Physical Stability: Ability of an ion-exchange material to resist breakage caused by physical manipulation or by volume changes.

Porosity: Term to describe that property of an ion-exchange material which allows solutes to diffuse in and out of the resin particle.

Regenerant: Solution used to convert an ion-exchange material to the desired ionic form for reuse.

Regeneration: Displacement from the ion-exchange material of the ions removed from the process solution or influent.

Regeneration Level: Amount of regenerant used per unit volume of resin.

Resin Fines: Extremely small particles of an ion-exchange material usually resulting from breakdown of resin in course of use. They increase the pressure loss through the bed and are therefore undesirable.

Rinse: Passage of water through the ion-exchange material to flush out excess regenerant.

R.I.P. Process: Resin in pulp process where large-mesh ion exchange resins loosely contained in stainless steel screen baskets move up and down in the mineral leaching liquor in order to avoid the preliminary filtration of finely grounded ore slurry.

Salt Splitting: Conversion of salts to their corresponding acids or bases by passage through strong-acid or strong-base ion-exchange materials.

Selectivity (Ion Exchange): The preference of an ion exchange resin for one species of counter ion over another.

Sorption: A general term which includes absorption, an engulfing, and adsorption, an interface or surface attraction. This term is frequently used to specify the non-stoichiometric uptaking of solutes (electrolytes or non-electrolytes) from the solution.

Sphericity: Unbroken spherical state of ion-exchange resin beads.

Void Volume: The space occupied by a settled volume of resin minus the actual volume of the resin particles. This is usually expressed as a percentage and for spheres of roughly the same size is generally around 0.35 to 0.4 or 35% to 40%.

Wet-settled Resin: The volume of resin in a column when immersed in the liquid to be treated (usually abbreviated to wsr).

APPENDIX 2

COMPILATION OF RESIN DATA

(Compiled by Y. Fujii)

Notes and abbreviations of the terms used in the tables.

Column		Term
Type of acid, base, or exchange	SA	strong acid
	WA	weak acid
	SB	strong base
	WB	weak base
	S/W	"strong" + "weak"
Functional group	$-NR_n$	alkyl amines, n = 4, 3, 2 and 1.
	$-NR_{3,2,1}$	the mixture of tertiary, secondary and primary amines.
	(I)	quarternary ammonium group type I, $-CH_2N(CH_3)_3$.
	(II)	quarternary ammonium group type II, $-CH_2N(CH_3)_2(C_2H_4OH)$.
Ion form	The charge signs "+" and "-" are omitted.	
	FB	free base form
Matrix & porosity	PS	polystyrene
	MAc	methacrylic polymer
	Ac	acrylic polymer
	EA	epoxy-amine polymer
	P	porous
	HP	high porous
	VHP	very high porous
	MP	macroporous (macroreticular resin)
Closslinking mat.	mat.	material
	DVB	divinylbenzene
Others	max.	maximum
	temp.	temperature
	var.	variable

Table 1. Cation Exchange Resins

Trade name	Type of acid	Functional group	Ion form	Exchange capacity		Matrix & porosity		Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
				dry (meq/g)	wet (meq/ml)								
Amberlite													
IR-116	SA	$-SO_3^-$	Na	4.5	0.3	PS	Gel	DVB 1*	90*	0.3-1.2	120	0-14	*approx. values
IR-118(H)	"	"	H	4.4	1.3	"	"	" 4.5*	60*	"	"	"	
IR-120PLUS	"	"	Na/H	4.4	1.9	"	"	" 8*	45*	"	"	"	
IR-122	"	"	Na	4.4	2.1	"	"	" 10*	40*	"	"	"	
IR-124	"	"	Na	4.4	2.2	"	"	" 12*	39*	"	"	"	
IR-130C	"	"	Na/H	4.4	1.9	"	"	-	46*	0.35-1.2	"	"	
200	"	"	Na	4.3	1.75	"	MP	DVB 20*	48*	0.3-1.2	"	"	
200C	"	"	Na/H	4.3	1.75	"	MP	DVB 20*	48*	0.35-1.2	"	"	
252	"	"	Na	4.4	1.75	"	MP	DVB 12*	49*	0.3-1.2	"	"	
IRC-50	WA	$-COO^-$	H	10.0	3.0	MAc	MP	DVB	48*	"	120	5-14	
DP-1	"	"	Na	8.1	2.5	MAc	MP	DVB	73*	"	"	"	
IRC-84	"	"	H	10.0	3.5	Ac	Gel	DVB	43*	"	"	4-14	
Diaion													
SK 1B	SA	$-SO_3^-$	Na	-	1.9	PS	Gel	DVB 8	43-50	0.3-1.2*	120	0-14	*effective size=0.4-0.6 mm
SK 102	"	"	"	-	0.6	"	"	" 2	72-82	"	"	"	
SK 104	"	"	"	-	1.2	"	"	" 4	57-67	"	"	"	
SK 106	"	"	"	-	1.6	"	"	" 6	47-57	"	"	"	
SK 110	"	"	"	-	2.0	"	"	" 10	35-45	"	"	"	
SK 112	"	"	"	-	2.1	"	"	" 12	32-42	"	"	"	
SK 116	"	"	"	-	2.1	"	"	" 16	27-37	"	"	"	
PK 208	SA	$-SO_3^-$	Na	-	1.2	PS	P	DVB 4	58-68	0.3-1.2*	120	0-14	*effective size=0.4-0.55 mm
PK 212	"	"	"	-	1.5	"	"	" 6	52-58	"	"	"	
PK 216	"	"	"	-	1.75	"	"	" 8	46-52	"	"	"	
PK 220	"	"	"	-	1.9	"	"	" 10	41-47	"	"	"	
PK 228	"	"	"	-	2.05	"	"	" 14	37-43	"	"	"	

Table 1 (cont.)

Trade name	Type of acid	Functional group	Ion form	Exchange capacity dry (meq/g)	wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
Diaion (continued)												
WK 10	WA	$-COO^-$	H	-	2.5	MAc, P	DVB	50-56	0.3-1.2	150	5-14	
WK 11	"	"	"	-	2.9	" "	"	45-52	"	"	"	
WK 20	"	"	"	-	3.5	Ac, HP	"	40-46	"	120	4-14	
Dowex												
HCR-S	SA	$-SO_3^-$	Na H	-	2.0* 1.8*	PS, Gel	DVB 8	44-48 50-56	0.3-1.2	150	0-14	*mimimum
HCR-W2	"	"	Na H	-	2.0* 1.8*	" "	"	44-48 50-55	0.4-1.2	"	"	
HGR	"	"	Na H	-	2.2* 2.0*	" "	DVB 10	42-46 46-51	0.3-1.2	"	"	
HGR-W2	"	"	Na H	-	2.2* 2.0*	" "	"	38-43 46-49	0.4-1.2	"	"	
MSC-1	"	"	Na H	-	1.7* 1.6*	PS, MP	DVB	44-50 50-56	"	"	"	
CCR-2	WA	$-COO^-$	H		3.8*	Ac, Gel	DVB	48-54	0.3-1.2	120	5-14	
MWC-1	"	"	"	-	4.0*	Ac, MP	"	44-50	"	"	4-14	
Duolite												
C-20	SA	$-SO_3^-$	Na	4.6	2.0	PS, Gel	DVB 8	45-50	0.3-1.2	120	0-14	
C-225	"	"	"	"	"	" "	"	"	0.4-1.3	"	"	=Zeolit225
C-204F	"	"	"	4.6	1.5	" "	DVB 2-8	50-65	var.	90	"	
C-206A	"	"	"	4.6	1.6	" "	DVB 6	55-61	0.4-1.2	100	"	
C-255	"	"	"	4.5	2.0	" "	DVB 10	40-45	0.4-1.3	140	"	=Zeolit525
C-26	"	"	"	4.5	1.85	PS, MP	DVB 12	47-52	0.3-1.2	"	"	
C-264	"	"	"	4.6	2.3	" "	DVB high	38-43	0.4-1.2	"	"	
C-265	"	"	"	4.3	2.0	" "	"	35-40	"	"	"	

Table 1 (cont.)

Trade name	Type of acid	Functional group	Ion form	Exchange capacity		Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating		Remarks
				dry (meq/g)	wet (meq/ml)					max.temp., (°C)	pH range	
Duolite (continued)												
C 433	WA	$-COO^-$	H	9.5	4.2	Ac, Gel		43-47	0.3-1.1	120	5-10	
C 436	"	"	"	9.0	3.7	" "		50-55	0.3-1.2	100	"	
C 464	"	"	"	8.8	2.7	Ac, MP		52-58	0.3-1.1	120	5-14	
ES-468	"	"	"	9.0	1.9	" "		62-67	"	"	"	
Imac												
C 12	SA	$-SO_3^-$	Na	4.8	2.0	PS, Gel	DVB 8	48	0.3-1.2*	120	0-14	*90 %
C 12A	"	"	"	4.8	1.9	" "	"	50	"	"	"	
C 8P	"	"	"	4.5	1.8	PS, MP	DVB 12	55	"	"	"	
C 16P	"	"	"	4.3	2.1	" "	DVB 16	48	"	"	"	
25	WA	-COO	H	9.	3.5	Ac, Gel		50	"	"	"	
TMR	S/W	$-SO_3^-$, $-S^-$	H		1.3	PS, MP	DVB	55	"	60	0-14	
GT 73	WA	weak acid	H		1.4	PS, MP	DVB	53	"	55	0-14	
Ionac												
C-240	SA	$-SO_3^-$	Na	4.6	1.9	PS, Gel	DVB 8	45-48	0.4-1.2	140	0-14	
C-242	"	"	H	"	"	" "	"	"	0.3-1.2	120	"	
C-249	"	"	Na	"	"	" "	"	"	0.5-1.2	140	"	
C-253	"	"	"	"	"	" "	"	"	0.6-1.2	"	"	
C-250	"	"	"	5.0	2.1	" "	DVB 10	38-43	0.3-1.2	"	"	
C-255	"	"	"	"	"	" "	"	35-38	"	"	"	
C-257	"	"	H	4.6	1.9	" "	DVB 8	45-48	0.6-1.2	120	"	
C-258	"	"	Na	5.0	2.1	" "	"	38-43	0.4-1.2	140	"	
C-267	"	"	H	4.9	1.9	" "	"	49-55	0.35-1.2	120	"	
C-298C-H	"	"	"	4.9	2.1	" "	"	52-58	0.4-1.2	"	"	
CF	"	"	Na	5.5	2.3	" "	"	43-49	0.3-1.2	140	"	

Table 1 (cont.)

Trade name	Type of acid	Functional group	Ion form	Exchange capacity dry (meq/g)	Exchange capacity wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
Ionac (continued)												
CF S	SA	$-SO_3^-$	H	5.0	2.2	PS, MP	DVB	45-50	0.3-1.2	120	0-14	
CF Z	"	"	"	5.1	2.4	" "	"	40-42	"	"	"	
CFP-110	"	"	"	5.0	2.2	" "	"	40-46	"	"	"	
CC	WA	$-COO^-$	H	9.5	3.5-3.7	Ac, MP	DVB	46-53	"	"	"	
CNN	"	"	"	10.0	3.9-4.1	" "	"	51-56	"	"	"	

Table 2. Anion Exchange Resins

Trade name	Type of base	Functional group	Ion form	Exchange capacity		Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
				dry (meq/g)	wet (meq/ml)							
Amberlite												
IRA-400	SB	NR_4,(I)	Cl/OH	3.7	1.4	PS, Gel	DVB	45*	0.3-1.2	60^{OH}, 80^{Cl}	0-14	*approx. values
IRA-400C	"	"	Cl	"	"	" "	"	47*	0.35-1.2	" "	"	
IRA-401S	"	"	"	3.2	0.8	" "	"	62*	"	" "	"	
IRA-402	"	"	"	4.2	1.2	" "	"	54*	0.3-1.2	" "	"	
IRA-410	"	NR_4,(II)	"	3.4	1.3	" "	"	42*	0.3-0.8	" "	"	
IRA-420C	"	NR_4,(I)	"		1.2	" "	"	54*	0.42-1.2	" "	"	
IRA-430	"	"	"	3.9	1.1	" "	"	50*	0.84-1.41	" "	"	
IRA-458	"	"	"	4.4	1.2	Ac, Gel	"	60*	0.3-1.2	38 80	"	
IRA-93	WB	NR_3	FB	4.6	1.2	PS, MP	"	58*	"	100	0-9	
IRA-94	"	"	"	"	"	" "	"	60*	"	"	"	
IRA-99	"	"	"	4.7	1.2	" "	"	58*	" / o.5-1.2	"	"	
IRA-45	"	$NR_{3,2,1}$	"	5.2	1.9	PS, Gel	DVB	43*	0.3-0.84	100	0-7	
IRA-68	"	NR_3	"	5.6	1.6	Ac, Gel	"	60*	0.3-1.2	60	"	
IRA-900	SB	NR_4,(I)	Cl	4.2	1.0	PS, MP	DVB	60*	"	60^{OH} 80^{Cl}	0-14	
IRA-900C	"	"	Cl/OH	"	"	" "	"	63*	0.35-1.2	" "	"	
IRA-904	"	"	Cl	2.6	0.7	" "	"	57*	0.3-1.2	" "	"	
IRA-910	"	NR_4,(II)	"	3.7	1.0	" "	"	55*	"	" "	"	
IRA-938	"	NR_4,(I)	Cl/OH	3.7	0.5	" "	"	73*	0.3-0.84	" "	"	
IRA-958	"	"	Cl	4.1	0.8	Ac, MP	DVB	69*	0.3-1.2	" "	"	

Table 2 (cont.)

Trade name	Type of base	Functional group	Ion form	Exchange capacity dry (meq/g)	Exchange capacity wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C) OH	Operating max.temp. (°C) Cl	pH range	Remarks
Diaion													
SA10A	SB	NR_4,(I)	Cl		1.3	PS, Gel	DVB	43-47	0.3-1.2	60	80	0-14	
SA11A	"	"	"		0.85	" "	"	55-65	"	"	"	"	
SA20A	"	NR_4,(II)	"		1.3	" "	"	39-44	"	40	60	"	
SA21A	"	"	"		0.8	" "	"	55-65	"	"	"	"	
PA306	SB	NR_4,(I)	Cl		0.8	PS, P	DVB 3	66-76	0.3-1.2	60	80	0-14	
PA308	"	"	"		1.0	" "	DVB 4	57-67	"	"	"	"	
PA312	"	"	"		1.2	" "	DVB 6	49-55	"	"	"	"	
PA316	"	"	"		1.3	" "	DVB 8	44-50	"	"	"	"	
PA318	"	"	"		1.3	" "	DVB 9	42-48	"	"	"	"	
PA406	"	NR_4,(II)	"		0.7	" "	DVB 3	61-71	"	40	60	"	
PA408	"	"	"		0.9	" "	DVB 4	54-64	"	"	"	"	
PA412	"	"	"		1.1	" "	DVB 6	46-52	"	"	"	"	
PA416	"	"	"		1.3	" "	DVB 8	40-46	"	"	"	"	
PA418	"	"	"		1.3	" "	DVB 9	38-44	"	"	"	"	
WA10	WB	$NR_{3,2}$	FB		1.2	Ac, Gel	DVB	50-56	"	60		0-9	
WA11	"	"	"		1.4	" "	"	45-52	"	"		"	
WA20	"	NR_2	"		2.5	PS, P	"	40-46	"	100		"	
WA21	"	"	"		2.0	PS, HP	"	63-69	"	"		"	
WA30	"	NR_3	"		1.5	" "	"	57-63	"	"		"	

Table 2 (cont.)

Trade name	Type of base	Functional group	Ion form	Exchange capacity dry (meq/g)	Exchange capacity wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
Dowex (continued)												
SBR	SB	NR_4,(I)	Cl		1.4	PS, Gel	DVB	43-48	0.3-1.2	50 ,100	0-14	
"	"	"	"		"	" "	"	"	0.35-0.8	" "	"	
"	"	"	OH		1.1	" "	"	max60	"	" "	"	
"	"	"	"		"	" "	"	55-65	0.3-1.2	" "	"	
SBR-P	"	"	Cl		1.2	PS, P	"	53-60	0.3-1.2	" "	"	
"	"	"	"		"	" "	"	50-67	0.35-0.8	" "	"	
"	"	"	OH		1.0	" "	"	60-70	"	" "	"	
11	"	"	Cl		1.1	" "	"	55-60	0.3-1.2	" "	"	
MSA-1	"	"	"		1.0	PS, MP	"	56-64	"	" "	"	
"	"	"	"		"	" "	"	"	0.35-0.8	" "	"	
21K	"	"	"		1.2	PS, P	"	50-58	0.8-1.2	" "	"	
												Particle size 0.6-1.2, and 0.4-0.8 are available.
XFS-43116	"	"	"		1.4	PS, Gel	"	43-48	0.4-0.8	" "	"	
SAR	"	NR_4,(II)	"		1.4	" "	"	38-45	0.3-1.2	35 77	"	
MSA-2	"	"	"		1.0	PS, MP	"	53-60	0.3-1.2	" "	"	
MWA-1	WB	NR_3	FB	4.5	1.2	" "	"	50-60	0.3-1.3	100	0-9	
WGR	"	NR_3	"	5.0	1.5	EA -	-	50	0.4-1.2	93	"	
WGR-2	MB	"	"	"	"	" -	-	"	"	"	"	

Table 2 (cont.)

Trade name	Type of base	Functional group	Ion form	Exchange capacity dry (meq/g)	wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)		pH range	Remarks
										OH	Cl		
Duolite													
A 101	SB	NR_4,(I)	Cl	3.7	1.3	PS, HP	DVB	50-55	0.3-1.2	60	,100	0-14	
A 102	"	NR_4,(II)	"	3.5	1.3	" "	"	45-50	"	35	, 75	"	
A 109	"	NR_4,(I)	"	3.5	1.4	PS, Gel	"	43-48	0.4-1.1	60	,100	"	
A 113	"	"	"	3.6	1.3	" "	"	48-55	0.3-1.1	"	"	"	
A 116	"	NR_4,(II)	"	2.2	1.4	" "	"	45-50	0.3-1.2	35	75	"	
A 161	"	NR_4,(I)	"	3.8	1.1	PS, MP	"	51-56	"	60	100	"	
A 162	"	NR_4,(II)	"	3.3	1.1	" "	"	48-53	"	35	75	"	
A 132	"	NR_4	"	4.0	1.25	Ac, Gel	"	51-57	0.3-1.1	35	70	"	
ES 137	"	NR_4,(I)	"	3.2	1.4	PS, Gel	"	40-50	var.	60	100	"	
A 30 B	WB	NR_3	FB	6.0	1.9	EA, Gel	-	58-63	0.3-1.2	25	40	0-9	
A 303	"	NR_3	"	4.0	1.3	PS, MP	-	45-55	0.3-1.0	60	100	0-7	
A 368	"	"	"	4.0	1.7	" "	-	45-52	0.3-1.1	"	"	"	
A 378	"	"	"	4.1	1.3	" "	-	52-58	"	"	"	"	= A368PR
A 369	"	"	"	4.1	1.1	" "	-	56-62	"	"	"	"	
A 374	"	PFA*	"	7.3	2.3	Ac, Gel	-	47-51	"	35	70	"	*polyfunct-
A 375	"	NR_3	"	4.7	1.6	" "	-	52-60	"	"	"	0-9	ional amine
A 561	"	NR_3	"	7.5	1.7	Ph, MP	-	50-55	0.3-1.2	50		0-6	
A 7	"	NR_2	"	9.0	2.0	Ph, VHP	-	53-60	"	40		"	
Imac-Asmit													
256 P	SB	NR_4,(I)	Cl	-	-	PS, MP	DVB	63	0.5-1.2		90	0-14	
Imac													
S 540	SB	NR_4,(I)	Cl	3.8	1.2	PS, P	DVB	53	0.3-1.2	60	100	0-14	
S 550	"	"	"	3.8	1.1	PS, MP	"	55	"	"	"	"	
S 542	"	NR_4,(II)	"	3.5	1.3	PS, P	"	48	"	35	75	"	

Table 2 (cont.)

Trade name	Type of base	Functional group	Ion form	Exchange capacity dry (meq/g)	wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)		pH range	Remarks
Imac (continued)											OH	Cl	
A 20 S	WB	NR_3	FB	4.1	1.4	PS, MP	DVB	57	0.3-1.2	60	100	0-7	
A 20 SU	"	"	"	4.1	1.1	" "	"	60	"	70	"	"	
A 20 R	"	"	"	4.1	1.7	" "	"	55	"	"	"	"	
A 24	"	"	"	4.0	1.7	" "	"	57	"	80	"	"	
A 24 F	"	"	"	"	"	" "	"	46	"	60	"	"	
A 327	"	$NR_{3,4}$	"	6	1.9	PA*, Gel	-	60	"	30	-	"	*Polyamide
Ionac													
A-540	SB	NR_4,(I)	Cl	3.6	1.0	PS, Gel	Ac	48-60	0.4-1.2	60		0-14	
A-550	"	NR_4,(II)	"	3-3.3	1.3	PS, Gel	Ac	43-47	"	40	100	"	
A-641	"	NR_4,(I)	"	3.9	1.15	PS, MP*	DVB	54-58	0.3-1.2	70	"	"	*Second generation type.
A-642	"	"	"	3.9	1.1	" "	"	57-62	0.4-1.2	"	"	"	
A-651	"	NR_4,(II)	"	3.5	1.15	" "	"	49-52	0.3-1.2	60	"	"	
ASB-1	"	NR_4,(I)	"	3.7	1.4	PS, Gel	"	43-49	"	"	"	"	=A-430
ASB-1P	"	"	"	4.3	1.3-1.4	" "	"	51-57	"	"	"	"	=A-440
ASB-1PC-OH	"	"	"	4.3	1.35	" "	"	50-55	"	"	"	"	
ASB-2	"	NR_4,(II)	"	3.5-3.7	1.5-1.6	" "	"	38-42	"	40	77	"	=A-450
A-305	WB	$NR_{2,1}$	FB	12.0	3.5	EA, MP	-	59-67	0.4-2.0	40		"	
A-328	"	NR_3	"	4.5	1.85	PS, MP*	DVB	46-52	0.3-1.2	100		"	
AFP-329	"	"	"	4.0	1.5	" "	"	44-52	"	60		"	=AFP-329K
A-365	"	$NR_{2,1}$	"	9.5	3.8	Ac, Gel	DVB	54-59	"	"		"	

Table 3. Nuclear Grade Ion Exchange resins

Trade name	Type of exchange,	Functional group	Ion form	Exchange capacity dry (meq/g)	Exchange capacity wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
Amberlite												
IRN-77	Cation,	SA, SO_3^-	H		1.75	PS, Gel	DVB	55	0.3-1.2	120	0-14	
IRN-163			Li									
IRN-169			NH_4									
IRN-218			Li-7									
IRA-78	Anion,	SB, (I)	OH		1.2	PS, Gel	DVB	60	0.3-1.2	60	0-14	
Bio Rex												
50W-x8	Cation,	SA, SO_3^-	H			PS, Gel	DVB 8		20-50 mesh			
			NH_4									
			Li									
			Li-7									
RG 1-x8	Anion,	SB, (I)	OH						20-50 mesh			
RG 2-x8	"	(II)	"						"			
Diaion												
SKN 1	Cation,	SA, SO_3^-	H	4.7		PS, Gel	DVB 8		0.4-1.2			
SKN 3			Li-7	4.6								
SAN 1	Anion,	SB,(I)	OH	3.7		PS, Gel	DVB 8		0.4-1.2			
Dowex												
HCR-S	Cation,	SA, SO_3^-	Li		1.8	PS, Gel	DVB 8	55max	0.3-1.2	150	0-14	H form is in Table 1
			NH_4		2.0			42-46				

Table 3 (cont.)

Trade name	Type of exchange	Functional group	Ion form	Exchange capacity dry (meq/g)	Exchange capacity wet (meq/ml)	Matrix & porosity	Cross-linking mat.(%)	Moisture (%)	Particle size (mm)	Operating max.temp. (°C)	pH range	Remarks
Duolite												
ARC 9351	Cation,	SA, $-SO_3^-$	H	4.9	1.8	PS, Gel	DVB 8		0.3-1.2	120		Parent =
ARC 9353	"	" "	Li-7	4.8	1.75	" "	"		"	"		Duolite C20
ARC 9359	"	",$-CH_2SO_3^-$	H	3.0	1.1	Ph,			0.4-1.2	60		= C 3
ARC 9359Na			Na	2.8	1.1							"
ARC 9360	"	" "	Li-7	2.9	1.1	Ph						"
ARA 9366	Anion,	SB, NR_4(I)	OH	4.0	1.0	PS, Gel			0.3-1.0	60^{OH}		= A 101
ARA 9366B	"	"	"	"	"	" "			0.3-1.2	" 100^{borate}		"
ARA 9371	"	MB, NR_3	FB	6.0	1.8	polyalkylamine			"	50		= A 30B
Ionac												
NC-10	Cation,	SA, SO_3^-	H		1.9	PS, Gel	DVB	$\leq$ 55	0.4-1.2	120	0-14	
NC 11	"		"		2.0	" "	"	"	"	130	"	
NA-30	Anion,	SB, (I)	OH		1.0	PS, Gel	Ac	$\leq$ 60	0.4-1.2	60	0-14	
NA-38	"	" "	"		1.4	" "	DVB	"	"	"	"	

Table 4. Mixed Bed Ion Exchange Resins

Trade name	Mixed resins Cation / Anion	Mixing ratio(C:A)	Functional group	Ion form	Capacity (meq/ml)	Moisture (%)	Particle size(mm)	Operating max.temp.(°C)	Remarks
Amberlite									
IRN-217	IRN-218/IRA-78			Li-7/OH	0.55	60	0.3-1.2		nuclear grade
IRN-150	IRN-77 /IRA-78			H/OH	"	"	"		"
IRN-154	IRN-163/IRA-78			Li/OH	"	"	"		"
IRN-170	IRN-169/IRA-78			NH_4/OH	"	"	"		"
IRN-277	AMB.200/IRA-938			H/ OH	0.25	"	"		"
IRN-300	IRN-77 /IRA-60			H/ OH	0.86	50	"		"
MB-1	IR-120/IRA-400	1:1.5			0.55	55		60	
MB-3	IR-120/IRA-410	1:1.5			0.55	55		40	
Bio-Rex									
RG 501-X8	RG 50W-X8/RG 1-X8	1:1		H/OH			20-50mesh		nuclear grade
	Other available ionic forms are Li/OH, Li-7/OH, NH_4/OH .								
RG 502-X8	RG 50W-X8/RG 2-X8	1:1		H/OH			20-50mesh		nuclear grade
Diaion									
SMN 1	SNK 1/SAN 1	1:1		H/OH			0.4-1.2		nuclear grade
SMN 3	SNK 3/SAN 1	1:1		Li-7/OH			"		"
Duolite									
ARM 9381	C 20/A 101			H/OH			0.3-1.2	60	Nuclear grade
ARM 9381D	C 225/A 113			H/OH			"	"	"
ARM 9381S	C 3/A 101			H/OH			"	"	"
ARM 9383	C 20/A 101			Li/OH			"	"	"
ARM 9386	C 20/A 101			Li-7/OH			"	"	"
ARM 9386S	C 3/A 101			Li-7/OH			"	"	"
ARM 9386T	C 20/A 101			Li-7/OH			"	"	"
ARM 9390	C 20/A 30B			H/OH			"	50	"
Ionac									
NM-40			$-SO_3^-$, NR_4(I)	H/OH	1.9^C, 1.0^A	60	0.4-1.2	60	Ultrapure grade
NM 49			" "	H/OH	2.1 , 1.0	"	"	"	"
NM-60			" "	H/OH	1.9 , 1.4	"	"	"	Nuclear applic.
NM-65			" "	H/OH	1.9 , 1.4	"	"	"	"
NM-75			" "	H/OH	1.9 , 1.4	"	"	"	"

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