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# Lead Removal from Synthetic Leachate Matrices by a Novel Ion-Exchange Material

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# ABSTRACT

This paper discusses the application of a novel polyacrylate-based ion-exchange material for the removal of Pb ions from water. Preliminary testing includes the establishment of the operating pH range, capacity information, and the effect of  $Ca^{2+}$  and anions in the matrix. Batch testing with powder indicates slightly different optimal operational conditions from those used for column testing. The ion-exchanger is excellent for removing Pb from aqueous solutions.

# **INTRODUCTION**

Lead in the water supply is an ever-increasing concern. Common sources include the corrosion of transport systems and material leached from the environment. The environmental sources are diverse, ranging from Pb paint in the soil to spillage at battery-cracking facilities.<sup>1,2</sup> Because of its extreme toxicity, acceptable concentration levels of Pb in potable water must be maintained at low parts per billion. One of the most common techniques for lowering the concentration of metal ions to suitable levels in potable water is ion-exchange treatment.

A proposed method of remediation technology is soil washing. This treatment appears to be extremely attractive

# IMPLICATIONS

This work demonstrates the ability of a polyacrylate ionexchange material to remove toxic metals from water. The material has significant affinity for Pb in the presence of considerable amounts of competing or complexing ions, and it also works well in the presence of hard water to readily remove other toxic metals. An important property of this material is that it can be fabricated in many forms, such as coatings, films, and conventional beads. because of the large quantities of contaminated soil that would otherwise have to be contained in a waste-storage facility.<sup>2,3</sup> In soil washing, the soil is pretreated to remove large Pb sources (e.g., bullets). The corroded Pb that has leached into the soil is stripped with a leachant. Because the Pb encountered in different washing situations occurs in different forms, the wash solution must be tailored to the site. Typical wash solutions that have been employed range from a simple acidification medium, such as dilute HNO<sub>3</sub> or fluosilicic acid, to strong complexing agents, such as ethylenediaminetetraacetic acid (EDTA). Although EDTA has been shown to solubilize Pb fairly well, it creates other problems with the soil to be subsequently recovered. Weak chelators have been employed as well, including nitrilotriacetic acid and acetic acid. Acetic acid is attractive because it is inexpensive, has been demonstrated to be a moderately good leachant, and is readily biodegradable. The leachate is then stripped by ion-exchange technology and recycled. This last step in the loop is often problematic, because a good leachant is often hard to strip of the solubilized Pb.

A novel polyacrylate-based ion-exchange material (IEM) was developed at NASA after the serendipitous discovery that a marginal battery separator retained Cu ions from distilled water. The source of the Cu in the distilled water used to wash the separator was traced to a corroding line in the still. In earlier versions of the separator, polyacrylic acid (PAA) was cross-linked with radiation to produce films. These materials had ion-exchange capacity but were readily fouled before reaching a useful loading capacity.<sup>4-7</sup> In subsequent versions of the material, polyvinyl alcohol (PVA) was incorporated in the film matrix, which solved the fouling problem.<sup>8-12</sup> The new IEM is chemically cross-linked at the PVA, leaving the PAA loosely trapped in the matrix. This configuration of the material provides additional flexibility for the PAA sites to exchange ions.

We have characterized the new IEM for removal of Pb in the presence of various anions that are commonly found in the environment. Chloride also was tested because it is ubiquitous and will be of interest in systems where noncomplexing leachants such as  $HNO_3$  are used. Acetic acid was investigated as a weak complexing agent associated with proposed soil-washing scenarios. The study includes the effects of pH, because it is important when using weak cation exchangers, and the Ca ion, which often fouls ion exchangers. For comparison, limited data on Cu and Zn also are presented.

# MATERIALS AND METHODS

The ion-exchange resin was obtained from Southwest Research Institute. The powder was manufactured by spray-drying a solution containing 8.4% solids (1:1 mixture of PVA and PAA) and 0.13% glutaraldehyde to crosslink the PVA framework.<sup>8,12</sup> The ion-exchange beads were manufactured by a novel patented process.13 The aqueous phase contained 14% solids (1:1 mixture of PVA and PAA) and 1.3% glutaraldehyde. This solution was mixed with mineral oil and fumed silica in a sufficient amount to cause droplets of resin to remain suspended after stirring stopped. The mixture was heated to 60-70 °C overnight. The spheres were strained, washed with hexane, and air-dried. All IEMs were received in the acid form. Before use in uptake experiments, they were converted to the Ca form. Powder was stirred with excess suspended Ca(OH)<sub>2</sub>, filtered, and washed prior to use. Bead conversion is described later in this section.

The capacity of the IEMs was determined by equilibrating the acid IEM with an excess of standard NaOH for at least 12 hr. The resin was filtered off and the excess OH- was determined by titration with standard HCl. For batch tests, the IEM (typically 100 mg) was stirred with the test solution (typically 100 mL), and aliquots were taken at defined time intervals. An aliquot was taken before the introduction of the IEM to the test. The amount taken was such that all aliquots totaled less than 5% of the original volume. Metal ion concentrations were determined on all aliquots by flame or graphite furnace atomic absorption spectrophotometry (AAS) using the conditions described in SW-846<sup>14</sup> or as close to that as possible. The pH was determined at the start and end of each experiment.<sup>15</sup>

Column testing was performed in glass columns with sintered glass frits at either end. The columns were typically packed with 1 g of beads 80% converted to the Ca form. Challenge solutions containing various concentrations of Pb and Pb with excess anions at varying pH were pumped continuously through the column. The effluent

was collected for AAS and pH analysis. The IEM was weighed in the acid form, converted to the correct extent with standard Ca(OH)<sub>2</sub> solution, and loaded into the column. The void volume of the column was monitored by the injection of a salt spike to generate a signal at a conductivity detector placed at the column effluent. Challenge solutions were prepared from the Pb salts with the corresponding anion. To prevent hydrolysis and subsequent precipitation of the Pb, the solutions were stabilized with a trace of hexamethylenetetramine (a weak complexing agent). The pH was then adjusted with HNO<sub>3</sub>. For challenge solutions containing excess anion, the solution was prepared such that an excess of 0.1-molar anion was generated from 0.09-molar Na salt and 0.005-molar Ca salt. Various challenge solutions, column geometries, and flow conditions were tested as described in the subsequent sections and figures.

#### RESULTS

The powder form of the IEM, nominally in the 5–75  $\mu$ m range, was used as received. Titration of this material indicated a capacity of 4.81 ± 0.11 meq/g IEM. Equilibration of the Ca form of the IEM with a large excess of Cu ions in an acetate buffer at pH 5.0 yielded a capacity of 4.8 meq/g IEM. Titration of two subsequent lots of powder yielded capacities of 5.29 and 5.36 meq/g IEM. By end point differences in the back titration of these materials, it is possible to determine the amount of PAA released from the cross-linked PVA during the reaction with the NaOH. The leakage numbers correspond to 1.72, 0.86, and 1.05 meq/g, respectively, indicating that the latter lots of IEM were cross-linked more efficiently and, therefore, yielded the higher capacities.

Figure 1 demonstrates the pH working range for the powder form of the IEM using Cu and Pb as test ions. Figure 2 illustrates the rate at which the powder and film forms of the IEM take up Pb ions in batch testing. For



**Figure 1.** Fraction of metal removed as a function of pH for Ca form of IEM powder.



Figure 2. Metal ion concentration remaining in solution as function of equilibration time for various resins.

comparison, the Na form of the Biorad cation exchange resin (AG 50W-X2, 38–75  $\mu$ m) for uptake of Cu ions is also presented. Table 1 summarizes the results of 16 separate conditions tested and demonstrates the immunity of the IEM against some common anions for the uptake of Pb ions when 100 mg of IEM powder is challenged with 100 mL of test solution under the conditions specified in the table.

The beads received from Southwest Research Institute were fractionated into two sizes (600–1400  $\mu$ m and <600  $\mu$ m). These were presumably manufactured as one lot having a similar composition. The <600- $\mu$ m lot was further sized into two fractions, <250  $\mu$ m and 250–600  $\mu$ m. The limited quantity of the latter fraction was saved for testing in column experiments and then was recycled for capacity testing. The other two fractions were subjected to several batch experiments. Table 2 gives capacity and leakage values for the limited testing performed on these materials. It is apparent that the recycled beads give considerably lower leakage values and that the capacity is in line with that of the original

Table 1	۱.	Recovery	of	Pb	from	various	matrices.
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	Lead Recove % (std. de Ani	ered in IEM eviation) <sup>a</sup> ion		Hydrogen Ion Concentration pH
None	Nitrate	Chloride	Acetate	
	10-ppm	Pb with 0.1-Mola	ar Anion	
92.2 (0.4)	92	91	81	5.0
9.2 (3.6)	21	5.5 (0.5)	0	3.0
	100-ppm	1 Pb with 0.1-Mo	lar Anion	
9.2 (2.4)	15	8	1	3.0
	500-ppm	1 Pb with 0.1-Mo	lar Anion	
10.4 (3.9)	16.2	11	14	3.0

<sup>a</sup>Standard deviation between replicate experiments.

Table 2. Capacity and leakage of IEM beads.

Bead Size	Cap	acity	Leakage		
μm	meq/g	Standard Deviation <sup>a</sup>	meq/g	Standard Deviation <sup>a</sup>	
<250	4.2	_	_	_	
250-600	4.3 <sup>b</sup>	0.07	0.4 <sup>b</sup>	0.03	
600–1400	5.4	0.02	1.2	0.02	

<sup>a</sup>Standard deviation, n = 2; <sup>b</sup>Determined on beads recycled from column testing.

material. Digestion of the beads resulted in a silica content of ~10% by weight from entrapped silica introduced during the manufacturing process.

For comparison, the beads packed into the columns were weighed and the column dimensions were recorded along with the experimentally measured void volumes. Typically, 1.00 g of the 80% converted beads packed into a 10-mm inside-diameter (id) column produced a bed 60 mm long (4.7 mL) with a void volume of 2.5 mL. The bulk density of the beads then was calculated to be  $0.2 \text{ g/} \text{ cm}^3$  (dry) and the void volume to be 53%. In most cases, the length of the bed decreased by 2–3 mm by the end of the experiment.

Two different experiments compared beads that were converted to the 20 and 80% Ca forms. Figure 3 is a plot of the Pb concentration of the exit  $C_e$  divided by the initial challenge concentration  $C_i$  versus the volume of Pb solution run through the column. It is apparent that



**Figure 3.** Fraction of original concentration of PbNO<sub>3</sub> and PbCl<sub>2</sub> in column effluent ( $C_g/C_1$  values × 1000) as function of volume of Pb solution through columns for IEM beads 80% and 20% converted to Ca form. Flow rate through columns, 1.0 mL/min.

breakthrough occurs early with the 20% converted beads. Even at a very low challenge concentration (100 ppm), the 20% converted beads are not as effective at removing Pb as is the 80% converted material. The behavior of the columns is understood by close examination of the associated pH profile of the effluent during a column experiment. In Figure 4, the effluent pH is plotted for the two 500-ppm Pb samples in Figure 3. Figure 4 demonstrates the relationship between percent of bead conversion to the Ca form and ability to maintain pH as Pb is removed from the influent solution.

A careful examination of the pH profiles for all column tests performed with the 80% converted IEM and Pb solutions containing Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> is shown in Figure 5. This figure is a plot of the pH of the first eluent collected (pH<sub>e</sub>) from the column versus the pH of the influent challenge solution (pH<sub>i</sub>). The figure reveals that the resin initially attempts to adjust the pH of the solution in the column to a value coincidentally close to the pK<sub>a</sub> of the IEM, ~5.5. A plot of (pH<sub>e</sub> - pH<sub>i</sub>) versus the pH of the challenge solution pH<sub>i</sub> is presented in Figure 6. This plot demonstrates the amount of pH adjustment on the solution by the column.

Figure 7 shows typical breakthrough curves for columns of varying length and the effect of  $NO_3^-$  ions. Excess  $NO_3^-$  ions only influence this system by providing a high ionic strength. In subsequent experiments, the longer length columns were used, because they provided more ideal curves. For comparison, the weights of resin used to vary the column length are included in the figure legend.



**Figure 4.** Correlation of fraction of original concentration of Pb in column effluent  $C_e/C_i$  as function of volume of Pb solution through column to pH of column effluent as function of volume through column for IEM beads 80% and 20% converted to Ca form. Note: pH of challenge solution is pH at volume = 0 mL.



**Figure 5.** pH of column effluent  $pH_e$  as function of pH of column influent  $pH_i$  (pH<sub>i</sub> taken as pH of challenge solution) for challenge solutions containing NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>.

It also is evident that the high ionic strength generally improves the performance of the IEM. In another experiment (not shown), the effect of ionic strength was a doubling of the apparent onset of column breakthrough for two flow rates. Figure 8 shows the effect of flow rate on column retention of Pb. Figure 9 is a plot of the Pb in the IEM at the end of the experiment normalized by the weight of IEM used in the experiment plotted against the final reading of  $C_{1}/C_{1}$  for 30 column experiments. The large scatter in the data is attributable to varying conditions of flow rate, column length, pH, anion associated with the Pb salt, and, in some cases, 0.1 molar excess of the corresponding anion. Extrapolation of the data having  $C_{a}/C_{i}$  > 0.01 (22 data points) to  $C_e/C_i = 0$  indicates that Pb loading of ~10% by weight (~20% of the calculated equilibrium capacity) leads to breakthrough in unoptimized conditions. In the most extreme data, at  $C_a/C_i > 0.8$ , the resin has, at best, taken up 28% of its weight as Pb, which is only 60% of the calculated equilibrium capacity.

The effect of Cl<sup>-</sup> was examined because it is ubiquitous, has complexing ability, and forms a sparingly soluble salt with Pb. Acetate is of interest because acetic acid has



**Figure 6.** Difference in pH between column effluent pH<sub>e</sub> and column influent pH<sub>i</sub> (pH<sub>i</sub> taken as pH of challenge solution) as function of pH<sub>i</sub>.



**Figure 7.** Fraction of original concentration of Pb in column effluent  $(C_e/C)$  as function of volume of Pb solution through column for columns of various lengths challenged with low- and high-ionic-strength Pb solutions. Flow rate, 2.0 mL/min of 500-ppm lead nitrate through 80% IEM converted to Ca form.

been used in soil-washing scenarios. Acetate has moderate complexing ability and acts as a solution-buffering agent. Figure 10 presents additional data for column experiments involving Cl<sup>-</sup> and acetate.



**Figure 8.** Fraction of original concentration of Pb in column effluent  $(C_e/C_i)$  as function of volume of Pb solution through column for various flow rates. Columns contained 0.5 g of 80% Ca-converted IEM challenged with 500-ppm lead nitrate.



**Figure 9.** Weight percent of Pb in IEM vs. ratio of concentration of Pb in column effluent  $C_{e}$  for final data point in run divided by concentration of Pb in challenge solution  $C_{i}$ .

# DISCUSSION

Preliminary investigations with laboratory samples of the IEM indicated that it has the following properties: high capacity; mechanical durability; immunity to Ca<sup>2+</sup>; immunity to Fe and several other nontoxic metal ions; high efficiency in the removal of Pb, Cd, and other toxic metal ions; easy recyclability or disposability; and easy formation into many shapes (e.g., beads, fibers, film, or coated magnetic beads).<sup>8-12</sup> Because of these properties, we decided to have the material manufactured by a commercially scalable process for evaluation as a potentially useful product. Proposed uses include drinking-water purification and application in environmental processes such as soil washing. To date, powder, beads, film (both porous fiberglass-reinforced and nonporous), and irregular granules have been produced at the pilot scale. These potential



**Figure 10.** Fraction of original concentration of Pb in column effluent  $(C_e/C_p)$  as function of volume of Pb solution through column for various anions. Pb concentration, 500 ppm.

products indicate that the manufacturing process for this material is feasible.

#### **Powder Properties**

The capacity numbers are consistent with the theoretically calculated value of just under 7 meg/g for a material containing 50% PAA. From prior experimentation with bead, granular, powder, and film IEM, there are a number of reasons for the leakage.<sup>12</sup> A small amount of initial leakage appears to be inherent in the structure of the material, in that the PVA is cross-linked into a matrix that entangles the PAA, the only mechanism for retention of the PAA in the resin. Some small amount of additional PAA leaks during the first conversion to the salt form, the active form of the resin. The conversion process with Ca2+ tends to shrink the resin, which causes the remaining PAA to be more strongly retained in the resin so that subsequent leakage is negligible. Consequently, the working version of the IEM uses the Ca salt, which is immune to leakage and deterioration of mechanical strength. Conversion with NaOH as in the titrations tends to expand the volume of the resin (prior unpublished studies indicate by as much as 40%), causing deterioration of the mechanical strength. Sodium conversion also may release more PAA than the working Ca form. Hence, the leakage numbers may be an overestimate and the actual capacities reported may be underestimates. In the formulation process, we have also observed that too little cross-linking or using a PAA with lower molecular weight facilitates leakage. This topic will be addressed further in the section titled Bead Properties.

The IEM is a weak acid cation-exchange resin estimated to have a pK<sub>2</sub> of ~5.5. The operational pH range for the IEM (see Figure 1) is limited at lower pH values because acid competes heavily for the resin sites. The powder does not appear to suffer the same shortcoming described in our earlier work, where many metal ions that exist as neutral precipitates or as anionic hydroxy species at the higher pH values (typically pH > 7) are not taken up by the film form of the IEM. In the present work, the powder IEM clearly effectively removed Cu to a pH approaching 8. In our earlier work with films,9 the Cu recovery had dropped from nearly 100% at pH 6.5 to 50% at a pH slightly greater than 7. The extended operational pH range probably is caused by the higher surface area of the powder, hence the better performance. The slowness in uptake for the film versus the powder (see Figure 2) is attributed to mass transfer problems associated with the film being a single entity in a large volume of solution. Nonetheless, it is equally effective at removing ions, provided that there is sufficient equilibration time. At the lower pH values, the anions evaluated in Table 1 are less problematic than the pH. At higher pH values, the acetate, which has a high formation constant with Pb,16 lowers the effectiveness of the IEM as discussed in the section titled Column Performance.

#### **Bead Properties**

Beads would be expected to have a 10% lower capacity than the powder because of the silica incorporated during manufacturing. The rest of the capacity reduction in the beads is attributable to a lack of bead porosity and the resulting mass diffusion problems. For the purpose of comparison, the calculated uptake of Pb based on a capacity of 4.3 meq/g IEM is 45% of the weight of the IEM. From prior comparative studies with the film and with irregular granular and powder forms of the IEM, the majority of the performance properties (e.g.,  $pK_a$  of the IEM, capacity, affinity for metal ions, and pH uptake profiles for various metals) are very similar. The two exceptions are the kinetic-related properties and the apparent extended operating pH range for the powder demonstrated in the single experiment reported herein (see Figure 1).

#### **Column Performance**

Even though the columns prepared with 20% converted beads do not work well at high-challenge concentrations, Figure 3 demonstrates that a substantial amount of Pb can be removed for low-challenge concentrations with a 20% converted material. The key to the behavior of the columns is that the resin behaves as a pH buffer by altering the pH of the medium passing through the column, as seen in Figure 4. For water at a pH of 5 passing through an 80% converted column (IEM pH of ~6.6), the column would be expected to pick up hydrogen ions from the medium and release Ca from the resin. This behavior should result in a slight increase in the pH of the column effluent; however, this activity is not what was observed. For Pb solutions passing through the column, the Pb was exchanged onto the column, releasing both Ca and hydrogen ions. The hydrogen release causes the drop in the pH of the solution passing down the column.

In columns where the percent conversion to the Ca form was greater, less hydrogen was released into the system to lower the pH of the medium passing through the remainder of the column (see Figure 4). For the 20% converted beads (IEM pH of ~4.9) in Figure 4, substantial hydrogen ions are released, dropping the pH of the medium to ~3. For higher Pb concentrations, the effect would be even more dramatic. From Figure 1, the equilibrium concentration of Pb in the solution over the IEM at pH 3 should be 60% of the original concentration, which is what was observed in the effluent. In all other studies, 80% converted beads were used, and the pH of the effluent was monitored as samples were collected.

Examination of the pH profiles for each column experiment is required for the correct interpretation of results. Interpretations tend to be complicated by a drifting pH and the inability to maintain the influent pH during runs, even for the highly acetate-buffered test solutions. Figures 5 and 6 show the effect of the column on the pH of the challenge solution. Figure 5 demonstrates that the column attempts to adjust the pH to a value coincidentally equal to the pKa of the IEM. A good linear correlation of the amount of pH adjustment initially performed by the column on the challenge solution to adjust the pH toward 5.6 is shown in Figure 6. Other percent conversions would be expected to produce a similar effect, although the pH value converged upon should be different.

In an unrelated experiment using the large beads to develop a home test kit for determination of Pb (ppb level) in drinking water that also contained Cu and Zn (ppm range), the pH of the challenge solutions was buffered to values between 3.8 and 4.5. At the lower pH, the majority of the Pb and a small fraction of the Cu is retained on the column, whereas no Zn is collected. At the higher pH, Pb and the majority of the Cu are retained by the column but only a small fraction of the Zn is removed from the challenge solution. These experiments further illustrate the effect of pH on the retention of metal ions on this IEM.

The optimization of column conditions presented in Figures 7 and 8 are as expected. The larger columns provide more reasonable-looking curves because flow patterns in the columns are more homogeneous. Slower flow rates provide better equilibration, particularly with respect to mass transfer in the ion-exchange media. Based on the results of these experiments, subsequent experiments used 1 g of IEM and a flow rate of 2 mL/min. The higher, unoptimized flow rate was used to expedite breakthrough conditions. The effect of ionic strength observed in Figure 7 is the result of several simultaneous processes, an advanced discussion of which is beyond the scope of this report. Briefly, the processes leading to the improved performance of the IEM include a combination of the change in activity of the exchanging ions along with a lowering of the surface tension of the solution. The ionic strength alters the activity of the exchanging ions in predictable fashion. The change in surface tension promotes mass transfer across the interface between the solution and ion-exchange resin.

A major drawback of the IEM is that mass diffusion in the resin is a limiting factor for the breakthrough of Pb. As the flow rate is slowed, there is more time for Pb at the surface of the resin to diffuse inwardly. Hence, in Figure 8, the amount of Pb removed per gram of IEM is dramatically improved at a flow rate of 0.5 mL/min. Because the intent of these experiments was to amplify the differences in column performance by various conditions in the challenge solutions, higher flow rates than optimal were used. The actual performance of the columns used in the following experiments could be improved greatly if a slower flow rate were used. The problems associated with mass transfer in the IEM are confirmed in Figure 9, which indicates that Pb loading of ~10% by weight leads to breakthrough for unoptimized conditions. To give a perspective, the 0.5-mL/min data having  $C_e/C_i = 0.0004$  at the end of the run has a loading of 17% by weight (38% of theoretical). This indicates that optimizing the conditions allows considerably more Pb to be removed before breakthrough is approached.

Chloride ion weakly complexes Pb ion, and in addition, PbCl<sub>2</sub> is sparingly soluble. From equilibrium constant calculations, the solubility of the Pb is complete under all conditions tested, including that in the presence of 0.1 molar excess Cl- ion. Furthermore, the concentrations of PbCl<sup>+</sup> and PbCl<sub>3</sub><sup>-</sup> are negligible at 500-ppm Pb with 0.1 molar excess Cl<sup>-</sup> ion.<sup>16</sup> In a preliminary experiment at pH 5.5 using 107 ppm PbCl<sub>2</sub> pumped at 2 mL/min through a 10-mm id column containing 1 g of 80% converted IEM, the Pb concentration in the column effluent was lowered to below the limit of instrumental detection (<2 ppb Pb) throughout the run (total volume of 240 mL). Effluent Pb concentrations in the low-ppb range were typical of the IEM performance before column breakthrough for challenge solutions containing modest Pb concentrations. Figure 10 illustrates the effect of various anions on the retention of Pb. The interpretation of the figure is complicated by the effect of pH on the system. Plots for NO<sub>3</sub><sup>-</sup> are complicated by the drift of the pH to unfavorable absorption values toward the end of the run. The pH started in the 5.8 range and drifted toward 4 or less for the last data points, demonstrating that Pb preferentially displaces Ca over hydrogen. The Cl<sup>-</sup> curves have a less pronounced pH effect and exhibit the same general trend as that for the ionic strength curves presented in Figure 7. The last data points on the Cl- curves show that in the presence of 0.1 molar excess Cl<sup>-</sup>, the Pb is retained more effectively, even with slightly less favorable pH (pH = 5.5 vs. 5.3 for the excess-anion run).

Acetate is a complexing anion that neutralizes the charge on the Pb, rendering it a neutral species.<sup>16</sup> According to the values of the stepwise formation constants, appreciable amounts of PbAc<sup>+</sup> can be generated as the acetate forms the neutral PbAc<sub>2</sub> species. Either the Pb<sup>2+</sup> or the PbAc<sup>+</sup> ion is capable of immediately adsorbing to the IEM; however, the equilibrium is probably reestablished rapidly enough to produce substantial cationic species as the IEM removes the Pb from solution. None-theless, acetate competes markedly with the IEM for Pb. For 500-ppm Pb prepared from PbAc<sub>2</sub>, substantial amounts of the Pb are in cationic species at pH 4 where the IEM is less effective. As the pH rises to 5 and 6, the amount of cationic species is on the order of two-thirds and one-half, respectively (exact calculations rely on an

iterative process). In the presence of a large excess of acetate (0.1 molar), the calculations are more exact and the concentrations of cationic Pb drop markedly from pH 4 (2% Pb<sup>2+</sup> and 1% PbAc<sup>+</sup>) to 6 (<0.5% Pb<sup>2+</sup> plus PbAc<sup>+</sup>). Under these conditions, the rapid establishment of equilibrium in the solution enables the IEM to remove Pb successfully (see Figure 10). The Pb breakthrough correlates directly with the amount and strength of competing ligands in solution. In unrelated beaker experiments with Zn and IEM films,17 similar results were achieved with EDTA. None of the Zn was removed from solution by the IEM because of the complexing strength of the ligand that creates an anionic complex, ZnEDTA2-.

A final note regarding the often-detrimental effects of Ca2+ in the matrices is that this resin operates most effectively in the Ca form for all divalent cations that have been tested with the IEM to date. This point is further demonstrated in the excess-anion experiments wherein the matrix is ~0.005 molar (200 ppm) in Ca. In experiments performed stripping Pb from seawater, the effect of Na was to eventually displace Ca and expand the resin, causing deterioration of the IEM and column performance. To this end, we spiked the matrices with small amounts of Ca to replenish the resin as the experiment proceeded. In all experiments using excess, noncomplexing anions, results were superior to runs without the excess anions. These results are more likely because of ionic strength considerations than Ca<sup>2+</sup> enhancement.

# CONCLUSION

The IEM, developed from battery separator technology, is composed of cross-linked PVA and entrapped PAA and can be produced in a variety of forms. The current evaluation is designed to demonstrate the ability of the material as a replacement for column ion-exchangers where weak acid exchangers are applicable. Data are presented for Pb adsorption under a number of physical and chemical conditions. Physical conditions were several geometries, the quantity of IEM in the test column, and flow rates. The chemical conditions were Pb concentration, pH, ionic strength, and effect of weakly competing organic complexing agents. The IEM removed Pb effectively under most conditions; however, the breakthrough characteristics for similar columns were greatly affected by pH and the presence of complexing anions. Under ideal conditions, this IEM will remove modest amounts of Pb (high-ppm concentration range) and reduce the Pb concentration to the low-ppb range.

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