

Purolite[®] Water Softening Resin Guide

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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) commonly referred to as carbonic acid.. The rain that falls into surface waters such as streams, rivers, ponds and lakes are 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) which 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 all our water supplies. Where the calcium and magnesium content is high these waters are described as "hard" waters.

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 you will notice the soluble calcium and magnesium salts will react with soap causing the familiar bathtub ring and soap scum. Needless to say, it is often desirable to remove hardness ions before using the water in residential as well as industrial applications.

Ion exchange is often the process of choice for removing hardness ions. In domestic applications a low level of hardness can be permitted. In industrial applications, particularly boilers, total hardness has to be almost totally removed.

Ion exchange was first observed and recognized by Thompson and Way in 1858 noting that when an ammonium salt was poured through soil, a different water composition trickled out of the bottom of the container. The soil had 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 onto by ion exchangers which will then release a less tightly held ion (which is often more desirable). It should be noted that mono-valent ions such as sodium or potassium do not cause scale and do not react with soap.

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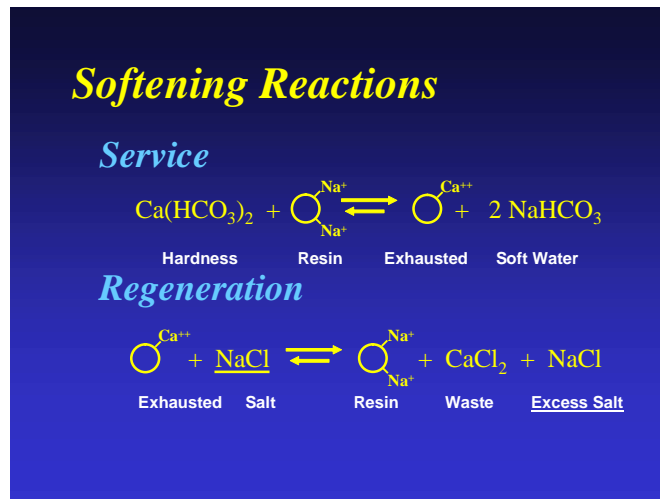
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Zeolites were synthesized in 1903 offering higher capacity and stability than the natural zeolites and German industrial pioneer, Robert Gans commercialized the first regenerable ion exchanger for removing hardness in 1905.

The synthesis of new chemistry gradually improved the efficiency of the regenerable softener through the 1940s when G.F. D’Alelio of GE produced the first suspension polymers of styrene and di-vinyl benzene (S/DVB) which gave 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:



The $\rightarrow \leftarrow$ means that there is equilibrium between the water composition and the amount of hardness that can be removed. It also means that the reaction is reversible should there be a high driving force applied to the exhausted resin. If that driving force is a concentrated brine (NaCl or KCl), the hardness on the expended resin is driven off and the mono-valent sodium or potassium takes its place.

This is called “regeneration”. So a softener system, consisting of resin beads in a bed that has the ability to pick up hardness by ion exchange (hardness exchanged for “softness”) and then be regenerated by a high concentration (10% brine) of salt and have its capacity restored. The system can be used over and over and lasts for years.



Water hardness is usually commonly reported in ppm (parts per million) or mg/l (milligrams per litre 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.

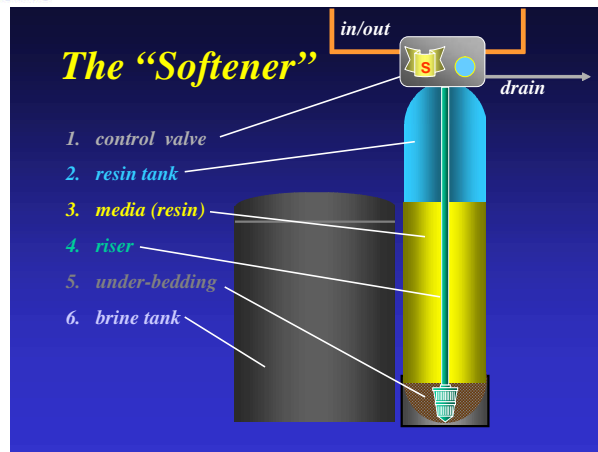
The factor for Ca⁺⁺ is 2.5. You then multiply the mg/l as Ca⁺⁺ by 2.5 to get mg/l as CaCO₃. For Mg⁺⁺, the factor is 4.1.

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

Regen Level g/l (NaCl)	Regen Level lbs (NaCl)	Capacity (g/l)	Capacity (Kgs/cf ³)
65	4	42	18
96	6	48	21
128	8	55	24
160	10	60	27
190	12	66	29
240	15	70	30

Once you have the capacity 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 in by the amount of hardness in the water supply in mg/l as CaCO₃ and this will indicate the amount of water that can approximately be treated between regenerations in m³ (x 1000 to get volume of water in litres).

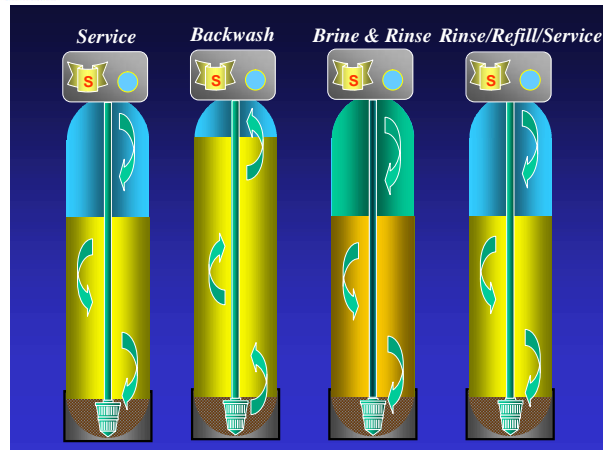
The basic softener consists of an exchange resin in a tank with a control valve (to control the regeneration cycles) and a brine source. Typically, it would look like this:



There are many factors controlling how well your softener works. One is the water composition. The higher the Ca and Mg of the raw water, the fewer gallons your system will produce between regenerations (cleanings). The more salt you use per regeneration, the better the performance (in terms of percentage of hardness removed) and capacity (how much it will treat). Typically, a 15 liter (1 cubic foot) unit regenerating with 160 g/l (8 lbs) of salt will produce 4500 liters (2100 gallons) of treated water with a feed of 200 mg/l (10 gpm) hardness

Regeneration is generally 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 a 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 litre bed = 105 litres (50 gal per ft³). The wastewater is discharged to the sewer or septic system.



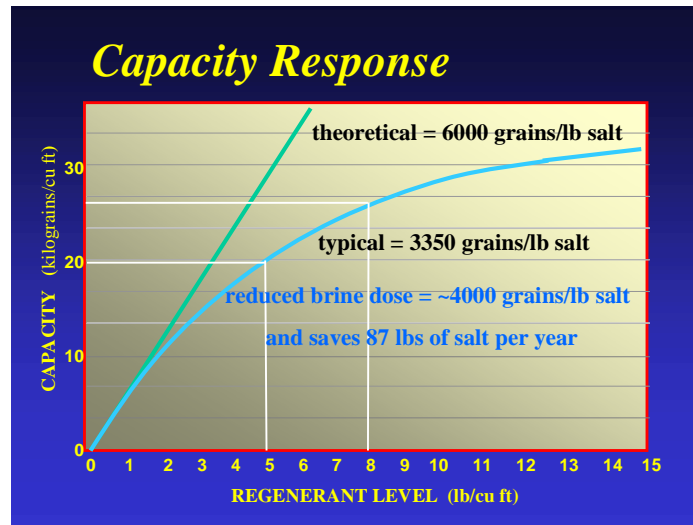
For a typical home use, a 15 liter (1 ft³) softener will serve most needs of a small home. If the water is very high in total hardness, (> 250 mg/l) (>25 gpm) or the family is large then a larger systems may be needed. Commercial and industrial systems are usually sized to produce a certain run length—say 8 hours. With a feed hardness 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) you divide the load (16 Kg) (144Kgr) by the capacity (say 50 g/l)(22 Kgr) and we see that we would need 0.32 m³ (320 liters) (6.55 ft³) resin volume in the softener.

At 10 m³/h (25 gpm) , the relative flow rate would be (10/0.32 = 31.25 BV/h) (25/6.55 = 3.8 gpm/ft³) This flow is generally considered acceptable for residential and commercial needs but critical applications (high pressure boilers) might choose to have a larger system with 650 litres (1 – 3 gpm/ft³) on a operating 12 – 24 hour 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 the need to minimize brine usage lower regeneration levels are now being employed (120 g/l or less) (8 lbs/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 hardness leaches off the resin creating a slight amount of hardness in the effluent. This is called “leakage”. The level of leakage 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 lbs/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) (lbs/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 due to oxidation and over time. Chlorine and any other oxidants are detrimental. Levels of 0.5 mg/l (0.5 ppm) have little affect on resin life but at higher levels the life of the resin can reduce dramatically. Also the presence of metal ions such as iron (which is common) or copper in the feed water will foul the resin and promote oxidative breakdown and shorten the life further.

The basics of ion exchangers have been chemically 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 1.2 mm. 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 Purolite PFC100E and PPC100 and 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 0.4 mm) 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 (a gain of about 10% can be realized).

The latest development is the SST bead (Shallow Shell Technology beads manufactured exclusively by Purolite primarily for the USA market) 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 which 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 and hence a reduction in the diffusion path results in easier and better regeneration giving 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 $m^3/m^2/h$) and volumetric flow (flow in BV/h of resin) need to be fully considered in the design. Surface flows should be between 10 - 40 $m^3/m^2/h$ 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.

PuroLite manufactures a full line of standard and specialty strong acid cation exchangers for your softening needs. PuroLite supply a wide range of softening resins some of which are listed below. Some are food grade treated, some offer enhanced performance and some are physically more robust. Consult your local PuroLite office or visit www.purolite.com for help in selecting the best resin for your duty and application.

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