Basic Ion Exchange for Residential Water Treatment

Part 1

By Michael C. Keller

When dealing with residential water treatment there are two basic classifications of water: groundwater and surface water. Any body of water exposed to the atmosphere is designated as surface water. Examples of surface waters include lakes, ponds, reservoirs, rivers, oceans and seas. Groundwater is self-explanatory and includes all water sources found underground. Rain and snow replenish these water sources. Precipitation forms in clouds when water condenses around dust particles. When the clouds become saturated with water, precipitation occurs. As rain passes through the atmosphere, it picks up gasses such as carbon dioxide, sulfur dioxide and oxygen. Many of the gasses assimilated by a drop of rain are acidic in nature or react with other compounds to form acids and this is why rain water will generally have a pH below seven. When a drop of water reaches the surface of the Earth, it starts to pick up certain substances that it contacts. For example, as water percolates through the soil it may come in contact with a limestone (calcium carbonate) deposit. The calcium carbonate will react with CO₂ forming calcium bicarbonate, which is a primary constituent of hardness in water.

On the whole, surface water will have a lower dissolved solids content than groundwater. However, surface water will tend to have a higher degree of organic matter (tannins) and suspended solids (silt, sand, etc.). Water that seeps down through the soil is much more likely to come in contact with mineral deposits than water that runs off into a river. Depending upon the source of water, different types of treatment may be required. Surface water may not need to be softened, but it may need a filtration and tannin removal system. On the other hand, groundwater may have hardness and iron, so softening may be sufficient. This article deals with the treatment of water as it pertains primarily to ion exchange resin in residential systems. Other treatment applications are discussed when their probability of success is equal to or greater than that of an ion exchange system. It is important to contact the manufacturer for proper operating conditions and limitations.

History of ion exchange

In 1850, Thomas and Way performed some of the first scientific research that indicated the existence of an ion exchange process. It was observed that fertilizers would function better in certain soils. In their experiment, a solution of ammonium sulfate was passed through soil. The filtrate collected was composed of calcium sulfate instead of ammonium sulfate. The ability of some soils to attract ammonia in preference to other positively charged ions (in this case, calcium) made it more suitable for agricultural purposes. The importance of this discovery (in ion exchange terms) was not fully understood until later in that decade, when Eichhorn found that this reaction was reversible. These soils were known as zeolites. In 1905, synthetic sodium alumino silicates were manufactured. This was the first practical substance used to remove hardness in water. The alumino silicates have their drawbacks, since they dissolve in water when the pH drops below seven. They also have very little exchange capacity. An alumino silicate can obtain a capacity of only 10,000 to 15,000 grains using 10 lbs of salt.

These alumino silicates could also be treated with manganese chloride and regenerated with potassium permanaganate to form manganese greensand, which is used mainly for iron removal.

The next step in the evolution of ion exchange was the ability to sulfonate coal. In this process, the coal receives a functional group that is able to exchange positively charged ions in water. This exchange was also found to be reversible. What made this discovery important was the fact that the sulfonated coal operated in a greater pH range, 1 to 10. This made the sulfonated coal more versatile, enabling it to be used in many more industrial applications. The deficiency of this material is due to the fact that it has a lower capacity than the alumino silicate. When regenerated with 10 lbs NaCl/ cu.ft., the capacity obtained is only approximately 5,000 grains. A few years later, the phenol formaldehyde polymer was synthesized. This polymer was sulfonated to form a strong acid cation. Using the same base polymer, only functionalized with an amine (NH₃), produced the first weak base anion. When the cation was used in the hydrogen form and the anion was used in the free base form (OH⁻), deionized water could be produced. Unfortunately, these polymers could not hold up to high pH levels and would release high amounts of color.

It wasn’t until the end of World War II that a styrene and divinylbenzene poly-
mer was synthesized. This polymer was used to manufacture both strong acid cation and strong base anion. The base polymer was treated with sulfuric acid to make a strong acid cation. The anion was first chloromethylated and then aminated. This is the basis of today’s resins used in softening and deionization processes.

Eventually, the macroporous and acrylic resins were synthesized, with each resin having its own niche in the water treatment industry.

**The manufacturing process**

The cation/ion exchange manufacturing process consists of the following steps: polymerization, sulfonation, neutralization and rinse. In the polymerization process, two monomers (styrene and divinylbenzene, see Figure 1) which are insoluble in water are mixed in a suspension system by an impeller at a speed that breaks the mixture into small spheres. These spheres eventually harden, forming spherical plastic beads. This is known as copolymer, which is unfunctionalized. The copolymer must then be dried and screened to specification and then placed into a sulfonator.

In this step, the copolymer is treated with sulfuric acid. The combination of time, acid concentration and temperature produce a functionalized copolymer or cation resin. At this point, the cation resin is in the hydrogen form. Cation resin in this form still cannot be used for residential water treatment. If raw water is passed through this resin, a low pH will result, which is not acceptable in residential water treatment.

The hydrogen form resin must now be neutralized to the sodium form (see Figure 2). This is performed by passing NaOH (caustic) through the resin. The excess caustic is then rinsed from the resin. The cation resin can now soften water; however, the resin can still release taste, odor and color. This resin could be used in industrial softening applications, but not in potable water processes.

The final step involves the cleaning of the resin. This is performed by hot water washing and steaming the resin. This rinse process reduces the amount of organic compounds left in the resin from the manufacturing process. Taste and odor throw are reduced to insignificant levels. However, even with this post-treatment, some color throw may be observed. Generally, color throw can be eliminated after one regeneration on properly treated softening resin. Before the softening resin is shipped, it will undergo a quality control inspection (see Table 1).

The total capacity is the resin’s theoretical capacity. To convert milli-equivalents per milliliter (meq/ml) to a more recognizable unit, multiply meq/ml by 21.8 and the result will equal kilograms per cubic foot (Kgr/cu.ft.). New standard softening resin will have a theoretical capacity of approximately 41.4-43.6 Kgr/cu.ft. This capacity will only be realized on the initial service cycle running the unit to complete exhaustion. Once the resin has been through one complete exhaustion cycle, the theoretical capacity will never again by achieved.

The water retention is the amount of water that is found inside the bead. When the resin is received there should be no moisture in the drum, bag or box. However, standard softening resin is made up of approximately 44-48 percent water. If the resin is allowed to dry out, a 40 percent reduction in resin volume will result. The analysis may also give moisture content. This value takes into account all water, both inside and outside the bead. The moisture content should always be the same, or slightly higher than the water retention. Typically, the moisture content should fall within two percentage points of the water retention.

The bead count measures the percentage of whole perfect beads, whole but cracked beads and broken beads. Generally, an analysis will state whole and broken beads. The whole bead count is the percentage of whole perfect beads and whole cracked beads. The most important parameter is the broken bead content. Most manufacturers place a specification on this parameter of five percent maximum. Excessive amounts of broken beads will cause pressure drop and channeling in the bed. Cracked beads are less of a concern, but are still important. If these beads are put under enough stress, they can break. Once the cracked beads become broken, pressure drop and channeling can occur.

The screen distribution or particle size distribution is a parameter that is run to show bead size. Standard softening resin has a distribution of 16 U.S. standard mesh to 50 U.S. standard mesh. This equates to 0.3 mm to 1.2 mm in diameter. The percentage of ~50 mesh resin is important, since the finer the resin, the greater the pressure drop.

P H is important since it is an indication of whether or not the resin was properly neutralized and rinsed. Resin is soaked in a neutral brine solution. If the pH drops below seven, a portion of the softening resin is still in the hydrogen form. This occurs since the resin picks up the sodium and hydrogen is released in its place. The hydrogen combines with the chloride from the salt solution to form hydrochloric acid. If a high pH is detected, the NaOH (caustic) was not completely rinsed from the resin. The pH range for this test should fall between 6.5 and 9.5.

Resin can be packaged into one cu. ft. bags, seven cu.ft. drums, 20 cu.ft. boxes or 40 cu.ft. boxes. Other packaging is available upon request. Additional cost may be levied with different packaging.

**The softening process**

Hardness in water is best known for the bathtub ring that is causes. When soap comes in contact with calcium and magnesium, a curd forms. This precipitate will adhere to many surfaces and is very difficult to remove. Water spots on fixtures are brought about by the evaporation of water containing calcium and magnesium. The scale that is formed is very tenacious and difficult to clean. Industrially, hardness forms scale on pipes, boilers, heat exchangers and cooling towers. These deposits will reduce the heat transfer capabilities of a system as well as increase the cost of operating the system. If the scaling is extreme, flow through the pipes can be reduced or terminated. For these reasons, water softening is beneficial. It is obvious that as hardness increases so does the potential for scaling.
The WQA’s level of hardness guidelines are as follows:
- Less than 17.1 ppm as CaCO_3 (1 grain) is considered soft.
- 17.1 to 60 ppm as CaCO_3 is considered slightly hard.
- 60 to 120 ppm as CaCO_3 is considered moderately hard.
- 120 to 180 ppm as CaCO_3 is considered hard.
- Greater than 180 ppm as CaCO_3 is considered very hard.

Standard softening resin used in the residential water industry is eight percent crosslinked. This means that the polymer matrix is eight percent divinylbenzene (DVB). The balance of the resin is composed of styrene and sodium sulfite (SO_3^-Na^+), as it is manufactured. The SO_3^-Na^+ provides the functionality of the softening resin. This resin can range from black to a golden color depending on the manufacturer. By modifying the screen distribution to a finer mesh size, the softening resin becomes more efficient.

Gel-type softening resins are translucent (light will pass through bead) while macroporous softening resins are opaque. Any type of resin can be manufactured with different percentages of crosslinking. However, macroporous resins are usually manufactured to be stronger, requiring high crosslinking. The DVB concentration will generally run from 10 to 20 percent. With this greater crosslinking the resin becomes more resistant to oxidation from substances like chlorine. It is important to note there is no resin on the market that is chlorine resistant: all resins will be degraded by chlorine. Higher DVB crosslinking also allows the resin to hold up to higher water temperatures. The theoretical capacity of the 12 percent crosslinked macroporous resin will be approximately 2.2 meq/ml. Even though it has a higher theoretical capacity, the operating capacity will be similar to standard softening resin. This occurs because the crosslinking is much tighter, so the kinetics (rate of reaction) of the resin is slower. Think of the resin as a sponge: the exchange sites are located throughout the ion exchange bed. The exchange that takes place is not just a surface phenomenon, it happens throughout the whole bead. With the tighter crosslinking, the internal sites are not as accessible to the ions in the water, thereby giving a lower operating capacity. The water retention of the higher crosslinked resins will generally range between 38-42 percent. Higher crosslinked resins are generally more expensive than standard resins.

<table>
<thead>
<tr>
<th>Total capacity, meq/ml</th>
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<tr>
<td>Water retention percentage</td>
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<tr>
<td>Bead count percentage Whole</td>
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<td>Screen distribution percentage</td>
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<td>Mechanical strength, gm/beam</td>
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### Table 1. Parameters used to check resin quality

**Taste and odor are subjective tests. Sybron has put together a “taste and odor panel” that judge both of these parameters. Softening resin will either get a pass or a fail.**

*The mechanical strength test, which is also known as the Chatillon test, checks the bed’s strength. No specification is used, but the average gms/beam is approximately 500.*

There are softening resins on the market that are non-solvent sulfonated. These resins do not use a swelling agent during the sulfonation process when the resin is functionalized. They will typically have a rough surface, which is often called the orange peel effect. Standard resins use a swelling agent to reduce the osmotic shock that occurs during the sulfonation. This is seen in the smooth spherical bead that is produced. Because the sulfonation process occurs in a very hostile environment, if a solvent is not used to reduce stress on the resin, the beads will have a rough surface. This will often have a higher concentration of cracked and broken beads than resins that are solvent sulfonated.

Lower crosslinked resins may look like high quality resins, but do not be deceived. The lower crosslinked resins will not hold up as well as higher crosslinked resins to chlorine or any other oxidants in the water. Lower crosslinked resin will also have a lower theoretical capacity (see Figure 3). The total capacity for a six percent crosslinked resin may only reach 1.6-1.7 meq/ml, with a water retention of 54-56 percent. A benefit of this type of resin is that it is less expensive than its higher-crosslinked counterpart. When this resin is purchased, one is buying more water and less resin.

Softening resin works on the principle of selectivity (see Figure 4). Monovalent ions, like sodium, have one positive charge and are held onto the resin less tightly than divalent molecules like calcium and magnesium (which have two positive charges). Therefore, a calcium ion will displace a sodium ion. The second factor that affects selectivity is the molecular weight of the ion; the greater the molecular weight, the greater the affinity of the resin for this ion. Calcium will displace magnesium, since calcium has a molecular weight of 40.1 and magnesium has a molecular weight of 24.3.

In the softening process, two sodium ions are released for one calcium ion or one magnesium ion (see Figure 5). The effluent from the softening resin will be sodium sulfate, sodium bicarbonate, sodium chloride and a small amount of hardness. This reaction is reversible with a high concentration of salt. Two sodium ions are placed back on to the resin for each calcium ion that is displaced. The waste regenertor will contain the excess sodium chloride (NaCl), calcium chloride (CaCl_2) and magnesium chloride (MgCl_2). Note that no matter how much salt is used in the regeneration process, the resin will never fully regenerate to the sodium form.

Potassium chloride (KCl), also known as potash, can be used as an alternative regenertant. Theoretically, for every pound of NaCl used, 1.27 lbs of KCl should be used. Based on prior testing by industry experts, it appears that the difference is not as great as the theoretical amount. Performance testing should be carried out to establish the difference in capacity in a given unit. A benefit to using KCl as a regenertant is the release of potassium into the water instead of sodium. In fact, sodium can even be reduced according to a study performed by PCL. When the system is sized to soften the water, one can expect to remove a portion of the naturally occurring sodium through a portion of the service run. When the resin’s capacity for sodium is exhausted, the levels of sodium will start to increase and even exceed the levels of naturally occurring sodium. This elevated sodium level is due to two processes. First, sodium is no longer being removed from the influent water. Second, hardness will displace sodium from the bed. The combination of these two properties causes sodium levels to be greater in the effluent water than in the influent water. Utilizing KCl as a regenertant is advantageous for people on low sodium diets, because sodium leakage from the resin is minimal if properly engineered.

Current research indicates that sodium may not be as big a factor as previously thought in causing high blood pressure. In addition to this, softeners regenerated with NaCl will add only a
small fraction of sodium in the daily diet. If the water has 10 grains (171 ppm) of hardness, the additional sodium added to the diet would be 78 mg/1Na as Na. For a person to get the equivalent amount of sodium as that of one piece of white bread, over two quarts of softened water would have to be consumed (based on 10 grains of hardness in the influent water to be treated.) This figure does not include any sodium that occurs naturally in the water.

The U.S. Food and Drug Administration (FDA) defines sodium levels in water as follows: sodium free, up to 28 mg/l; very low sodium, up to 197 mg/l; low sodium, up to 789 mg/l. As can be seen from these guidelines, hardness concentrations up to 100 grains will still only put what is considered a low amount of sodium into the treated water (this does not include the naturally occurring sodium in the water).

In order to size a softener properly, a thorough water analysis is required. Generally, the following parameters should be run: calcium (Ca), magnesium (Mg)—Ca and Mg make up total hardness—sodium (Na). Total Dissolved Solids (TDS), pH and iron content are also helpful to know. When a water analysis is run, the Ca, Mg and Na are usually expressed as the ion. These must be converted to their CaCO₃ equivalent, the industry standard. This permits the comparison of one ion to another, which is performed by multiplying the ion by a conversion factor. These conversion factors are derived from the equivalent weight of the ion, which is divided into the equivalent weight of CaCO₃. Ca has a conversion factor of 2.5. To calculate the conversion factor, do the following: Ca has a molecular weight of 40.1 by 2 which equals 20. CaCO₃ has a molecular weight of 100.1 and it also has two positive charges, so the equivalent weight is 50. The conversion factor is calculated by dividing 50 by 20, which gives a conversion factor of 2.5. A comprehensive water analysis will include the anions as well as the cations. Table 2 shows a typical water analysis with conversion factors.

Total hardness takes into account both Ca and Mg and is expressed as CaCO₃. TDS is also expressed as CaCO₃. To check the water analysis for accuracy, the total cations (Ca, Mg, K and Na) as CaCO₃ should be equivalent to the TDS. If the anion constituents are present in the analysis and converted to their CaCO₃ equivalent, they should also be equivalent to the total cations.

A comment should be made about alkalinity. Alkalinity is based upon the bicarbonate ion (HCO₃⁻), the carbonate ion (CO₃⁻) and the hydroxide ion (OH⁻). Total alkalinity is always expressed as CaCO₃. The bicarbonate ion will be prevalent in water when the pH ranges from 4.3 to 8.3. Once the pH exceeds 8.3, CO₃⁻ becomes prevalent and at a pH above 10, OH⁻ will exist.

When sizing a water softener the total hardness, TDS and salt dosage must be known. It is not uncommon to see a softener rated for 30,000 grains when 15 lbs of NaCl/cu.ft. is used to regenerate the system. This simplified rating will work on the vast majority of systems installed. To calculate throughput for this system, take the Ca and Mg as CaCO₃ (total hardness) and divide by 17.1; this will convert ppm as CaCO₃ to grains per gallon. The conversion of total hardness from ppm as CaCO₃ to grains per gallon can be calculated using the following formula:

\[
250 \text{ ppm Ca as CaCO}_3 + 206 \text{ ppm Mg as CaCO}_3/17 = 26.7 \text{ grains/gallon.}
\]

To calculate the throughput capacity, divide the capacity by the grains of influent hardness (30,000/26/7 = ~1,120 gallons/cu.ft.).

However, when TDS values exceed 1,000 ppm, the capacity will start to drop below 30,000 grains at 15 lbs NaCl cu.ft. Another type of water that will lower capacity occurs when the ratio of hardness to TDS falls below 15 percent. Both of these conditions indicate elevated hardness leakage. Consult the resin manufacturer regarding capacity and leakage when one of these water types is encountered.

As previously stated, resin cannot be fully regenerated back to the Na form. There will always be a heal of exhausted resin somewhere in the bed. The Ca and Mg in this heal produces hardness leakage during the service cycle. The leakage graphs are based upon TDS and salt dosage. In most residential applications, the goal is to obtain a hardness leakage of less than one grain (also known as zero hardness). This is not true when treating water for industrial applications. Many specifications call for water hardness to be less than one ppm (0.06 grains). To be specific, there is no such thing as zero hardness.

When checking hardness leakage from a system, always remember to run the water for a short period of time before the sample is taken. This will give the system time to rinse so a true hardness reading is obtained. When a system is on stand-by, the resin and water will try to reach an equilibrium state. What this means is when the system is not in operation, the resin will release hardness back into the water. This occurs until the concentrations in the water and resin are equivalent. When the system goes back on line, the first water out of the unit can have excess hardness. Once this excess hardness is washed out of the unit, hardness readings will return to normal. Iron can act the same way.

**Regeneration**

When the system has exhausted, the first step in the regeneration process is the backwash. The backwash is used to remove debris that has been filtered out in the bed. It will also classify the resin bed (big beads on the bottom and little beads on top). It is recommended that the flow rate be high enough to expand the bed a minimum of 50 percent. This usually requires a flow rate of approximately 5 gpm/sq.ft. Cold water temperatures will require lower flow rates, while warmer waters require higher flow rates. As the water temperature decreases, the water becomes more viscous (thicker). Caution should be taken when setting up a system in July so that the resin is not backwashed out of the unit in January. Fluctuations in water temperature will usually only occur in surface water sources. A top screen in the valve will prevent the loss of resin.

Salt starts out as a granule or pellet in the brine tank. The salt is then dissolved in water at a concentration of approximately 26 percent (saturated brine). When it is time to regenerate the bed, the salt solution is generally educted into a stream of dilution water. The concentrated brine is diluted down to approximately 10-13 percent. The regeneration flow rate through the bed should be approximately 0.25 to 0.5 gpm/cu.ft. Optimaly, the resin should be in contact with the salt for approximately 20 to 30 minutes. If the contact time is reduced to under 20 minutes, shorter service cycles and greater leakage may result (system design is important). The slow rinse simply displaces the salt solution from the bed; terminating the salt eduction so only the dilution water is running through the bed performs this function. A total of one to two bed volumes is usually adequate for the slow rinse. The fast rinse is performed by running the water at the service flow rate and it is used to rinse the excess salt from the unit. This will usually require three to 10 bed volumes depending on the distribution of the system. If there are dead spots in the bed, it will take longer for the resin to rinse up to quality. Since one cubic foot of resin is
approximately eight gallons, one bed volume is approximately eight gallons of water.

The service flow rate should be 2-5 gpm/cu.ft. or 5-10 gpm/sq.ft. A higher flow rate will cause shorter service cycles. High flow rates can exceed the kinetics of the resin. This means the resin cannot work fast enough. An exhaustion band forms that contains both regenerated and exhausted resin. As the flow rate increases, this band will expand. This expansion reduces the amount of usable resin in the unit. However, in many applications, higher flow rates can be used since the hardness leakage is not as critical. Flow rates of 20 gpm/sq.ft. or more are not uncommon. When higher flow rates are used, it is important to know that the hardness leakage will increase, the capacity will decrease and the pressure drop will increase. As long as these parameters stay within specification of the equipment and customer requirements, no excessive damage should occur to the softening resin. In condensate polishing applications, flow rates can be as high as 50 gpm/sq.ft. If the flow rate is too low, water can channel through the bed. Since the water pressure is reduced, the water follows the path of least resistance, causing pockets of resin (regenerated) to be bypassed and the service cycles will be shorter than expected. The unit’s distribution must also be good, whether the flow rate is high or low, so all the resin is utilized. Equipment testing is suggested to optimize the flow rate for a given system.

**About the author**

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This article is Part 1 in a series. Watch for Part 2 in an upcoming issue.