Iron, Manganese, Barium, Strontium and Radium Removal With Shallow Shell™ Technology Resin

Shallow Shell Technology resin beads can be more completely regenerated, making them ideal for reducing metal fouling and leakage during service.

ECOLAB®

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Shallow Shell Technology (SST) Resins provide unique advantages when removing bulky slower-diffusing cations from water such as iron, manganese, barium, strontium and radium versus standard resins. The cores of standard resin beads eventually become irreversibly fouled with such metals, leading to higher leakage and poorer water quality during service. SST resin beads are manufactured with an activated outer shell area and an inert central core that eliminates fouling of the core of the beads. The shorter diffusion path of the shell area results in more efficient removal of especially slower-diffusing cations, resulting in higher regeneration efficiency, better water quality, and longer resin life.

Contents

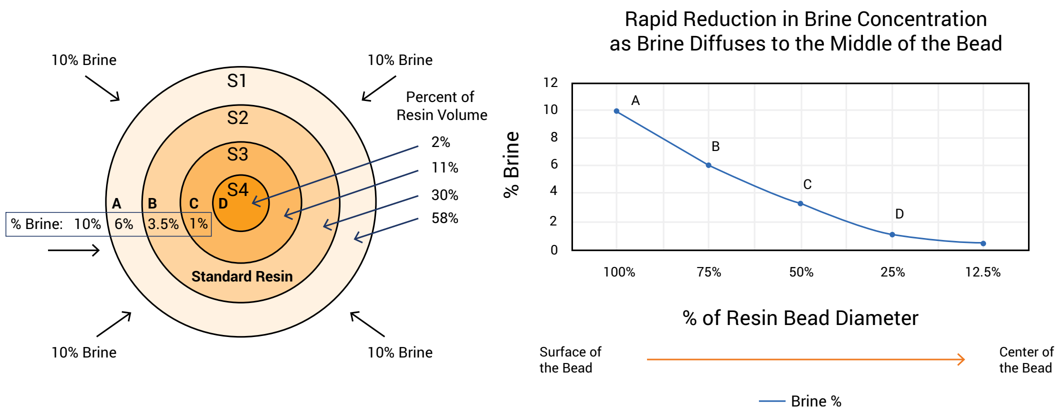
Inefficient Regeneration of Standard Resin

Brine regenerated strong acid cation exchange resin has been a popular method of softening water, including removing bulky cations such as iron, manganese, barium, strontium and radium. Decades of experience show that such bulky cations present a two-fold challenge to the life of the resin and the quality of the water produced. Bulky high molecular weight cations diffuse relatively slowly through the resin beads during the service uptake and brine elution step. The short duration of the brining step (e.g., 30–60 minutes) compared to the service phase (e.g., hours to days) results in insufficient time for the slower diffusing cations to be completely removed from the center of the resin beads. The problem is accentuated with larger beads, such as the 800–1200-micron beads that form part of the standard range of 300–1200-micron beads supplied as standard (or Gaussian type) resin.

Incomplete regeneration of the center of standard beads is easy to visualize from the example shown in Figure 1. The extreme case of all sites being fully saturated with metal cations is considered using modeling software developed by Ecolab. A 10% sodium chloride brine concentration is assumed to be applied to the surface of the bead. The brine first reacts with metals loaded on the bead's surface and continues to diffuse inward toward the center of the bead. Metal cations are released from the ion exchange sites while sodium ions are picked up as the brine moves through the outer segments of the bead (e.g., segments S1, S2, etc.). The graph in Figure 1 shows that the residual brine concentration quickly drops from 10% (Point A) to about 6% (Point B) as it diffuses through the outer segment S1; then it decreases to about 3.5% as it diffuses through segment S2. It then falls to less than 2% as it moves from segment 2 to segment 3 (Points C to D) and continues to decrease as it moves toward the center of the bead. It indicates that merely utilizing one bed volume of brine when all sites are fully loaded with metal cations is likely not enough to elute all cations. A higher brine dosage is likely better if adequate control over leakage is to be maintained during subsequent service cycles. This extreme case is not usually encountered in actual practice since most ion exchange plants are designed and operated to utilize less than 70% of the available ion exchange sites on the resin. This in itself helps to limit fouling. But it serves to show that with time incomplete regeneration will likely lead to a gradual buildup of such foulants at the center of the beads, leading to reduced operating capacity and higher leakage.

FIGURE 1

Rapid Reduction in Brine



The fouling problem is compounded when metals such as iron and manganese are trapped in the center of the bead because they can eventually be converted to their oxide form by oxygen or other oxidants that may be present in either the water being treated or the regenerant brine. These oxides are more significant in volume than the metals and tend to become permanently wedged and trapped, especially at the center of the beads (see Image 1 on the next page).

1. Iron oxide fouling of resin center

Such fouling results in shorter service cycles, longer rinse times, and more wastewater to dispose of — all of which drive up the cost of production.

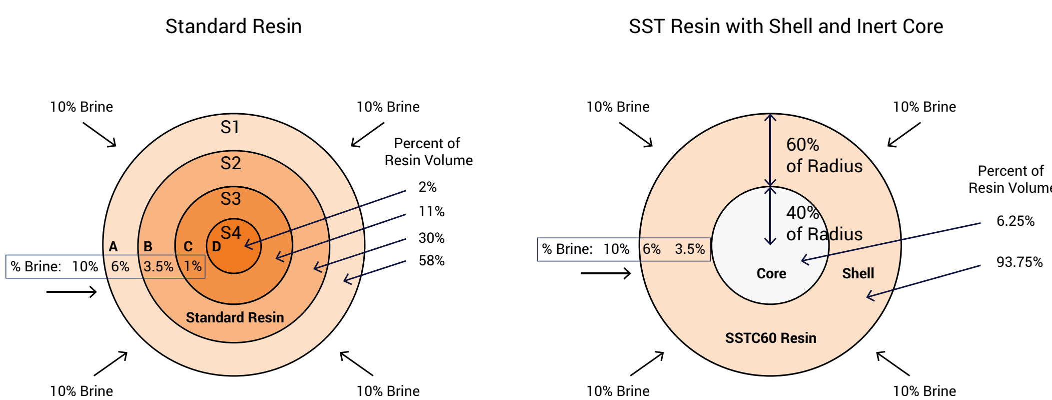
Care must be taken to prevent air from coming into direct contact with the water before the ion exchange process. Well water should be pumped directly through pressurized ion exchange units and not be passed through storage tanks where it can potentially absorb oxygen from the atmosphere. Even a leaky pipe joint on the suction side of the well pump can suck in enough oxygen to precipitate iron and manganese. In addition, the brine tank should be kept covered as much as possible to avoid introducing oxygen-containing brine that can oxidize the metals during the brining step.

Shallow Shell Technology has proven to reduce metal fouling of cation resin significantly. With standard resin beads, the ability of the regenerant to elute metals trapped at the center of the beads is severely compromised since regenerant concentration diminishes as it travels to the center of the bead. With time, the beads become increasingly metal-fouled, requiring increasing amounts of rinse water and time to adequately reduce metal leakage to specification levels for the treated water.

With the innovative SST resin bead, all ion exchange functional groups are located in the 'SHELL' area of the bead while the 'CORE' is inert and inactive (see Figure 2 below) with no ion exchange taking place — thus, no metal and metal oxide fouling can occur in the core. More regenerant is therefore available to elute cations from the outer shell of the bead, allowing for higher chemical conversion and regeneration of the ion exchange sites at any given regenerant level. With the SST bead, the diffusion path length is shorter, going from the outer periphery of the bead to the deepest part of the shell versus the longer path to the center of the standard bead. Shallow Shell SSTC60 is one of several types of SST beads produced by Ecolab, with a nominal 60% shell and 40% core. This means that the core volume is less than 7% of the total volume and results in no material loss in operating capacity vs. standard resin. Since diffusion is proportional to the radius of the bead, it also means that regenerant reaches the innermost part of the shell much faster than it takes to reach the center of the standard bead. Because there are no extra metals trapped at the center of the SST beads to be eluted, all of the regenerant is available to provide higher regeneration efficiency of the shell area. Therefore, rinse down of the resin is quicker, and leakage of metal cations is significantly reduced versus standard resin.

FIGURE 2

Comparing Standard Resin to SST Beads With a Shorter Diffusion Path



SST resins have been used successfully for several decades since their development early in the 1990s for softening applications and the removal of relatively high levels of iron and manganese. SST resins demonstrate high regeneration efficiency, even at relatively high influent iron and manganese levels. Table 1 below showcases three such SST examples of commercial installations in which iron and manganese are efficiently removed as part of the softening process.

TABLE 1 Efficient Removal of High Levels of Iron and Manganese with SST Resin

Case	Inlet Hardness, ppm	Inlet Fe, ppm	Inlet Mn, ppm	Salt Dose at 15% conc'n, lb/ft³ (g/L)	Fe Leak, ppm	Mn Leak, ppm
1	120	26	0.66	14 (225)	0.05	0.02
2	140	9	0.4	8 (128)	0.05	0.02
3	320	4.4	0.52	10 (160)	0.05	0.02

In these cases, iron ranged from 4.4–26 ppm (mg/L) while manganese ranged from 0.4–0.66 ppm (mg/L). Salt regenerant dosage ranged from 8–14 lbs/ft^3 of resin (128–224 g/L) and was generally applied at 15% concentration. All systems were regenerated in the co-flow mode. Iron and manganese leakage were consistently reduced to 0.05 ppm (mg/L) and 0.02 ppm (mg/L), respectively. In addition, in all cases, either a high grade of salt with a built-in resin cleaner was used, or a resin cleaner specific for iron fouling was used annually.

Removal of Other Bulky Cations

Barium, Strontium and Radium

In addition to iron and manganese, SST resins are ideal for removing bulkier high molecular weight cations like barium, strontium and radium from water since the same principles apply as bulky cations diffuse very slowly through the resin matrix and thus require much longer elution time for efficient removal. Barium, in particular, can form insoluble barium sulfate precipitate, which can accumulate in the matrix of the resin. The same applies to a lesser extent for strontium and radium. Such precipitates can be slowly re-dissolved if adequate contact is made with elevated levels of sodium chloride brine. The shorter diffusion path length of SST beads facilitates this by providing higher brine concentrations at the interface of the shell and core versus that present at the center of standard resin beads. Thus, it is easier to re-dissolve such precipitates.

Design Recommendations

The softening module of our "Purolite Resin System Modeling Software (PRSM™)" can be used to design a treatment system to remove hardness in conjunction with the bulky cations mentioned above.

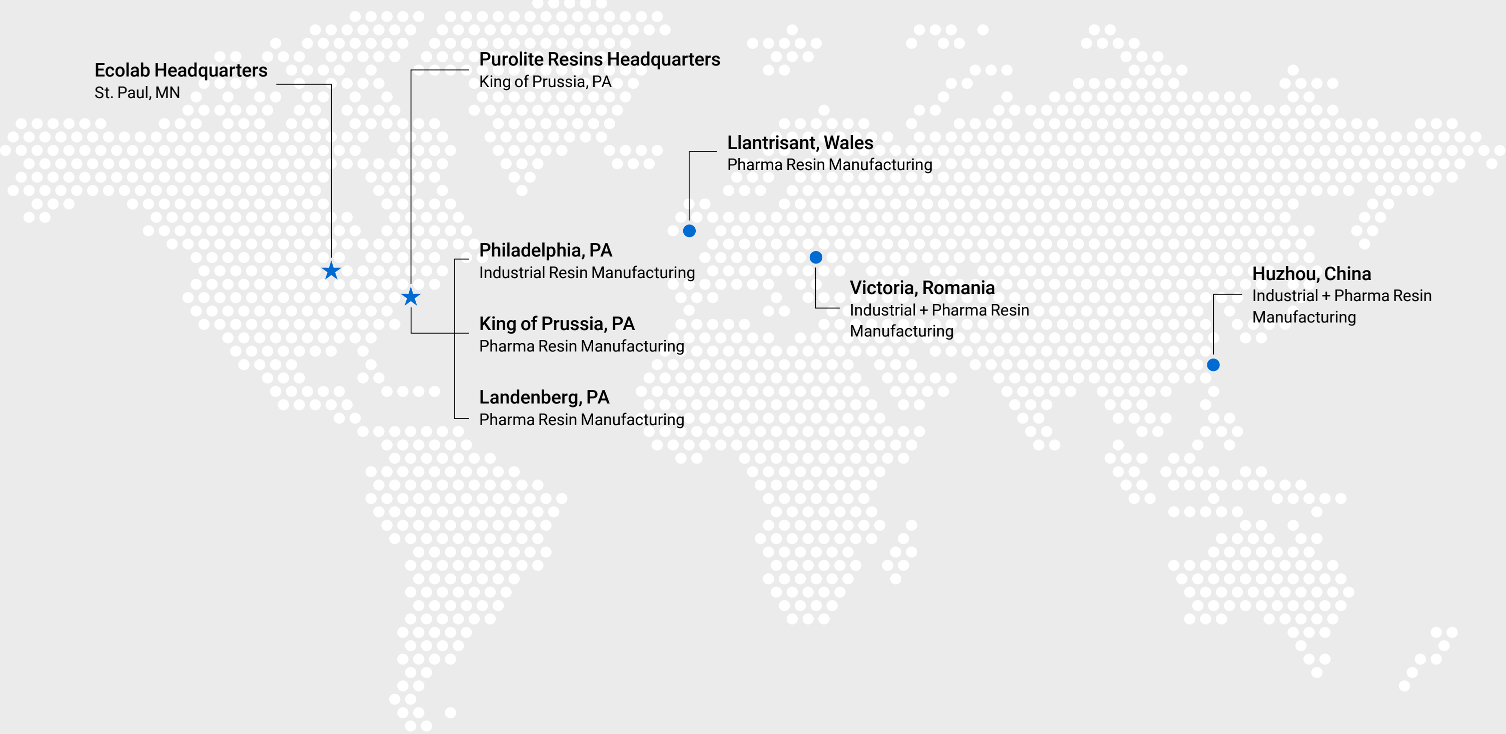
It is recommended to use a hardness breakpoint to determine the length of the operating cycle. When using counter-flow regeneration, the salt dosage should range from 160–192 g/L (10–12 lbs/ft^3), while with co-flow designed systems, the dosage should range from 192–240 g/L (12–15 lbs/ft^3). A minimum brining time of 60 minutes is recommended. Please contact your Ecolab representative for additional help.

Acknowledgment

Thank you to Craig Winter, President, Advanced Quality Water Solutions, who supplied much of the information on the case studies for iron and manganese removal found in Table 1.

Ecolab is a global developer, manufacturer, and supplier of Purolite™ Resins including ion exchange, catalyst adsorbent and advanced polymers that make the world cleaner and healthier.

PuroliteResins.com



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