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**Evaluation of New Macroporous Resins
for the Removal of Uranium and
Plutonium from Waste Streams**

John W. Koenst and William R. Herald

December 20, 1976

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MOUND LABORATORY

Miamisburg, Ohio

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Abstract

Organic ion exchange resins were evaluated for $^{238}\text{Pu}(\text{IV})$, $^{238}\text{Pu}(\text{VI})$, and $^{233}\text{U}(\text{VI})$ removal from water. The capacity of the resins and equilibrium coefficients (K_d) were compared with each other and to bone char - an inorganic adsorbent consisting of hydroxyapatite (HAP) for which data is available. Bone char gave the best results for the removal of $^{238}\text{Pu}(\text{IV})$, Amberlite XE279 (one of the new macroporous resins) gave the best results for $^{238}\text{Pu}(\text{VI})$, and another macroporous resin, Dowex-MSA-1, gave good results for $^{233}\text{U}(\text{VI})$. K_d values were shown to be a function of pH.

Introduction

Mound Laboratory is evaluating macroporous ion exchange resins for the removal of plutonium, uranium, and various colloids from process waste treatment effluents. These ion exchange resins, in use for some time, were recently improved giving greater resistance to particulate, iron, and organic/oil fouling. Resin bed capacities and equilibrium constants for specific isotope removal and interaction of various radioactive nuclides with other chemical species and the resultant effect on ion exchange resin performance are unknown. Only the performance of these resin beds based on a composite waste stream has been measured.

Ion Exchange - Status of Technology

Ion exchange is a process involving the mass transfer of ions between a polar solvent and an inert liquid or solid matrix containing highly polar groups which can be ionized. Generally, there is exchange of equivalent amounts of ions between the solution and the solid exchanger. A large number of natural and synthetic materials have ion exchange properties, but the important commercial exchangers are the zeolites and polymeric resins.

Shortly after World War II, new types of resins were produced which greatly expanded the scope of ion exchange applications. These new materials were produced by suspension polymerization of styrene and divinylbenzene or acrylic monomers and divinylbenzene followed by

formation of functional groups by secondary chemical reaction. Four types of functional groups are employed in these systems: strongly acidic sulfonic; strongly basic quaternary ammonium; weakly acidic carboxylic; and weakly basic primary-secondary amino.

Ion exchange has been used in processing radioactive solutions in many ways, including ore processing, isotope separations, decontamination, and waste treatment. Many different wastes have been treated including reactor coolants, condensates, steam generator blowdown, etc. The processes used generally include the conventional fixed bed gel resin, either in separate cation and anion beds or in mixed beds.

Conventional ion exchange resins require pretreatment of waste streams which contain suspended solids and colloids, the most common pretreatment being the addition of a coagulant followed by sedimentation and filtration. An alternative procedure is to remove organics, particulates, and radioactive colloids by a small adsorbent resin column and then use a conventional demineralizer to remove the remaining dissolved solids. However, there is little information about this procedure.

Wastes with very low ionic concentrations, such as condensates, can be economically treated with ion exchange resins and the resins discarded as solid waste.

Recently, macroporous ion exchange resins have been developed which have been successfully used to demineralize raw waters with appreciable organic content. The porosity allows the organics to be absorbed in the resin matrix without blocking the diffusive exchange of ions. For water that is heavily contaminated with organics, special adsorbent resins have been developed which are used as a pretreatment to conventional ion exchangers. These types of resins would also adsorb colloidal metal oxides.

The main advantages of these new resins are their high porosity, resistance to organic and iron fouling, ability to operate in highly oxidative environments, ability to operate in polar organic solvents, and their ability to remove colloids and organically complexed species. In contrast, presently used gel resins foul readily, need a higher level of

pretreatment, and result in high pressure drops within operating columns.

Because these macroporous resins are newly developed, basic design parameters, such as capacity, equilibrium constants, loading rates, etc., need to be obtained for such radionuclides as plutonium and uranium.

Experimental Procedure

Table 1 lists the resins that were used in this study. Samples of the resins were weighed wet and corrected for moisture content. These samples were then added to flasks containing 50 or 100 ml of solution buffered with ammonium or acetate salts to keep the pH between 4 and 10. Flasks were shaken for 72 hr using a mechanical shaker. Samples were then taken from the flasks containing the various concentrations of resins and counted using an alpha disintegration counter.

The solutions contained 20,000 to 50,000 dis/min/ml of alpha activity (plutonium-238 or uranium-233) initially, however, some of the activity adsorbed onto the glass. The amount of activity adsorbed onto the glass was ascertained by running a blank sample flask. The initial concentration was determined from the blank flask, thereby automatically correcting for adsorption onto the glass surface. Adsorption onto the glass was affected by pH, as can be seen from the results in Tables 2 and 3. In all cases, the initial amount of activity was the same, and any change in concentration was due to adsorption on the glass surface. This effect, at times, is quite large. The pH values reported were initial values. The pH's changed because the buffering salts were adsorbed by the various resins, depending on the strength of the resin, and the various ions removed by the resin were exchanged for OH⁻ or H⁺, depending on the resin type.

Results

Organic ion exchange resins were evaluated for the removal of ²³⁸Pu(IV), ²³⁸Pu(VI), and ²³³U(VI) from water. The capacity and equilibrium distribution coefficients (KD) (see Tables 2 and 3) were compared with each other and to bone char, an inorganic adsorbent consisting of hydroxyapatite (HAP). It was apparent that pH values could not be maintained due

to adsorption of the buffering agent and exchange for H⁺ and OH⁻. In the removal of polymeric plutonium, ²³⁸Pu(IV), considerable adsorption onto the glass surface occurred at pH 10 (initial value), no noticeable effect was apparent at pH 7, while at pH 4 a precipitate formed. With the uranium, considerable adsorption onto the glass occurred at pH 10, while at pH 4 and 7 no effect was noticed. Only a slight effect was noticed with ²³⁸Pu(VI).

The equilibrium distribution coefficient is defined as

$$K_d = \frac{\text{dis/min/gm}}{\text{dis/min/ml}} = \frac{\Delta c/g}{c}$$

where Δc = (Initial Concentration) - (Equilibrium Concentration),
g = grams of adsorbent, and
c = concentration of solute in equilibrium.

The various types of adsorbents showed that the extent of removal and Kd's were a function of pH. The values for adsorption reported (Kd's) are not at total capacity but at a low enough concentration of adsorbent (high capacity) where the Kd values are not expected to change a great deal.

For removal of polymeric plutonium, ²³⁸Pu(IV), the best results (higher Kd's) were achieved using the inorganic adsorbent, bone char (hydroxyapatite), at pH 7. This had been shown previously in work done at Mound Laboratory for DPR.¹⁻⁴ However, Amberlite XE270, a macroporous weak base anion exchange resin, also showed reasonable Kd values at pH 7. Therefore, the best removal of polymeric plutonium can be achieved using chemisorption or weak base anionic exchange (indicating strongly ionized anions). XAD2, a resin which removes solute by a pure adsorption process (hydrophobic), also showed some promise. That is, it performed better than the remaining resins but not as good as bone char and XE270.

For removal of ionic ²³³U(VI), the strongly acidic cation exchangers gave the better results; the Kd values were on the order of 10² better than bone char. Again, performance was a strong function of pH. In most cases, pH 4 and 7 gave the better results. However, for anionic resins, the better results occurred at pH 7 and 10. Adsorbent resins which remove constituents by physical adsorption (XAD2 and XAD7) did not perform well for

Table 1

PROPERTIES OF ION EXCHANGE RESINS

(This table is not to be construed as an endorsement of any of these resins)

Bone Char	inorganic adsorbent - chemisorption hydroxyapatite (HAP), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
Amberlite XAD2	polymeric adsorbent (hydrophobic) crosslinked polystyrene polymer macroreticular physical porosity been used for dye waste and phenol removal
Dowex-HRC-W	high capacity cation exchange resin medium porosity styrene-divinyl benzene matrix hydrogen form
Dowex-SBR-P	strongly basic anion exchange resin quaternary ammonium function groups (good for removal of weakly ionized anions, especially silica) porous resin high resistance against organic fouling hydroxide form
Amberlite XE270	macroporous weak base resin macroreticular porosity useful for colloidal removal no organic fouling
Amberlyst XN1010	strongly acidic cation exchange resin catalysis of organic reactions in non-aqueous solutions cation removal from non-aqueous solutions hydrogen form
Amberlite XAD7	acrylic ester - polymeric adsorbent has been used for treating dye wastes and antibiotic recovery
Amberlite 200	styrene - DVB strongly acidic cation exchanger sulfonic acid functionality resistant to oxidation used for water conditioning, separation of rare earths, separation of amino acids, and chemical processing sodium form
Amberlite IRC50	weakly acidic cation exchanger will selectively adsorb organic bases such as metals present in alkaline solution been used for copper and nickel recovery carboxylic functionality hydrogen form
Amberlite IRA938	strongly basic anion exchanger quaternary ammonium functionality removal of colloidal silica and hydrous metal oxides from various water streams well suited for removal of radioactive colloids chloride form
Amberlite XE279	strong base resin macroreticular porosity acrylic backbone no organic fouling useful for colloid removal
Dowex-MSA-1	strong base anion exchange resin macroporous no organic fouling hydroxide form
Dowex-MS-1	strong acid cation exchange resin macroporous recovery of metal catalysts, recovery of metals from plating baths, sorption of high molecular weight cationic materials hydrogen form
Dowex-AG-1x4	commercial anionic gel resin chloride form

uranium removal. In comparing the strong base anion exchange resins, the gel resin, Dowex-SBR-P, had much lower Kd values than the macroporous resin, Dowex-MSA-1, thus showing the main advantage of using the new macroporous resins. In fact, for the Dowex resins, both cationic and anionic macroporous resins gave Kd values on the order of 10^5 at various pH's, while the gel resins gave Kd values of the order of 10^2 .

Excellent results for removal of $^{238}\text{Pu}(\text{VI})$, were achieved (see Table 4) using a strong base macroporous anion exchange resin, Amberlite XE279. The Dowex-SBR-P strong base anion exchange gel resin gave Kd values lower than bone char, while the XE279 gave Kd's a factor of 10 better than bone char. The best results were achieved using Amberlyst XN1010, which gave Kd's a factor of 20 better than bone char. The XN1010 is a strong acid cation exchange macroporous resin used mainly for catalysis in organic liquids, and also for cation removal from nonaqueous solutions.

Conclusions

It seems that the new macroporous resin technology gives great promise as an

improvement over the present ion exchange resin technology. The new resins compare favorably with bone char, an inorganic adsorbent which removes solutes through the mechanism of chemisorption. In the case of ionic solutes, such as uranium and hexavalent plutonium, a definite edge in Kd values goes to the resin while for polymeric plutonium the bone char has a slight edge in removability.

As stated previously, the data was used only for initial screening of the resins. No great concern was shown over the fact that the pH changed while solute removal was taking place. Also, the capacity used in determining the Kd values was not the theoretical total capacity of the material. However, it was felt that for basis of comparison, the Kd values would not change significantly with further loading of the adsorbent material. Further tests are planned which would determine isotherms for each material, and determine various engineering parameters, such as loading rates, bed capacity, residence time and removals for the various resins, and if it is possible to maintain constant pH. Isotherms will be run on a batch basis while engineering parameters will be determined using small bench scale columns.

Table 2

REMOVAL OF $^{238}\text{Pu}(\text{IV})$ POLYMER BY ION EXCHANGE/ADSORPTION

Adsorbent Type	Adsorbent Concentration (mg/ml)	Initial Concentration of Solute (dis/min/ml)	$K_d = \frac{\Delta C/q}{C}$	pH Initial Value
Bone Char	0.245	34291	1.2×10^6	7
	0.260	44710	9.8×10^3	8
	0.304	19167	1.9×10^3	10
Amberlite XAD2	1.075	12733	3.0×10^3	4
	0.660	59651	7.0×10^2	10
Dowex-HRC-W	0.878	13597	8.5×10^2	4
	0.738	25088	1.34×10^3	7
	1.380	38899	2.1×10^2	10
Dowex-SBR-P	1.116	8359	1.0×10^1	4
	0.631	15558	3.5×10^2	10
Amberlite XE270	0.575	19717	1.56×10^4	7
	0.500	20106	1.42×10^3	10

Table 3

REMOVAL OF $^{233}\text{U(VI)}$ BY ION EXCHANGE ADSORPTION

Adsorbent Type	Adsorbent Concentration (mg/ml)	Initial Concentration of Solute (dis/min/ml)	$K_d = \frac{\Delta C/g}{C}$	pH Initial Value
Amberlite 200	0.098	11166	4.25×10^5	4
	0.082	11370	1.05×10^6	7
	0.036	8623	3.58×10^3	10
Amberlite IRC50	1.160	10966	1.68×10^3	4
	0.076	10934	7.5×10^4	7
	0.046	7869	1.3×10^4	10
Amberlite IRA938	0.030	21647	1.6×10^2	4
	0.028	22162	5.0×10^1	7
	0.054	6605	9.0×10^4	10
Amberlite XAD7	0.0492	21172	6.4×10^2	4
	0.082	21593	2.1×10^2	7
	1.14	4141	1.0×10^2	10
Amberlite XAD2	0.110	21599	6.0×10^1	4
	0.032	21844	1.14×10^3	7
	0.038	4861	7.7×10^2	10
Amberlite XE279	0.027	21875	3.8×10^2	4
	0.028	21731	1.24×10^3	7
	0.016	7386	9.0×10^4	10
Dowex-MSA-1	0.046	22332	1.9×10^2	4
	0.054	21980	1.65×10^5	7
	0.052	13772	2.7×10^5	10
Amberlite XE270	0.432	21294	6.0×10^3	4
	0.162	21743	1.72×10^3	7
	0.12	14065	5.6×10^2	10
Bone Char	0.14	12548	8.0×10^4	7
	0.266	12361	8.5×10^4	8
	0.22	8976	3.5×10^4	10
Dowex-HRC-W	0.72	21964	2.0×10^1	7
	0.53	16290	1.4×10^2	10
Amberlyst XN1010	0.12	10690	3.3×10^5	4
	0.02	12599	9.5×10^6	7
	0.08	8034	1.62×10^3	10
Dowex-MSA-1	0.15	12310	5.5×10^5	4
	0.12	11036	5.0×10^5	7
	0.19	10148	5.0*	10
Dowex-SBR-P	0.12	21122	2.8×10^2	4
	0.19	10984	4.8×10^5	7
	0.24	17334	8.0×10^2	10
Dowex-AG-1 x 4	0.058	21958	3.0×10^2	4

*The value, 5.0, as shown, is correct

Table 4

REMOVAL OF $^{238}\text{Pu(VI)}$ BY ION EXCHANGE/ADSORPTION

Adsorbent Type	Adsorbent Concentration (mg/ml)	Initial Concentration of Solute (dis/min/ml)	$K_d = \frac{\Delta c/g}{c}$	pH Initial Value
Amberlite XE279	0.109	21675	5.24×10^2	4
	0.0144	30906	3.17×10^3	7
	0.0102	22218	4.53×10^3	10
Amberlyst XN1010	0.0088	29925	2.55×10^5	4
	0.0144	26970	6.23×10^5	7
	0.0315	27860	9.4×10^3	10
Bone Char	0.244	29449	3.31×10^4	4
	0.1097	26340	5.34×10^4	7
	0.178	30048	3.97×10^4	10
Dowex-SBR-P	0.0047	23567	5.37×10^3	7
	0.0121	20765	6.05×10^4	10

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