SLEEP ON IT

Overnight Soaks Work Miracles in Mixed-Bed Regeneration for PEDI Service

By Francis J. DeSilva and Bill Hanson

Summary: *Dealers may not always get acceptable results during rinsing of mixed-bed resins after regeneration. But there's something to be said about sleeping on a problem, and an overnight soak can often be the solution your resins need. Here we explain how self-neutralization saves rinse water and improves product water quality.*

The portable exchange deionization (PEDI) business is one of the fastest growing segments of the ion exchange industry. Customers receive canisters of freshly regenerated resin, use them to produce deionized (DI) water and—when they are exhausted—the resins are replaced with another regenerated set in a new exchange tank. The exhausted canisters are brought back to a central regeneration facility.

It's easy to see why PEDI is such an attractive idea. The customers who use PEDI services don't need to store any chemicals on site, maintenance and monitoring is minimized and accountability for DI water quality is very well defined.

The PEDI regeneration facility performs a complete regeneration of the resin. Separate bed cation and anon canisters can be regenerated in the canister or batched into larger regeneration vessels for external regeneration. Chemical dosages are relatively high, usually in the range of 6-to-8 pounds per cubic foot.

Hydrochloric is the acid of choice for regenerating cation resins, although sulfuric acid can also be used. Anion resin is regenerated with caustic (sodium hydroxide). Separate bed regeneration consists of backwash, chemical dosing, slow rinse and fast rinse to quality.

Effluent water quality

The classic pairing of cation and anion units to form a two-bed deionizer will produce DI water with a resistivity better than 100,000 ohms (corresponds to 10 micromhos conductivity or 4-to-5 parts per million, or ppm), commonly referred to as "100 K" water. Conductivity is the property of water to conduct an electrical current and is measured in micromhos (mhos). It is the reciprocal of resistivity. More ions in the water enable it to conduct more electricity. High-purity water exhibits poor conductivity and, therefore, high resistivity. Many systems in use utilize a quality light that indicates when the water quality drops to 100 K at the end of the service run, signaling exhaustion. The water quality of a two-bed system is usually higher than this and can approach 1 megohm or higher resistivity.

Some end-users require higher purity water—microelectronics, pharmaceutical, medical, surface finishing preparation and others. They need ultrapure water, a term usually assigned to water with a resistivity of 18.3 megohms, the theoretically pure limit. This is a higher quality level than can be achieved by a two-bed system. A mixed bed unit must be used.

Mixed-bed canisters contain a mix of regenerated cation and anion resins. Cation resin has a higher capacity per unit volume so, to make a mixed bed that has an equal amount of cation and anion capacity, a higher ratio of anion resin volume is needed in the mix. The ratio of the mix for a mixed bed that's made of standard strong acid cation (SAC) resin and Type 1 strong base anion (SBA) resin is 60 percent anion with 40 percent cation.

Mixed bed units can be used as a polisher following a two-bed DI or a reverse osmosis (RO) system. Some mixed beds are also used as "working mixed beds" on waters with low total dissolved solids (TDS).

Regeneration

Exhausted mixed beds are brought back into the PEDI plant for regeneration but the regeneration process is more complicated than two-bed canisters. The cation and anion resins must be separated first. Here's a simplified account of what takes place:

The mixed-bed resin is taken out of the canisters and transferred to a separation vessel.

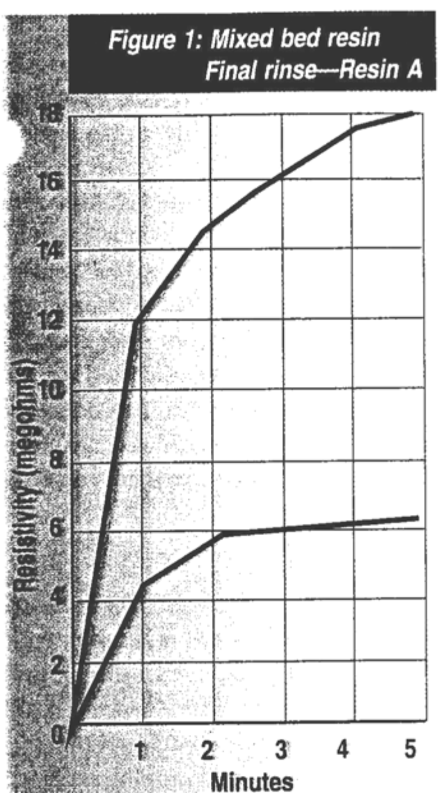

Figure 1: Mixed bed resin Final rinse—Resin A

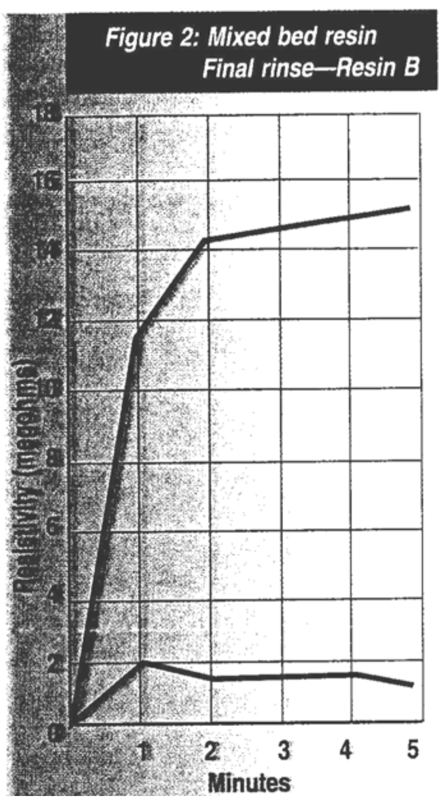

Figure 2: Mixed bed resin Final rinse—Resin B

A backwash step is then performed that separates the resin into layers. The backwash step uses softened or DI water (most plants use softened). Some regeneration plants use a brine-assisted backwash separation, where a salt solution (around 10 percent) is used as the backwash water. The brine separation step helps separate resins that may be hard to separate with a normal backwash using only water. The brine increases the density of the backwash solution and can help "de-clump" stubborn mixed-bed resin. For particularly hard-to-separate mixed beds, a solution of saturated brine can be used. Anion resin floats in saturated brine, cation resin sinks. Cation resin has a density of 52 pounds per cubic foot (lbs/ft^3) while anion resin has a density of 43 lbs/ft^3 both measured in the exhausted form. This differential in density is enough to allow the cation resin to settle faster and migrate downward during backwash to form the bottom layer of resin. Most mixed-bed systems use a black cation resin and a light-colored anion resin so that the resin interface is easy to see.

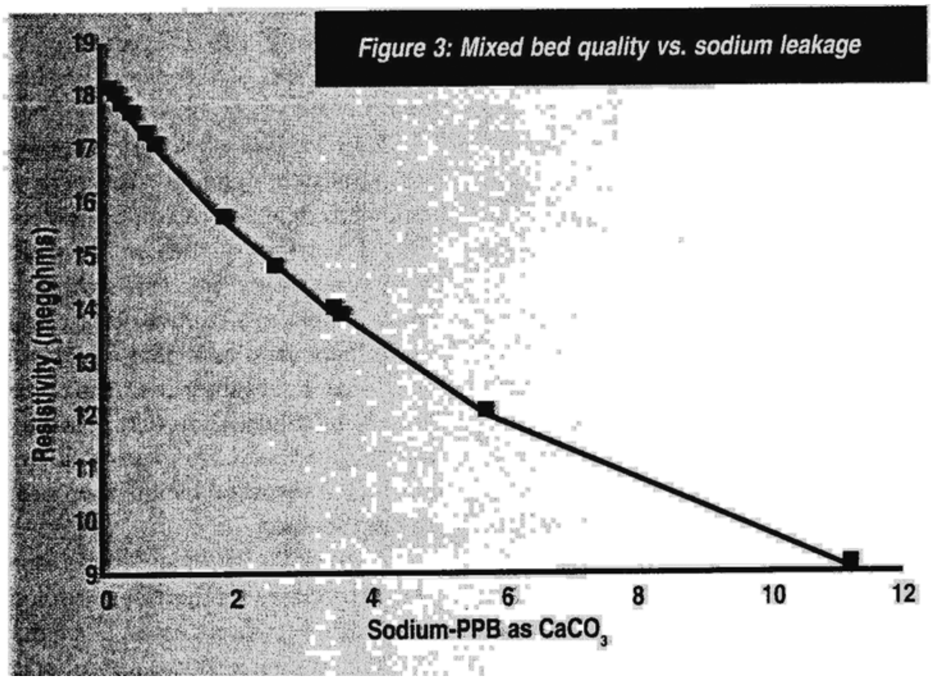

Figure 3: Mixed bed quality vs. sodium leakage

The anion resin is sluiced to the anion regeneration tank and the cation resin is sluiced to the cation regeneration tank or left in the separation vessel. Sluicing is a term that describes transport by a flow of water or compressed air or both. Resin can be sluiced into and out of vessels or sluiced through piping. The resins go through a typical regeneration—backwash, chemical dosing, slow rinse and fast rinse. They are then mixed together and rinsed again to quality. Rinse water quality should at least be softened; some plants use DI water. Warmer water is better and can give a quicker rinse. That's why some plants may notice shorter rinses during summer months. The final quality achieved is tied into many variables. Those that control final quality include: flow, temperature, distribution, influent composition, resin type, resin ratios and condition of the resin—taking into account fouling and aging effects.

Plant operators at PEDI facilities are familiar with a phenomenon that occurs during and after the final rinsing. For reasons described below, a mixed-bed resin may not achieve 18-megohm quality during the first fast rinse. After letting this same resin soak overnight, however, the mixed bed achieves much higher quality when the rinse is resumed (see *Figures 1 and 2).*

The overnight soak of the mixed bed resin allows a diffusion process to take place. The resin beads self-neutralize each other and come into equilibrium (see *Reactions).*

Organic contamination

Gradual falling off of water quality below 18 megohm can be the result of organic fouling of the anion component. Initial rinse down will take a long time. One batch of badly organically fouled anion resin can destroy the capability to consistently make 18-megohm water. The difference between 18 megohm and 17 megohm is only about a tenth of 1 ppm, and an organically fouled anion resin can easily cause this. A caustic/brine cleaning of the anion resin and several subsequent clean water cycles can remedy the problem.

Organic fouling of anion resins places weak organic acids onto the resin that aren't easily removed during caustic regeneration. These organic acids can contain carboxylic acid groups that behave like weak acid exchangers during caustic regeneration, capturing sodium ions from the caustic. These sodium ions are then slowly bled off of the resin by hydrolysis during the rinsing step. The appearance of this sodium (actually present as sodium hydroxide now) in the rinse effluent is what can make achieving 18 megohm so difficult. The sodium ions can be neutralized during an overnight soak by diffusing off of the carboxylic groups onto the cation component of the mixed bed.

Cross contamination

When resins aren't separated completely, the cation resin portion that ends up in the anion resin layer gets exposed to sodium hydroxide (caustic) during regeneration. This puts the cation resin into the sodium form. When anion resin ends up in the cation resin, it's exposed to acid during regeneration, usually hydrochloric acid, which puts the anion resin in the chloride form. (Also, older anion resins contain weak-base anion sites. These sites get converted to the •HC1 form; that is, they absorb the whole acid molecule when exposed to acid during regeneration with hydrochloric acid.) These sites are now in the exhausted form and are not available for exchange in the subsequent cycle. In addition, • HC1 can throw off a chloride molecule during hydrolysis by water.

After the resins are mixed, a long rinse-to-quality (or the final rinse of the mixed bed preceding the service cycle) may occur. The service cycle doesn't begin and the water is not sent to service until quality is reached. But an overnight soak will vastly improve the effluent quality. The resin probably will not be able to attain 18 megohm, however. At reasonable flow rates (5 gpm/ft^3) better quality will be seen; at higher flow rates (20 gpm/ft^3), expect lower quality.

REACTIONS

These formulas explain self-neutralization and equilibrium:

$AR^{\cdot ORG\cdot Na} + H_2O \rightarrow AR^{\cdot ORG\cdot H} + NaOH$

Organically fouled anion resin has exchangeable sodium ion present after regeneration. This sodium ion can be hydrolyzed off the resin by water.

$CR^{\cdot H} + NaOH \rightarrow CR^{\cdot Na} + H_2O$

Cation resin in hydrogen form exchanges for the sodium ion hydrolyzed off the anion resin.

AR = anion resin
CR = cation resin
ORG = organic

Temperature influences

Mixed-bed resins that rinse well in the summer may not rinse as quickly during the winter when water temperatures are lower. This is particularly true of older anion resins that have slower reaction rates. Older anion resins usually have some degree of organic fouling that slows down the time it takes to remove ions, and cooler water temperatures exacerbate the problem. To overcome this and avoid wasting so much water, end the rinse cycle before the desired quality is reached but after the bulk of the rinsing has taken place. Then, remix the cation and anion resins and perform an overnight soak.

The neutralization that takes place during the overnight soak is governed by diffusion and dissociation rates. Diffusion and dissociation are constant rate processes that are affected by temperature—colder is slower, warmer is faster. Using warmer water for rinsing will result in a faster rinse to quality and consume less water.

The role of sodium

Poor rinse characteristics of mixed bed resins are usually due to the appearance of sodium in the effluent (*Figure 3).* This sodium is sloughed, o~ hydrolyzed, off of the anion resin. The rate of sloughing, or hydrolysis, is affected by temperature, and the amount of sodium is determined by the amount of organic fouling and carboxylic groups present. If the desired mixed-bed effluent quality is not achieved during the initial rinse, try an overnight soak and resume the rinse the following day.

Conclusion

Regeneration of mixed bed resins may not always immediately yield acceptable results after the initial final rinsing. Upon overnight soaking, however, the same mixed bed may perform beautifully. This is due to the phenomenon of self-neutralization that occurs when a freshly regenerated resin is allowed to soak in water for a period of time. The self-neutralization that occurs compensates for several effects that may be present in the mixed bed.

1. *Hydrolysis of sodium ions.* As anion resins age, the processes of oxidation and organic fouling can both put carboxylic groups on the resin. These sites grab sodium ions during caustic regeneration and these same sodium ions can be hydrolyzed off during rinsing. During an overnight soak, however, the cation resin in the mixed bed can pick up these sodium ions.
2. *Hydrolysis of chloride or sulfate ions. Another thing that happens to anion resins as* they age is the formation of weak-base sites on the resin. These weak-base sites, when exposed to acid after cross contamination, will remove the acid as . HSO_4 if sulfuric acid is used. In either case, the corresponding chloride ion (Cl) or sulfate ion (SO_4) can be hydrolyzed off during rinsing or absorbed by an anion resin during soaking.
3. *Precipitation.* Mixed-bed resins can sometimes be hardness fouled, especially working mixed beds that don't have reverse osmosis or separate