

Basic Ion Exchange for Residential Water Treatment

Part 3

By Michael C. Keller

This third installment (see our February and March issues for parts one and two, respectively) of Mike Keller's popular WQA session talks about the removal of specific contaminants.

Other metals

Up to this point, this article has discussed the removal of positively charged ions such as calcium, magnesium and iron. Cation softening resin will remove most positively charged ions in water. Metals like lead, radium, barium, aluminum and copper are effectively removed with softening resin. There are, however, exceptions and guidelines to be aware of in these applications.

Lead Pb

Lead is generally found in water due to the corrosion of lead from solder and pipes found in many older buildings. In most cases, the corrosion is due to an acidic environment (pH below seven). At those pH levels, standard softening resin will remove lead very readily. Please remember that if lead removal is performed at the point of entry (POE), any plumbing past the water treatment system may corrode, adding more lead to the water. If the lead is a corrosion product from solder and/or pipes, point of use (POU) equipment is recommended.

The first treatment that should be considered is pH adjustment at POE. By increasing the pH, the water should be less corrosive and the lead levels may return to acceptable limits. This may eliminate the need for any additional treatment methods. Lead has a high molecular weight and a valence of 2+, so it has a very high affinity toward resin. Lead will displace most positively charged metal

ions from the resin. During the regeneration process, where salt is used, the lead will not strip easily. Even strong acids do not strip lead efficiently from the resin. Softening resin will eventually foul with lead. In most cases, this fouling will occur over a long period of time, since it is customarily found in low concentrations in water. If the pH of water is above seven, lead may be in a precipitated non-ionic colloidal form, which cannot be removed by an ion exchange process. This type of lead must be physically filtered and may require the use of a submicron filter. If the pH of water is 10 or higher, the lead can found as a plumbate. This type of lead has a negative charge. An anion would have to be utilized to remove this form. The U.S. EPA has set a primary drinking water standard of 0.015 ppm (15 ppb).

Radium Ra/Radon Rn

Radium is one of the more common radionuclides in water. It is formed when its unstable parent, thorium, undergoes a transformation in which its nucleus emits a particle of energy, producing radium. Radium has a more stable nucleus than thorium; however, the radium nucleus is also unstable and will decay, producing radon. The emission of a particle with a transfer of energy produces radiation. Alpha, beta and gamma are the most typical forms of radiation. The length of time that passes to cause half of a material to transform is called the half-life (see Table 8). The half-life of radium is 1,620 years, while the half-life of radon is only 3.8 days.

Alpha decay is the least haz-

ardous form of radiation. The particle released has a short range and will not penetrate skin. If the particles of radiation are ingested, inhaled or come into contact with an open wound, they can be a health risk.

Beta decay is more dangerous. The particle released has more penetrating power than alpha decay and will penetrate skin. Beta decay is an external radiation health hazard as well as an internal health hazard.

Gamma radiation is the most dangerous. The transformation of the parent nucleus involves the release of gamma ray or photon of electromagnetic energy. Gamma rays have a much higher penetrating power than alpha or beta radiation, making them a significant health risk.

Radium is an alkaline earth metal

Table 8. Uranium decomposition

Decomposes to:	Symbol	Half life
Uranium 238	U	4.5 x 10 ⁹ years
Thorium 234	Th	24 days
Protactinium 234	Pa	1.2 minutes
Uranium 234	U	2.5 x 10 ⁵ years
Thorium 230	Th	7.7 x 10 ⁴ years
Radium 226	Ra	1,620 years
Radium 222	Rn	3.8 days
Polonium 218	Po	3.1 minutes
Lead 214	Pb	26.8 minutes
Bismuth 214	Bi	19.7 minutes
Polonium 214	Po	1.6 x 10 ⁻⁴ seconds
Lead 210	Pb	22.3 years
Bismuth 210	Bi	5 days
Polonium 210	Po	138 days
Lead 206	Pb	stable; no further decomposition

that is a divalent cation much like calcium and magnesium, the primary components of hardness. Radium is naturally occurring and is typically found in groundwater as two isotopes, Ra 226 and Ra 228. Radium enters the ground water through a leaching process when water contacts rock deposits containing radium. Radium levels also tend to be elevated in areas where phosphates are mined (Florida) or in run-off from uranium mines (Colorado and New Mexico). The U.S. EPA has set a primary drinking water standard of five picocuries/l (pCi/l) for radium 226 plus 228, since it is a carcinogen. This concentration translates to 0.000005 mg/l (5 parts per trillion) as radium 226. Many water supplies have a measurable amount of radium, albeit well below the U.S. EPA limits. A recent study performed in southern New Jersey found that one third of 170 wells had a radium level exceeding the U.S. EPA limit. Other areas where radium levels frequently exceed the maximum contaminate level (MCL) are Iowa, Illinois and Wisconsin. Radium emits alpha, beta and gamma radiation.

There are a number of effective treatment methods for radium removal from water. The primary focus of removal will

be by cation ion exchange (softening). Radium is a divalent ion like calcium, however, it has a much higher molecular weight. Since the molecular weight of radium (226) is much greater than calcium (40.1), radium has a greater affinity to the cation ion exchange resin. Cation ion exchange resin should remove greater than 95 percent of radium in water. A water softener will continue to remove radium long after it no longer removes hardness. The radium ion will replace calcium and magnesium hardness on the ion exchange bed (see Table 9). When the softening system has reached exhaustion for hardness it is best to regenerate at this time, even though longer runs can be achieved if system goes to a radium breakthrough. Regenerating based on hardness capacity will help to prevent a build-up of excessive radium levels in the softener. It will also reduce the amount of radon formed upon the decomposition of radium and will also prevent hardness scale from forming in the distribution system.

Care must be taken when utilizing a valve that has a demand initiated regeneration (DIR). A water softener used for radium removal should not be allowed to stand for long period in the partially

exhausted state. Radon gas can develop from the decomposition of radium on the resin. Softening units should be flushed with a minimum of two bedvolumes of water (16-gallons/cubic foot) or regenerated before use, if the unit has been dormant for more than a week. Both sodium chloride (NaCl) and potassium chloride (KCl) will strip radium from the cation softening resin.

Potassium chloride is an alternative regenerant to sodium chloride. KCl is able to displace the radium to a greater degree earlier in the regeneration than NaCl. KCl has a better regeneration capability than NaCl since the potassium (K) has a higher affinity to the softening resin than sodium. The disadvantages of KCl are the additional cost (versus NaCl) and the additional KCl required to produce an equivalent capacity to NaCl use.

Care must be taken when iron is found in the water with radium. Ion exchange softening will remove both of these ions when they are soluble and have a positive charge. Iron that builds up on the resin and precipitates as an iron oxide can adsorb radium. The sludge that is produced will be radioactive. The iron oxides will also blind exchange sites, ultimately reducing capacity. The iron can

either be removed prior to the softening resin or the resin bed should be kept clean with some type of resin cleaner for iron.

Disposal of the waste brine can normally be done to the sewer or septic system. This waste is considered a low level, naturally occurring, radioactive material, as such no additional radioactivity is being added to the environment. Some states or municipalities may have different regulations, like brine discharge to septic systems. In N.J., the waste brine cannot be discharged into a septic system. Instead, the waste brine must be sent to a separate dry well. Waste brine containing radium would be disposed of in the same fashion. Answers to regulatory questions can be obtained from the state EPA or the DEP. Manmade radioactive materials fall under the jurisdiction of the Nuclear Regulatory Commission (NRC) and a license is required for disposal.

People often incorrectly use radon and radium interchangeably. They are two different contaminants. In fact, radon is a daughter or progeny of radium and both have a different detection technique. The transformation of the radium nucleus causes radon, a gas, to be formed. The half-life of radon, as noted previously, is just under four days. Like radium, radon is a carcinogen and it emits both alpha and beta radiation. The related health effects occur when radon is inhaled and/or consumed orally. The National Cancer Institute says that radon is the second-leading cause of lung cancer after cigarettes. The risk of illness brought about by radon-bearing water is considered to be low. The EPA in N.J. does not make any recommendation for radon removal from water. The amount of radon the body comes into contact with due to water is small. There is no U.S. EPA drinking water standard (for radon) at this time, however, that agency is proposing one. Water Quality Association sources say the standard will probably range between 300 and 1,000 pCi/l, if such a standard is adopted. The greatest health risk comes from radon found in the air. The largest percentage of the radon found in a house will emanate from the ground. Removing radon from air is beyond the scope of this article; however, the following website has information on reduction techniques and approximate costs: www.physics.isu.edu/radinf/radon2.htm. Radium cannot be removed from water by ion exchange softening. As a matter of fact, most of the treatment methods that remove radium from water will not remove radon and vice versa.

There are two primary methods for removing radon from water: carbon filtration and aeration. Carbon will remove

Table 9. Radium treatment methods

Media	Removal (%)	Regeneration	Comments
Ion exchange softening	>95	NaCl or KCl	Run to hardness break
Reverse osmosis	>90	None	May need to pretreat for hardness, cost effective for POU
Lime softening	75	Backwash filter	A municipal treatment; possible disposal problem; removal better at pH >10
Manganese greensand	50	Backwash/KMnO ₄	Treat levels <10 pCi/l
MnO ₂ adsorbent	50-75	None, permanently held by MnO ₂ ; backwash post filter	Problem with disposal; Silt, dirt and iron fouling; low cost; municipal treatment
Activated alumina	70	HCl/NaOH	Municipal treatment; best on water with pH >8
Alumina	80	H ₂ SO ₄ /BaCl ₂	Municipal treatment; much longer service cycle than plain alumina
Other adsorbents	>95		Disposal problem since Ra capacity is so high

the radon from water with varying degrees of success. Coconut shell carbon has the characteristics required to remove radon, while the coal-based carbons may not be as effective. A major coal-base carbon manufacturer does not recommend the use of carbon for radon removal. Contact your local carbon sales representative. Typically the unit is installed at the POE so the whole can be treated. Once radon-bearing water is exposed to the air, radon gas will be released and can be inhaled, so whole house treatment is recommended. The WQA recommends that carbon can be used in applications where radon levels are less than 5,000 pCi/l. The carbon unit can give off low levels of radiation, therefore it is further recommended that an area around the unit be fenced off. The local landfill and/or the EPA or DEP in your area should be consulted for proper disposal recommendations.

Aeration is probably the most effective method for treating water with radon. Removal efficiencies run from 65-95 percent. Water temperature along with water to air contact play important roles. Henry's Constant, a numerical system evaluating how easily a compound can be removed through aeration, is high for radon (see Table 10). The greater the Henry's Constant value, the more easily the compound can be removed by aeration. This information was presented by BGC Technologies in Stanford, Conn. As water is aerated, radon will be removed from the water into the air. The air is then vented to the outside of the house. The vent should be high enough so the ra-

don-bearing air cannot come into contact with people. Iron should be removed from the water prior to the aeration.

If radon is present in residential water, the homeowner should check for radon gas in the house and take appropriate action if it is found to be present. The EPA and DEP are good sources for information concerning all aspects of radium and radon from uptake to proper disposal.

Barium

Barium is another metal that the U.S. EPA regulates with a primary drinking water standard of 1 ppm. Barium is a divalent (two positive charges) cation that is effectively removed by softening resin. Barium will precipitate as barium sulfate at very low concentrations (approximately two ppm). If the sulfate concentration in water is less than one ppm, there is very little chance that barium sulfate will precipitate and the softening resin pick up and release barium. If greater than two ppm, the portion of barium greater than that amount will be in a colloidal, non-ionized form. Softening resin will not remove this type of barium and physical filtration must be used. If the sulfate is greater than two ppm and the barium is less than two ppm, the barium will be picked up by the resin. It will concentrate on the resin and once it exceeds the solubility point, it will precipitate and foul the resin. The bottom line is that barium will eventually foul softening resin and such fouling is permanent. The resin should be replaced.

Aluminum

Aluminum is another common metal found in water, since municipalities feed alum (aluminum sulfate) into the water as a coagulant to remove turbidity and suspended solids. If alum is overfed, aluminum will be found in the water. Aluminum can be removed by standard softening resin. It is not released efficiently with salt, so the resin will foul. This fouling will usually occur over a long period of time (since the aluminum will be found in low concentrations). Excessive amounts of aluminum can be identified as a gelatinous precipitate that coats the resin. This will make the exchange sites inaccessible and cause poor hydraulic properties. A stronger acid (like phosphoric) will strip the aluminum from the resin. Reducing agents like sodium hydrosulfite and sodium bisulfite will not effectively strip aluminum from the resin.

Copper

Soluble copper can be removed by softening resin. Copper will displace calcium from the resin. To ensure the system will remove the soluble copper, it should be sized to remove hardness. Copper can oxidize, which can foul the softening resin. To test for copper on the resin, take a small sample and treat with hydrochloric acid. If the acid turns a blue or green color, copper is probably present (although in some cases, copper may not cause the acid solution to turn color). The only true way to check for copper is to quantitatively run a copper analysis by atomic adsorption or some other method. Phosphoric acid should strip copper from a copper-fouled resin.

Most of these metal removal applications can cause fouling of the resin. Strong acids are the most effective cleaning agents. When utilizing one of these products, the softening resin may be converted to the hydrogen form. Resin left in this form will have an effluent low in pH; therefore, be sure to fully regenerate the resin back to the sodium form with salt. The equipment and plumbing must also be compatible to any acid cleaning application.

It is important to mention that a mixture of chlorine and certain types of metal such as copper will cause the resin to breakdown at a greater rate. The metal acts as a catalyst and enhances the oxidative properties of chlorine.

Ammonia

The frequency at which questions are being asked concerning ammonia (NH₃) removal is increasing. Ammonia will find its way into the water supply from runoff in agricultural areas, indus-

Table 10. Henry's Constant

Gas	Henry's Constant
Oxygen	43,000
Radon	2,260
Carbon Dioxide	1,510
Benzene	240

trial waste and potentially even municipal water systems that utilize chloramines. Most fertilizers use a nitrogen-based substance such as nitrate or ammonia. These compounds act as nutrients for plants. Industrially, ammonia can be used as a refrigerant or in the manufacturing process of many chemicals. Municipalities will feed ammonia into the water along with chlorine to form chloramines used for disinfection. Chloramine will not form trihalomethane like chlorine. It is important to remember that trihalomethane is considered to be carcinogenic. Ammonia is fed in excess to ensure that monochloramine is formed. A one:three or a one:four ratio of ammonia nitrogen to chlorine is generally used in this process. Since an excess of ammonia is used, it may be found in trace amounts.

Ammonia (NH₃) is also a cation, since it has one positive charge. Ammonia will not be removed by softening resin. A hydrogen form cation resin must be utilized to effectively.

Maintaining IX resin based systems

Ion exchange resins use a process based on ion selectivity. In this method, ions of greater preference will displace ions of lower preference. For example, in water softening, objectionable ions such as calcium and magnesium are exchanged onto the resin and sodium or potassium ions are released in their place. To regenerate the bed a strong regenerate solution must pass through it. In water softening, a five percent to 26 percent of sodium chloride (NaCl) or potassium chloride (KCl) is used. Because of high concentrations of sodium potassium, hardness is displaced from the resin. In this way, ion resin can be used over and over again. The resin will also act as a filter to incoming water, although this is not recommended. When substances like oil, grease, metal precipitates (iron, manganese, copper, etc.), high molecular weight metals (aluminum, lead, etc.), chlorine, organics (tannins, polymers etc.), silt and sand come in contact with resin, the exchange mechanism can become inhibited. These factors can produce poor water quality, shorter service cycles, lower flow rates and shorten the

useful life of the resin.

Properly manufactured eight percent cross linked softening resin can have a life expectancy in excess of 20 years when placed in unstressed situations. Anion resins do not last as long with a life expectancy of four to seven years. When fouling and /or degradation occurs, the resin can either be thrown out or cleaned and put back into service. There are many different forms of fouling/degradation that will manifest in or on the ion exchange resin. The following section deals with cleaning and preventative maintenance of ion exchange systems.

Iron fouling

Probably the greatest threat to softening resin is iron fouling. Cation resin will exchange ferrous iron (Fe²⁺) for sodium onto its structure. As long as iron stays in the ferrous form, salt will be able to regenerate the iron off the resin. If there are any oxidizing agents like chlorine and/or oxygen in the water, the ferrous iron (Fe²⁺) can be oxidized to ferric iron (Fe³⁺) (rust). This is known as precipitation and can occur both on the surface as well as on the internal matrix of the bead. Ferric iron cannot be regenerated from the resin simply with salt. A quick test procedure for iron fouling is to obtain approximately one ounce (50gm) of resin and place it into a beaker. Add the same amount of HCl (muriatic or hypochloric acid) to the beaker and let it sit for two hours. If the solution is heated, the contact time can be shorter. The acid will turn from clear to a yellow to tea color. The darker the color, the heavier the iron fouling. Reducing agents, such as sodium hydrosulfite and sodium bisulfite, can be effectively used to clean iron-fouled beds (see Table 11). One half pound to one pound of reducing agent can be added to one gallon of water. This mixture is immediately poured into the brine well, or directly into the salt and will treat one cubic foot of resin. These compounds decompose rapidly and should be used immediately after mixing. Always remember to add the chemical to the water (not water to the chemical). A manual regeneration is performed to clean the bed.

Acids, such as HCl, phosphoric acid and citric acid are commonly used to clean iron-fouled resin beds. These acids will generally produce better results than the hydrosulfite and bisulfite cleaning compounds. However, precautions must be taken when using acid. Hydrochloric acid is very corrosive. In most instances when HCl comes in contact with a metal surface, corrosion will occur. When an acid is used, some of the exchange sites

Table 11. Iron cleaning chemicals—reducing agents

Sodium bisulfate	NaHSO ₃
Sodium hydrosulfite	Ha ₂ S ₂ O ₄ + 2H ₂ O
Hydrochloric acid	HCl
Phosphoric acid	H ₃ PO ₄
Citric acid	OHCCH ₂ (COOH) ₃

on the resin will be converted to the hydrogen form. If the resin is not fully regenerated to the sodium form with salt, a low pH can result during the first service cycle after cleaning. A double regeneration with salt will usually prevent a low pH from occurring.

The most effective way to keep iron fouling to a minimum is the use of a salt that contains a cleaning agent. There are salts on the market that contain one or more of the following cleaning agents: hydrosulfite, bisulfite, citric acid and phosphoric acid. When salt bearing one of these compounds is used, the resin will be cleaned during the regeneration. These compounds are not harmful and will help increase the life of the softening resin.

Filterable solids

Ion exchange resin can act as a physical filter. Although not recommended for this application, particles of dirt, precipitated metals (rust), silt, etc. can be filtered out by a resin bed. Cation resin can filter particles down to a size of approximately 40 microns. Finer mesh resin systems can filter even finer particles. If these particles are not backwashed from the systems, increased pressure drop and channeling can occur, resulting in poor system performance. Most ion exchange resin systems require a 10-15 minute backwash. Lower backwash times can be used on systems that have prefiltration for suspended foulants in the influent water. The bed should be expanded a minimum of 50 percent although there are exceptions to this rule. If the bed is already experiencing pressure drop and channeling, an extended and/or increased backwash flow should be used to clean the bed. If the bed is severely fouled, an air lance may be required to break up the bed.

Oil and grease

Oil and grease entering a water treatment system can be filtered out to some degree by the ion exchange system, whether it is an anion or a cation. These substances will coat the resin causing short service cycles and poor product water quality. Dirt particles and broken beads will also cling to oil and grease, causing in-

creased pressure drop and channeling. A non-ionic surfactant (any detergent that is not cationic or anionic) can be used to clean a cation or anion resin. Agitating the resin while it is immersed in a warm detergent solution will enhance the cleaning process.

Organic fouling

Tannins in water can foul anion resin. This large organic molecule will pass through a softening resin without any detrimental effect. Tannins have a weak negative charge that will allow them to exchange onto anion resin. Once on the anion resin, they tend to migrate into the inner matrix of the bead and become very difficult to remove. Tannins will block exchange sites causing short service cycles.

The use of soda ash along with brine has been effective at cleaning organically fouled anion resin. By increasing the pH of the brine, tannins become more soluble. The beads will also swell, allowing better elution of the tannins from the resin. In industrial applications, a solution of brine and caustic (sodium hydroxide) can be used. Caustic is very corrosive and is not recommended for residential water treatment. If one of these alkaline brine solutions is not effective and the resin is going to be disposed, chlorination can be used as a "last ditch" effort to clean the resin. Place four ounces of household bleach in the brine well and pass it through the anion resin bed until a chlorine odor is detected in the effluent. The regeneration cycle should then be interrupted for two hours. After that time the regeneration can be completed. A second regeneration should then be performed to be certain that the bed is free of bleach. This should be used as a last resort. Chlorine will degrade the softening resin. The bed should be regenerated with salt prior to the introduction of bleach. Otherwise, metals that are oxidizable may precipitate and foul the unit.

Bacteria

Most municipal water treatment uses some type of disinfection. Disinfected water will not usually contribute to bacterial growth in an ion exchange system, untreated water may. Regeneration of the resin will usually keep bacterial treated with standard household bleach. This treatment is hard on the resin, but is a necessary evil. The treatment method is the same as treating an organically fouled resin (see previous paragraph).

Oxidation

The last topic to be discussed focuses on resin degradation instead of fouling.

Oxidizing agents such as chlorine will attack resin. There is no resin on the market that is totally chlorine tolerant, but there are resins that are more resistant. Standard softening resin is 8 percent crosslinked; the greater the crosslinking, the greater tolerance the resin has for chlorine. Chlorine attacks the skeletal structure of the resin, causing the resin to breakdown. A general rule that can be used is, for each one ppm of chlorine in the influent the resin's life will be reduced by half. Standard softening resin that is in constant contact with one ppm chlorine will have a life expectancy of seven - 10 years. It should be noted that applications operating at high temperatures or water that contains metals like copper (a catalytic reaction can occur between the oxidant and the metal) would degrade the resin at a faster rate. If resin turns to powder when rubbed between the index finger and thumb, it indicates the resin has been oxidized by chlorine. In severe cases, the bed will compress, causing increased pressure drop and channeling. There is no procedure to restore such resin to a usable condition. Once chlorine or any other oxidation has occurred, the resin must be replaced.

Correct cleaning and preventative maintenance procedures will help to prevent equipment downtime. It is also important to know the limitations of a given water treatment process and to stay within the guidelines. Following these recommendations will decrease service calls, increase the viability of resin-based systems and increase customer satisfaction. The cation resin will remove soluble positively charged ions from water. The bed of resin will also remove dirt and other debris through physical filtration. The buildup of solids must be kept to a minimum, as channeling and/or pressure drop will result.

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This is Part 3 in a series. Watch for Part 4 in an upcoming issue.