

LEAD REMOVAL BY ION EXCHANGE

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ABSTRACT

A number of tests looking at lead removal using ion exchange resins of various types from various aqueous streams have been undertaken. The tests focused on strong acid cation (SAC) and weak acid cation (WAC) resins. It was found that the mechanism of lead removal is partly by lead filtration rather than solely by ion exchange in a large portion of the applications studied. This is not surprising since lead carbonate is essentially insoluble and almost all water supplies contain at least some carbonate alkalinity. Regeneration of lead from exhausted resins containing significant amounts of lead may not be practical in some cases because of the large chemical and waste volumes involved. Since lead, along with many other very insoluble metals, is often present as a suspended solid rather than in ionic form, ion exchange is probably not always the best technology for bulk lead removal.

INTRODUCTION

Ion exchange is well known for its ability to concentrate various ionic contaminants and to produce very low effluent concentrations. For common ions found in natural water supplies, there is very good operating data to support this; sufficient in fact to design a system without pilot testing. However, for waste streams, particularly those containing lead and other heavy metals, very little operating data is available.

Published data for ion exchange resins implies that the selectivity for lead is very high and that lead should be removed preferentially to almost any other common cation. Both weak acid cation resins and strong acid cation resins are widely used in lead removal systems. Do these resins really work in all cases? At ResinTech, we recently performed an extensive series of experiments to determine how well certain metals including lead could be removed from an acidic waste water with a moderate TDS (around 1000 ppm) containing lead as well as manganese, some hardness, and traces of other divalent transition metals. The surprising answer was that, although both types of cation resin do remove lead, the primary mechanism, at least for these studies was usually filtration and not ion exchange.

Although lead is removed preferentially by cation exchange resins, lead salts are not very soluble in most water supplies. Of course, this also means that lead in ionic form (as a cation) is not present in most water supplies. When lead is present, it is generally present as a suspended solid. Other potential forms of lead include anionic complexes and neutral organic molecules that contain lead, either as part of a complex or as part of the organic molecule itself. In our investigation, when lead was removed by a cation exchange resin, we found that it was usually by a combination of filtration and ion exchange. In this paper, we will explore lead chemistry, its solubility, ion exchange selectivity and the various mechanisms of removal by cation exchange resin.

MEDIA USED FOR LEAD REMOVAL

There are a number of media that can be used for lead removal from aqueous streams. They include ion exchange resins and adsorbents as broad families of media. Ion exchange resins can be further divided into strong acid cation (SAC) resins, weak acid cation (WAC) resins, and chelating cation resins as discussed below. The selectivity coefficients of these three types of ion exchange resins for various cations is summarized in Table I.

Table I – Typical Selectivity of Ion Exchange Resins for Various Cations

Cation	Selectivity Coefficient		
	SAC Resin	WAC Resin	Chelating Resin
Hydrogen	1.0	-	-
Sodium	1.5	0.01	0.002
Calcium	3.9	1.0	1.0
Lead	7.5	160	1200

Chelating resins have specialized functional groups that form coordinate bonds with certain metallic cations in solution. The functional groups are usually either weakly basic or weakly acidic. They usually have a relatively low capacity (usually 1 equivalent per liter or less) and exchange ions very slowly compared with traditional resins. They are most useful for exchanging low concentrations

of transition metals from solutions that have relatively very high concentrations of non chelated divalent and monovalent cations or monovalent ions. Chelating resins will not be discussed in detail in this paper.

Adsorbents include granular activated alumina and zeolites. Granular activated alumina is commonly used for lead removal. Activated alumina is an adsorbent rather than an ion exchanger. It has limited capacity for lead, but it is often capable of reducing lead to very low concentrations. The exact mechanism of lead removal by activated alumina is not well documented, but probably includes both filtration and formation of coordinate (chelating) bonds. Lead removal by activated alumina will not be discussed in detail.

Ion Exchange Theory

Ion exchange resins are small (approximately 0.5 mm diameter) plastic beads. Typically, they are made from either styrene or acrylic polymers, crosslinked with divinylbenzene. The “co-polymers” are functionalized with acidic or basic chemical groups such that the completed structure is a solid acid or base with a mobile counter ion. Ion exchange resins are classified according to the relative strength of their acid or base groups. They exhibit varying preferences for ions in solution depending on the functional group of the resin, and the nature and concentrations of the ions being exchanged, such as valence and hydrated ionic radius, and other factors.

“Strong” resins are essentially fully ionized, while “weak” resins are ionized only when in their salt form. This leads to several basic differences in behavior.

“Strong” resins can split salts, meaning they can operate in practically any pH environment and can remove weakly ionized salts from solution. They also exchange ions rapidly between the liquid phase and the solid polymer structure.

“Weak” resins, when in their non-ionized form, can only neutralize acids or bases according to their immobile functional group (weak cation resins can only neutralize alkalinity, while weak anion resins can only neutralize acidity). When in their salt form, weak resins are true ion exchangers and are nearly as fully ionized as their “strong” counterparts.

The terms Relative Affinity and Selectivity refer to the preference of an ion exchange resin for one ion over another. The selectivity relationships between various ions can be quantified using the mass action relationships in a manner similar to the equilibrium expression used to define acid and base ionization constants and solubility products. In the case of ion exchange resins, the constants are referred to as Selectivity coefficients and they always include the two ions involved. These relationships can be combined algebraically to derive others, for example $K_{A/B} * K_{B/C} \rightarrow K_{A/C}$.

SAC (strong acid cation) resin has an internal ion concentration of about 2 equivalents per liter. SAC resin has a greater affinity for almost every other cation than the hydrogen ion. Hydrogen form SAC resin shrinks about 5 to 10% as it exchanges hydrogen ions for most other cations. SAC resin has relatively high affinity for lead. However, high concentrations of sodium (and other ions) interfere with lead removal, and lead is difficult to regenerate off the spent resin.

WAC (weak acid cation) resin has an internal ion concentration of about 4 equivalents per liter when in the hydrogen form. It prefers the hydrogen ion more than every other type of cation. The hydrogen form of WAC resin is only slightly ionized. This means that the resin can not exchange ions rapidly. Compared to SAC, the hydrogen form WAC resin has very slow kinetics. Due to their extreme affinity for hydrogen ions, WAC resins in the hydrogen form only remove cations when there is sufficient alkalinity present to neutralize the hydrogen liberated during the exchange. The result is that

in many situations, hydrogen form WAC resin tends to remove cations inefficiently, often leaving significant amounts of a divalent contaminant.

Since hydrogen form WAC resin cannot effectively remove lead in most cases, at least part of the resin's capacity has to be in the salt form. Sodium form WAC resin is a good ion exchanger and is known to have very a high selectivity for lead. Hydrogen form WAC resin swells about 100% when converted to the salt form by use of sodium hydroxide or other base. Therefore, the sodium form WAC resin has an internal ion concentration of about 2 normal. However, regeneration involves both acid and caustic, and the resin cannot operate well at a low solution pH (below 6).

WAC resin has a much higher affinity for lead than SAC resin and its sodium form WAC capacity is relatively unaffected by the concentration of monovalent cations such as sodium. It can operate in solutions that have much higher TDS (total dissolved solids) than SAC resins. However, lead cations do not normally exist at the pHs where WAC resins are effective.

Column Tests

Since we are stressing the importance of performing bench scale pilot testing for any contaminant where operating data is not already well known, it is worthwhile to include a few words about the setup and operation of ion exchange columns. If there is only one thing that the reader should remember from this paper, it is to document what was done. All too often investigators neglect to document how they achieved success (or even more importantly failure) and those who follow in their footsteps are forced to start over. Following are a few words of advice.

First, characterize the wastewater to be studied to make sure that it is similar to the preliminary analysis. As a minimum, check for lead and other contaminants of interest such as hardness, alkalinity, inorganic ions such as sodium, chloride, and sulfate, pH, conductivity, suspended solids, and the pH point at which precipitation of lead occurs. Perform other tests that may be helpful.

Typical laboratory ion exchange columns are 1 inch diameter, and hold anywhere from 50 to 250 mls of resin, although smaller columns are sometimes used. In certain cases, such as when there is only a limited sample volume, small columns can be made from burettes by placing a small wad glass wool in the bottom. The solution is pumped or siphoned through the columns at 0.25 to 0.5 bed volumes per minute. The flow rate through the columns should be held constant. Flow rates greater than 0.5 bed volumes per minute often cause problems such as premature breakthrough, high pressure loss, and resin fouling.

The column should be operated long enough to obtain meaningful long-term information about the leakage of various ions including the contaminant of interest. It often requires tens or hundreds of bed volumes for an ion exchange column to stabilize. Very short column runs (less than 10 bed volumes of product collected) often give misleading results. However, short column runs can often give a quick yes or no answer to determine whether or not ion exchange is an appropriate technology for a particular application.

Longer duration column tests that include cycling between exhaustion and regeneration should be performed to verify operating capacity and column throughput. Here, the column is operated until it exhausts and the effluent concentration of the contaminant of interest has increased to a high concentration. This should be at least twice the steady state leakage and preferably around 50% of the inlet concentration. Unfortunately, the exhaustion of lab columns does not occur any more rapidly than full sized exchangers and it can take many days to obtain capacity data.

A minimum of 10 data points along the expected exhaustion curve should be taken in order to obtain a realistic profile of the effluent. If the expected run length will be several days (or longer), take three or four samples during the first 24 hours and then one or two per day afterwards. As a minimum, take data on conductivity and pH long enough to know that the outlet is stable with respect to the inlet. Record as much data as practical, no matter how obvious or unimportant it may seem at the time. Later, when you review your notes, even something as unimportant as recording the time of day or raw water and room temperatures could be helpful.

If the initial effluent concentrations for the contaminant, whose removal is of interest, are higher than the treatment objective, it may be worth adding a second polisher column to the setup in series with the first column. This will depend on how close to the limit the concentrations are. If the process will involve pretreatment of the solution prior to the ion exchange columns (pH adjustment, filtration, etc.), this should also be done to the solution sample before it is used in the lab test.

Column Regeneration

Column regeneration can be a very complicated task, more so than simply running exhaustion tests. Flow rates and solution concentrations are significantly different and more critical for regeneration experiments than for exhaustions. Even when analysis and other measurements are carefully made, mass balances frequently do not come anywhere close to balancing. In this case, a mass balance generally consists of a calculation of the mass of contaminant loaded on to the resin during the exhaustion cycle compared to the mass removed from the resin during regeneration.

LEAD REMOVAL USING ION EXCHANGE

Figure 1 shows the lead removal performance of an H-form weak acid resin in a low hardness, low alkalinity water. The results clearly show that lead removal is sensitive to flow rate through the resin. Figure 2 shows the lead removal performance of an H-form weak acid resin in a high alkalinity, high hardness solution. Due to the alkalinity, much of the lead is not dissolved; the column is removing lead by filtration, as well as by ion exchange. The removal efficiency depends to a significant amount on the ability of the device to act as a filter rather than as an ion exchanger. The overall removal of lead is extremely variable and probably depends on minor changes in the flow rate through the column more than any other factor. Certainly, the leakage mechanism does not seem to be related to the ion exchange capacity of the resin.

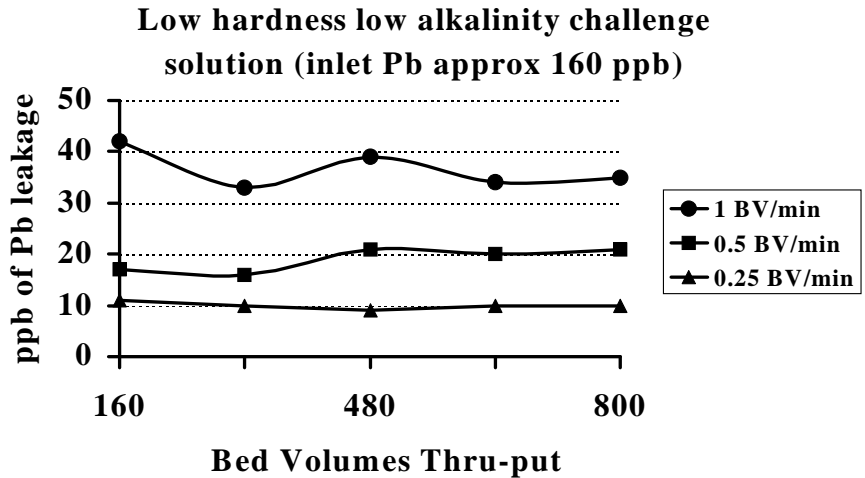


Figure 1 – The Effect of Flow Rate on Lead Removal by H-Form WAC Resin

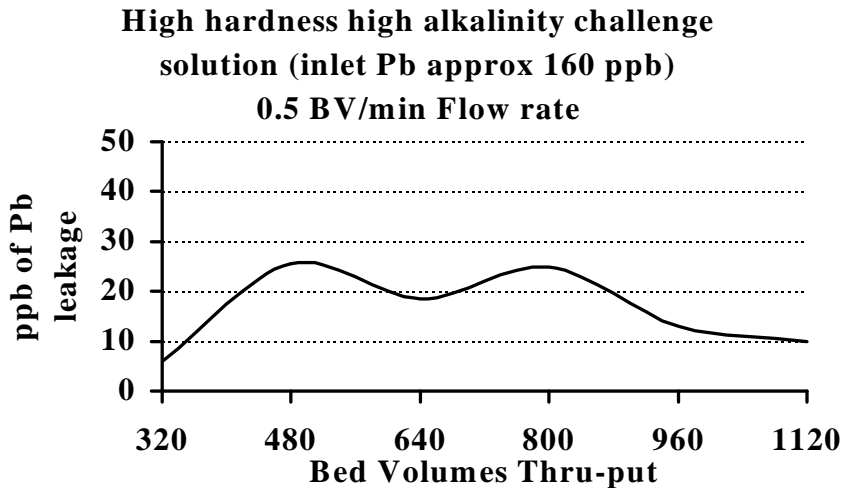


Figure 2 – Lead Removal by H-Form WAC Resin as a Function of Bed Volume Passed

RESINTECH LEAD EXPERIMENTS

At ResinTech, we performed an extensive bench scale study that included lead removal. The column studies included multiple exhaustion cycles for both SAC and WAC resins, with primary and polisher columns. We also performed regeneration experiments to try to determine the best way to remove lead and other metals from exhausted ion exchange resins. Several hundred of gallons of actual industrial wastewater were used containing approximately 1,000 ppm TDS, pH of 2, and about 12 part per million (as calcium carbonate) of divalent cations. The sum of the divalent cations was about 20% lead and 80% manganese with significant minor amounts of calcium, nickel, and copper, plus trace levels of several other divalent cations. The dominant anion was chloride, with minor amounts of nitrate and almost no sulfates or alkalinity present.

Two parallel experiments were set up, one with a strong acid cation (SAC) resin and one with weak acid cation (WAC) resin. Each experiment consisted of a primary column and a polisher column. All exhaustion tests were performed with virgin resins at a flow rate of 0.5 bed volumes per minute. A number of column exhaustions were performed with each resin. In a separate series of regeneration experiments, the resins were preloaded with 20% lead and 80% manganese.

Exhaustion of SAC Resin

Several sets of SAC resin columns were run at 0.5 bed volumes per minute in a “leadlag” fashion, with a primary and a polishing column. Typical performance is shown in Figure 3. Based on the sum of divalent cations in the influent, the calculated column throughput should have been approximately 8,500 bed volumes. In the first exhaustion, the primary column was run for a total of 5,200 bed volumes and was stopped when the particulate matter at the top of the primary column reached the point where the column plugged up. It should be noted that the influent was completely crystal clear and that the precipitant formed as the solution hit the resin bed.

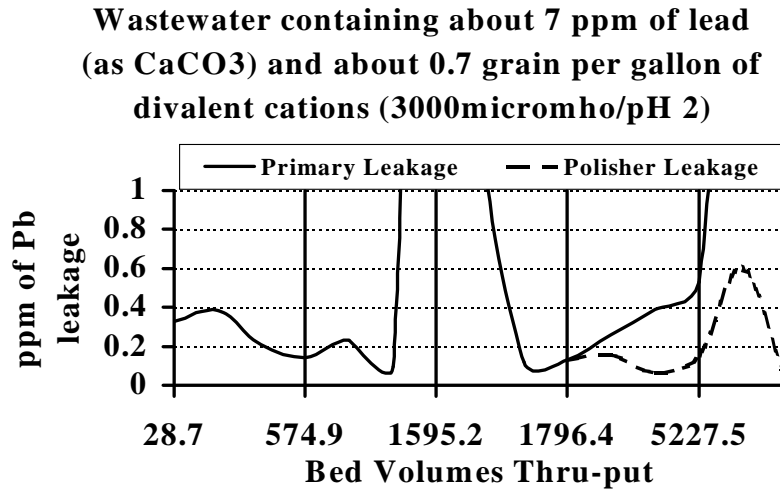


Figure 3 – Lead Removal by Na form SAC Resin

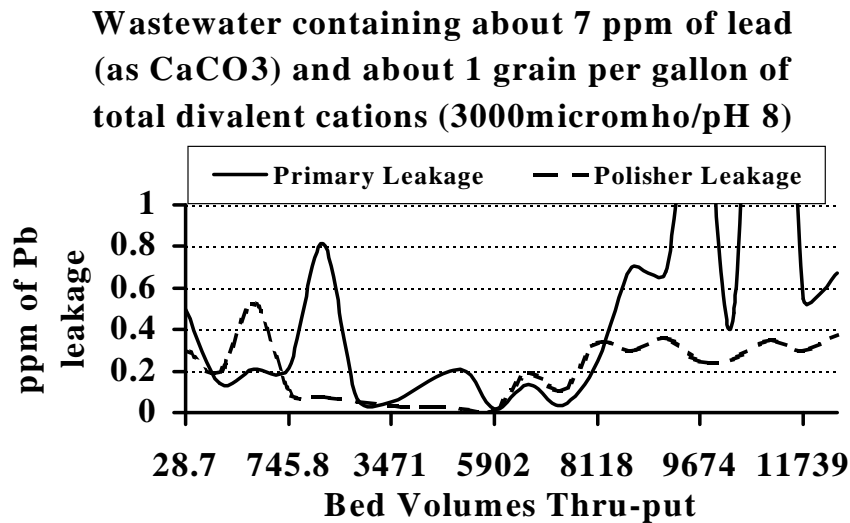
In the next set of experiments, the influent solution was prefiltered through a 0.5 micron nominal string wound cartridge filter. This test was terminated after 4,300 bed volumes, due to lack of solution. However, the same phenomenon occurred as in the first set of tests. The resin bed plugged up with particulate matter at the surface of the primary column. Leakage was quite similar to the first exhaustion.

Since the leakage of lead from the primary and polishing columns were similar, and the primary column developed a distinct crud cap, we suspected that the leakage mechanism was due to particulate matter, rather than ionic lead. We used 0.45 micron absolute syringe filtration prior to lead analysis to try to distinguish between particulate and dissolved lead. The syringe filtered effluents were all below the ICP detection limit of approximately 0.07 ppm.

Weak Acid Cation Experiments

WAC resin is only able to operate when sufficient alkalinity exists to drive a neutralization reaction or when the weak acid resin is in the salt form. One experiment was performed with the WAC resin in the sodium form but the pH of the inlet solution was left at 2. At first, the increase of pH across the sodium form WAC resin caused much of the lead to precipitate. The precipitated lead rapidly plugged up the surface of the primary WAC resin bed. As the experiment continued the hydrogen ion of the pH 2 solution began to convert the WAC resin into the hydrogen form. When the resin returned to the hydrogen form, it dumped all of the lead that was previously loaded, resulting in no net lead removal. Still, it took quite a lot of bed volumes through the WAC resin before it dumped the lead. At best, this would be a risky way to operate.

Figure 4 – Lead Removal by Na form WAC Resin



For the next series of tests, the inlet pH was increased to approximately 8 and the solution was well filtered before putting it through the columns. The primary and polishing WAC columns reached more than 12,000 bed volumes of throughput. The theoretical loading approached that of the resins total capacity. However, it was clear from the color change of the resin in the primary column that the resin was only about half exhausted. Again, it was visually obvious that most of the lead was being removed by filtration in a crud layer at the surface of the primary column.

A third WAC run was performed also pH 8 but with prefiltration through a 0.45 micron nominal string wound filter. However, the same phenomenon occurred and the primary column plugged up with precipitants. The primary mechanism of removal still appeared to be filtration rather than ion exchange, as observed by the crud layer buildup on the surface of resin bed. The primary and polishing column leakages were very similar. Again, the syringe filtered effluents confirmed that the leakage of ionic lead was below the ICP detection limit of less than 0.07 ppm.

Our conclusion from these experiments is that both SAC and WAC resins are suitable for removal of ionic lead. However, the primary mechanism of removal at certain alkaline pHs is filtration rather ion exchange. We also conclude that 0.5 micron nominal string wound cartridges were not suitable for removing the particulate lead from the solution, suggesting that the particle size was quite small or that string wound cartridges do not work very well.

It should also be noted that these tests were performed over a period of approximately four months and there were several time periods where the columns sat idle. During this time frame, the resins grew mold on the surface of the resin beds. This is fairly typical of other experiences that we have had with long term operation of ion exchange systems. Even though the wastewater contained a lot of metals at low pH and also contained at least 100 ppm of hydrogen peroxide, the stagnant columns were able to support biological growth. This is one of the more troublesome aspects of trying to operate columns for very long periods of time. Regardless of the theoretical throughput, it seems likely that column operation beyond about 5,000 or 10,000 bed volumes is seldom going to be practical for reasons of resin bed pluggage and/or biological growth.

Regeneration Experiments

In order to determine the ease of removing lead from ion exchange resins, we performed a separate series of experiments with both WAC and SAC resin. We exposed the two resins to equal amounts of lead and manganese, such that the resins were about 50% exhausted into the lead form and 50% exhausted into the manganese form. We then regenerated them using various chemical solutions.

According to theory, the highest chemical concentration that does not cause precipitation should work best as a regenerant for the SAC. However, for WAC resin, the concentration of acid or acid salt should not make much difference provided sufficient hydrogen ions are present fully convert the resin to the hydrogen form.

Conventional Wisdom

Since SAC resin is always fully ionized, it can be regenerated by a variety of solutions including neutral salts as well as acids and bases. WAC resin cannot be regenerated by neutral salts or by bases; it can only be regenerated by acids. When the salt form of a WAC resin is desired, a WAC resin must be forced into the salt form by use of bases such as sodium hydroxide after its regenerated with acid.

For SAC resin regeneration, the use of a sodium salt has three advantages over acid. First, it is a stronger regenerant with respect to lead removal. Second, since concentration is very important when using a monovalent ion to displace a divalent ion, it is important to use a relatively high solution concentration, which is safer and easier to do with sodium chloride than with acid. Third, salt is much less expensive than acid.

Since WAC resins cannot be regenerated with neutral salts, the regeneration is performed with acid, and then the resin is neutralized with caustic or with some other alkaline solution. Since the resin prefers hydrogen over all other cations, a low concentration of regenerant should work at least as well as a high concentration. However, contact time is very important, in order to allow the resin sufficient time to fully react with the regenerated acid. Therefore, a lower concentration acid can be beneficial.

Reality

In fact, two competing factors preclude the use of high regenerant concentrations. First, lead is a rather large and heavy ion, and it does not leave the resin rapidly during regeneration; thus, contact time, which is controlled by regenerant flow rate, is an important parameter. High regenerant concentrations lead to smaller solution volumes, which are difficult to pass through the resin slowly. Secondly, lead salts, such as those formed by common regenerants are only sparingly soluble. Lead sulfate is very insoluble, while lead chloride is only sparingly soluble. In every regeneration experiment performed by ResinTech, high regenerant concentrations did not remove as much lead

from the resin as low concentrations did. It should also be noted that none of the regenerant solution was particularly effective at removing lead from the resin, and therefore in most applications regeneration of lead laden resins will not be practical with common regenerants unless some leakage in subsequent cycles can be tolerated since this would allow partial regeneration at economic levels. However, this was not studied. There are other regenerants that could be used but they are mostly impractical due to high cost or safety concerns.

When a contaminant such as lead must be removed and it is not known what form the lead will be in or what competing ions may be present, it is a good idea to perform a bench scale test

Strong Acid Cation Regeneration

The primary advantage of a SAC resin over a WAC resin is that it can often be regenerated with a neutral salt solution, as opposed to more expensive and difficult acids or bases. In the first series of experiments, we attempted to regenerate the resin with sodium chloride and sodium nitrate. Neither solution was very effective. The sodium nitrate was more effective than the sodium chloride and lower concentrations were more effective than higher concentrations. This is probably due to the solubility of lead chloride and the fact that lead is a very large, heavy ion that is not very fast moving. The longer contact time with the resin created by the lower solution concentrations is probably responsible for the better removal.

The next series of tests were performed with hydrochloric acid. These tests also confirmed that the removal of lead from the resin is much better at lower concentrations.

In all cases, the chemical dose required to remove most of the lead from the resin was enormous, resulting in rather impractical regenerations. It would probably be less expensive to dispose of the resin than to attempt to fully regenerate it. In no case did the regeneration remove as much as 90% of the lead that had been loaded on the resin. However, effective operation can be achieved even at low lead removal. For example, common water softeners typically operate at regeneration levels that leave 50% of the resin in the hardness form. This area will be looked at in a future effort.

Weak Acid Cation Regeneration

Since WAC resins cannot be regenerated with neutral salts, only acids were attempted. Since the nitrate salts of lead are soluble, we were not surprised to see that nitric acid was relatively effective in removing lead. Hydrochloric acid was not very effective. Even with nitric acid, very large doses were required to remove the bulk of the lead from the resin. However, the nitric acid regeneration is somewhat promising and, if we were to attempt to optimize regeneration in the future, this is one of the candidate acids we would look at in more detail.

It should be noted that nitric acid has significant drawbacks over hydrochloric acid in that it is more expensive and because it is a strong oxidant. Nitric acid can both damage the resin and in certain scenarios could create explosive mixtures with ion exchange resins. For these reasons, nitric acid is usually not considered a practical regenerant for ion exchange resins.

CONCLUSIONS

The technical difficulties involved in column tests for sparingly soluble contaminants such as lead make this type of lab work a frustrating experience.

The mechanism of lead removal is partly filtration partly by ion exchange in most applications. This is because lead carbonate is virtually completely insoluble and almost all water supplies contain at least some alkalinity, which can liberate carbonates.

Regeneration of lead from exhausted resins was not practical in most cases because of the very large chemical and waste volumes produced

Unless the TDS and/or hardness concentrations are very high, it is probably just as well to use a strong acid cation (SAC) as a weak acid cation (WAC) resin.

If a stringent guarantee for lead removal is required it should be made mandatory to perform bench scale tests. The treatment system must include filtration and the filtration must be an absolute cutoff size significantly smaller than 1 μm .

It is important to remember that an ion exchange column is designed to remove only ions and that with wastewater contaminants, such as lead, the real story is that these types of contaminants are frequently not in an ionic form or may interact with and then precipitate in the resin. In such cases, ion exchange may not be suitable as the single technology for their removal.