Authored by water technology expert Chubb Michaud, this Application Guide reviews the basics of how ion exchange resins remove calcium and magnesium "hardness" in residential and industrial water softening systems. The document also goes over basic terminology and calculations used to determine the amount of brine needed during regeneration.
WATER SOFTENING BASICS

This Application Guide reviews the basics for using ion exchange resins in household and industrial water softening systems. For more detailed information on any product, or to find a product for an application not mentioned, visit www.purolite.com or contact the closest Purolite regional office listed on the back cover.

INTRODUCTION

Founded in 1981, Purolite is a leading manufacturer of ion exchange, catalyst, adsorbent and specialty resins. With global headquarters in the United States, Purolite is the only company that focuses 100% of its resources on the development and production of resin technology.

Responding to the needs of our customers, Purolite has built the largest technical sales force in the industry, the widest variety of products and five strategically located Research and Development groups. Our ISO 9001 certified manufacturing facilities in the U.S.A, Romania and China, combined with more than 40 sales offices in 30 countries, ensure complete worldwide coverage.

PREMIER PRODUCTS

The quality and consistency of our products is fundamental to our performance. Throughout all Purolite plants, production is carefully controlled to ensure that our products meet the most stringent criteria, regardless of where they are produced.

RELIABLE SERVICE

We are technical experts and problem solvers. Reliable and well trained, we understand the urgency required to keep businesses operating smoothly. Purolite employs the largest technical sales organization in the industry.

INNOVATIVE SOLUTIONS

Our continued investment in research & development means we are always perfecting and discovering innovative uses for ion exchange resins and adsorbents. We strive to make the impossible possible.
Water, passing through the atmosphere as snow or rain, picks up carbon dioxide (CO₂) and other acid gases and reaches the Earth’s surface as a weakly acidic solution (CO₂ + H₂O → H₂CO₃) known as carbonic acid. The rain that falls into surface waters such as streams, rivers, ponds and lakes is normally low in dissolved solids and hardness.

As this water soaks in, it passes through various strata containing limestone (CaCO₃), which neutralizes the acid forming a soluble calcium bicarbonate salt (H₂CO₃ + CaCO₃ → Ca (HCO₃)₂).

This then dissociates into ions: Ca⁺⁺ ions with a plus 2 positive charge is a cation and HCO₃⁻ with a single negative charge contributes two anions. This is how calcium (and magnesium) end up in the water supply. When calcium and magnesium levels are high, water is described as being “hard.”

When hard water is heated, the Ca (HCO₃)₂ decomposes to CaCO₃ and evolves CO₂ gas and H₂O (water). CaCO₃ is insoluble and deposits on the surfaces of water heaters, often found in boilers, coffee makers, pipes and on to fabrics, creating a hard scale (known as calcite, lime scale, boiler scale or hardness scale). This scale is a poor conductor of heat and so it takes more energy to heat water if the heater element or boiler tube is covered with this scale. Scale can also clog pipes and appliances and reduces the life of fabrics due to its abrasive nature. In addition, when washing, the soluble calcium and magnesium salts will react with soap causing the familiar bathtub ring and soap scum. It is desirable to remove hardness ions before using the water in residential and industrial applications.

Ion exchange is a preferred process for removing hardness ions. In domestic applications low level hardness is acceptable. In industrial applications, particularly boilers, hardness has to be removed.

Ion exchange was first recognized by Thompson and Way in 1858 who observed that when ammonium salt was poured through soil, the water trickling out from the container had a different composition. The soil captured the ammonium ion and released sodium. Natural soil contains clays and zeolites that have ion exchange capabilities. By order of selectivity, multi-valent ions are grabbed by ion exchangers, which will then release a less tightly held, more desirable ion. It should be noted that mono-valent ions such as sodium or potassium do not cause scale and do not react with soap.

Zeolites were synthesized in 1903 to offer higher capacity and stability than the natural zeolites. In 1905, German industrial pioneer Robert Gans commercialized the first regenerable ion exchanger for hardness removal. Synthesis of new chemistry gradually improved the efficiency of the softener through the 1940s when G.F. D’Alelio of GE produced the first suspension polymers of styrene and di-vinyl benzene (S/DVB), giving birth to the modern ion exchanger.

The basic chemistry of softening resins has remained unchanged since that time. Ion exchange softening systems use reactive plastic polymer beads with chemical functionality that selectively captures the di-valent ions such as calcium and magnesium and releases less tightly held mono-valent ions, normally sodium. The reaction is as follows:

Ion exchange reactions:

**Softening Reactions**

Service

\[
Ca(HCO₃)₂ + Na⁺ \rightleftharpoons Ca⁺⁺ + 2 NaHCO₃
\]

Regeneration

\[
Ca⁺⁺ + NaCl \rightleftharpoons Na⁺ + CaCl₂ + NaCl
\]
The equilibrium between the water composition and the amount of hardness that can be removed. It also means the reaction is reversible if a high driving force is applied to the exhausted resin. If that force is concentrated brine (NaCl or KCl), hardness on the expended resin is driven off and mono-valent sodium or potassium takes its place in a process called “regeneration.”

A softener system consists of a bed of resin beads with the ability to pick up hardness by ion exchange (hardness exchanged for “softness”). It can then be regenerated by a high concentration (10% brine) of salt to restore its capacity. The system can be used over and over for many years.

Water hardness is usually commonly reported in ppm (parts per million) or mg/l (milligrams per liter as CaCO₃ (calcium carbonate), and fortunately 1 ppm = 1 mg/l.

The term CaCO₃ defines a convention representing the number of ions to be exchanged. The water analysis is usually presented in mg/l (as the ion) which has to be converted to mg/l as CaCO₃ using conversion factors. The factor for Ca⁺⁺ is 2.5. To get mg/l as CaCO₃, multiply the mg/l as Ca⁺⁺ by 2.5. For Mg⁺⁺, the factor is 4.1.

Once calcium and magnesium as CaCO₃ is calculated, add them to get total hardness (as CaCO₃). Resin capacity will vary depending upon the salt dose per cubic foot of resin and can be approximated from the following table.

### Table 1 – Resin capacity estimates per level of NaCl

<table>
<thead>
<tr>
<th>REGEN LEVEL NaCl (g/l)</th>
<th>REGEN LEVEL NaCl (lbs)</th>
<th>CAPACITY (g/l)</th>
<th>CAPACITY (Kgs/ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>4</td>
<td>42</td>
<td>18</td>
</tr>
<tr>
<td>96</td>
<td>6</td>
<td>48</td>
<td>21</td>
</tr>
<tr>
<td>128</td>
<td>8</td>
<td>55</td>
<td>24</td>
</tr>
<tr>
<td>160</td>
<td>10</td>
<td>60</td>
<td>27</td>
</tr>
<tr>
<td>190</td>
<td>12</td>
<td>66</td>
<td>29</td>
</tr>
<tr>
<td>240</td>
<td>15</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

Once capacity is calculated in g/l or ft³, multiply that number by the number of liters or cubic feet of resin in the system to get system capacity. Then, divide that number by the amount of hardness in the water supply in mg/l as CaCO₃ to indicate the approximate amount of water that can be treated between regenerations in m³ (x 1000 to get volume of water in liters).

The basic softener consists of an exchange resin in a tank with a control valve (to control the regeneration cycles) and a brine source looks like the following:
There are many factors controlling how well the softener works. One is water composition. The higher the calcium and Magnesium of the raw water, the fewer gallons the system will produce between regenerations (cleanings). The more salt used per regeneration, the better the performance (in terms of percentage of hardness removed) and capacity (how much it will treat). Typically, a 15 liter (0.53 cubic foot) unit regenerating with 160 g/l (5.3 lbs) of salt will produce 4500 liters (1189 gallons) of treated water with a feed of 200 mg/l (10 gpm) hardness.

Regeneration is initiated by a time clock, gallons meter or an electronic sensor. During regeneration, the service water may bypass the treatment system giving a hard water effluent. To avoid this, industrial systems are designed with twin alternating operation mode using two systems.

The first step in regeneration is to backwash the system by running water backwards through the bottom of the bed. This lifts the bed and dislodges dirt and debris. The bed is then settled and regenerated with a 10% salt solution. This step drives off the hardness and restores capacity. The bed is then rinsed and returned to service. The total time to regenerate is <2 hours and the total water used is about 7 x the resin volume: 15 liter bed = 105 liters (50 gal per ft³). The wastewater is discharged to the sewer or septic system.

For a typical home use, a 15 liter (0.53 ft³) softener will serve most needs of a small home. If the water is very high in total harness, (> 250 mg/l) (>25 gpm) or the family is large, a bigger system may be needed. Commercial and industrial systems are usually sized to produce a certain run length — about 8 hours. With a feed harness of 200 mg/l (12 gpm) and a flow of 10 m³/h (25 gpm), the challenge is (200 x 10 / 1000 = 2 Kg load per hour) (12 x 25 x 60 min/hr = 18,000 grains per hour) and if the run length needed is 8 hours (2 x 8 = 16 Kg)(18,000 x 8 = 144,000) divide the load (16 Kg) (144Kgr) by the capacity (50 g/l)(22 Kgr). This shows0.32 m³ (320 liters) (11.3 ft³) resin volume is needed in the softener.

At 10 m³/h (25 gpm), the relative flow rate is (10/0.32 = 31.25 BV/h) (25/6.55 = 3.8 gpm/ft³).

This flow is considered acceptable for residential and commercial needs, but critical applications (high pressure boilers) might choose a larger system with 650 liters (1 – 3 gpm/ft³) on a 12 – 24 hour operating cycle. Residential systems often operate intermittently at flow rates of up to 80 BV/h (bed volume per hour) (10 gpm/ft³) of resin. Typical flows are much lower (average is closer to 20 – 30 BV/h) (2.5 gpm). As a result of higher flow peaks and need to minimize brine usage, lower regeneration levels are now being employed (120 g/l or less) (8 lb/ft³). Residential systems generally experience higher levels of hardness in the effluent but still less than 20 mg/l (1 gpg (17ppm). When a resin system regenerates, only about 60% of the total capacity is restored. Some hardness is left on the resin. When next in service, some of this residual harness leaches off the resin creating a slight amount of hardness in the effluent. This is called “leakage.” The leakage level is determined, in part, by the total amount of salt used to regenerate. Systems requiring very low leakages (<1 mg/l) (<1 ppm) may require high doses of salt (200 g/l or greater) (20 lb/ft³).
Leakage is the primary factor in determining the system design. For any given water analysis, a given quality (leakage) is produced by a given salt dose (g/l) (lb/ft³). The product engineering notes determine this. Once the salt dose (for the quality needed) is determined, the capacity is set and the system design can be initiated.

Although synthetic resins are very durable, they are subject to degradation. Chlorine and other oxidants are detrimental. Levels of 0.5 mg/l (0.5 ppm) have little effect on resin life, but higher levels dramatically reduce resin life. The presence of metal ions such as iron or copper in feed water will foul the resin and promote oxidative breakdown, further shortening resin life.

The basics of ion exchangers have remained unchanged for more than 60 years. However, much has been done to improve the efficiency by modifying the bead structure. Normal beads range in particle size from 0.3 to 1.2mm. This is called “standard Gaussian distribution.” This mix gives good capacity and minimal pressure loss. Most of what has been written about softening pertains to this particle size distribution. The efficiency of softening resins has been improved by newer manufacturing techniques which are capable of producing beads that are more uniform in size. Uniform bead products such as Purofine® PFC100E, Puropack® PPC100 and Purofine® PFC100 produce systems with lower pressure drops and better brine efficiencies (up to 10 to 15% over the standard beads). Finer mesh (0.2 to 0.4mm) beads have also been introduced by Purolite. These small narrow grade resins are kinetically faster. Using fine mesh resin such as Purolite® C100EFM allows systems that are smaller in size with higher capacity and better brine efficiency (about 10% improvement).

The latest development is the SST bead (Shallow Shell Technology) manufactured exclusively by Purolite, which are not fully functionalized by depth. This gives the performance of both fine mesh and uniform particle size resins while producing higher capacity and lower leakages than any other bead forms at any given salt level.

With the uniform bead, fine mesh bead and SST bead products, the enhanced performance comes from reduced diffusion paths that are critical during the regeneration step when the large calcium and magnesium ions have to migrate to the surface of the bead—while the resin is in contact with the brine solution. Calcium and magnesium ions migrate slowly, therefore a reduction in the diffusion path results in easier and better regeneration. This, in turn, gives rise to better performance and higher working capacity.

In designing industrial plant, consideration should be given for proper hydraulic flow rates. Both the superficial flow (flow in m³/m²/h) and volumetric flow (flow in BV/h of resin) need to be fully considered in the design. Surface flows should be between 10 - 40 m³/m²/h and volumetric flows should be between 8 – 40 BV/h. Peak flow can go up to 60 BV/h if designed correctly. Residential systems generally operate on the upper end of good design while major industrial systems trend towards the lower and more conservative end.