

a new family of Resins

The efficiency of an ion exchange operation is determined by how much excess chemical is used to drive the regeneration reaction. Regeneration efficiency not only determines the economics of the ion exchange process but also limits new ion exchange considerations because of restrictions on regenerant waste disposal. Recent developments in the resin bead fictionalization technique have led to a new family of resins with improved regenerant utilization and reduced waste discharge.

By Don Downey

Improving operations with shallow-shell resins

The capacity of an ion exchanger, be it a softener or demineralizer, is incrementally improved with increases in the regenerant dosage. The highest efficiencies, however, are with the lower doses, while the lowest leakages are with the higher doses.

In recent decades, the increased need for wastewater reclamation and waste discharge reductions has spawned much research dedicated to methods of improving regenerant efficiency.

Overall, ion exchange efficiency is limited by the rate at which regeneration can take place. Decreasing the path the regenerant needs to travel by partial (surface) fictionalization and leaving an inert core allows ion exchange resins to regenerate more completely, reducing excess chemical

usage with no sacrifice in capacity or leakage. The advent of shallow-shell resins (SSR) allows co-current regenerated systems to offer similar capacities and leakages previously only achieved in counter-current regenerated systems.

Ion Exchange History

When minerals dissolve in water, they dissociate or separate into oppositely charged ions. The ion exchange process, a relatively modern discovery, allows us to remove undesirable ions and replace them with less objectionable ones. Typical examples are replacing hardness with sodium or nitrates with chlorides. The exchange of ions has been observed and documented as far back as biblical times, but the understanding of the processes and applications for it are less than 100 years old.

The modern styrene divinylbenzene ion exchange resins used today for water softening and demineralization are about 50 years old. Although we may have discovered new ways to use these resins, the basic chemistry has not changed in half a century.

The rate at which similar resins regenerate is proportional to the square of their diameters. In other words, if one bead is four times the size of another, the larger beads take 16 times longer to regenerate to the same degree as the smaller ones. The result is that the smaller beads are highly regenerated while the larger ones are still loaded with hardness.

Because these smaller beads will sit at the top of the resin column, the feed stream will see the least regenerated resin last, which compromises quality by increasing the water required for rinsing and raises background leakage in a normal co-current regeneration scheme.

Uniform particle size (UPS) resins will demonstrate higher chemical efficiencies than nonuniform resins because they regenerate at about the same rate, resulting in less "overkill" or "starvation." The beads on the bottom of the vessel, however, will still be the least regenerated in the column.

Counter-current regeneration improves the efficiency of regeneration that results in the cleanest resin at the bottom of the column and leakages 70% to 80% lower than co-current. Proper counter-current regeneration requires the resin bed be held in place with a mechanical screen, completely filling the vessel with resin, or the use of blocking flows of air or water. Combining UPS resins with counter-current regeneration can produce various degrees of improvement over conventional systems.

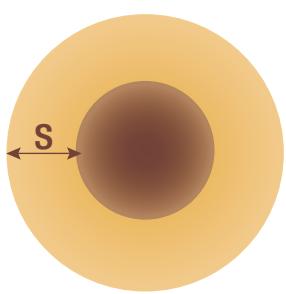
Shallow-Shell Technology

Several years ago, researchers looked at methods of improving the relatively poor efficiency of standard resins for decationization. The cation exchange process is rapid, taking only a fraction of a second to go from influent of 200 ppm cations to nearly zero within the column.

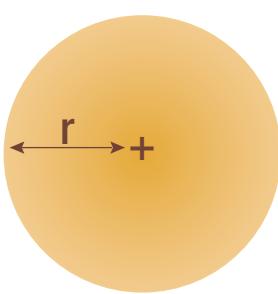
Why couldn't the regeneration process be as fast and complete? The reason, they discovered, is that the concentration of regenerant needed to drive the regeneration reaction diminishes rapidly as chemical enters the bead. More chemical is required to keep the reaction driving toward the center.

In the case of conventional resins, the larger beads are left with an almost solid core of sodium due to their relatively low regeneration level. The sodium equilibrates with its neighboring exchange sites, diffusing back to the surface where it is then rinsed off during service, resulting in sodium leakage. This

Table 1. Shell Radius & Volume Ratio



where: $\frac{s}{r}$ shell radius



Standard resin

Shell radius	.4	.5	.6	.7	.8	.9	10
Volume ration	78.4%	87.5%	93.6%	97.3%	98.7%	99.9%	100%

leakage necessitates longer rinses to reach quality, which consumes capacity and water, and shorter runs because less additional sodium throws the product water out of conductivity specification.

The volume of a sphere, such as a resin bead, is proportional to the cube of its radius. In other words, if bead A is half the size of bead B, it will contain $\frac{1}{8}$ the volume. Conversely, if we penetrate only halfway into the bead, we have accounted for $\frac{7}{8}$ of its volume. Therefore, if we produce a resin that only has surface functionality contained in the outer half of its shell, we can improve the efficiency of regeneration by cutting the workload effort by 75% because we do not have to spend all that energy and excess regenerant trying to clean the inside of the resin bead.

Nearly 30% of a resin's reactive sites lie just below the surface in the first 10% of its outer radius. Nearly 60% of its volume is 25% of its shell and 95% is contained at about 60% of the radius depth (see Table 1).

Over the past 25 years, scientific papers have promoted the idea that if resin had a shorter diffusion path or shallow shell, it could be more readily

regenerated. This, in turn, would yield higher regenerator efficiency, produce lower leakages and conserve water. Ion exchange manufacturers experimented with the concept of the shallow-shell technology (SST) by sulfonating the raw beads to a certain depth and leaving an inert core.

The structure somewhat resembled a boiled egg, except rounded. It was discovered that the shallow shell was also a very uniform shell. Not all beads were fictionalized to the same percentage depth, but they were fictionalized to the same uniform depth, and that was controllable. A resin could now be manufactured that would duplicate the positive attributes of uniform beads.

One of the problems encountered early on was that the functionalized shells and the inert cores had vastly different swell/shrink ratios during exhaustion and regeneration. This resulted in a highly efficient resin bead that could not hold itself together. Recent improvements in basic core bead strength have solved the problem and led to the development of a family of SST resins.

Operating capacity of SST in the H⁺ form—when evaluated in a lab

with synthetic water containing 100% sodium as the cation to be adsorbed and regenerated with HCl—was slightly higher than standard resin at 3 lb of HCl/cu ft (48 g/L). However, when regenerated at 5 and 7 lb of HCl/cu ft (80 and 112 g/L), SST capacity was comparable or slightly below that of standard cation.

An important aspect of SST is the lower sodium leakage achieved in a co-flow regenerated system. This resin achieves a more complete elution of sodium from the bead during regeneration, resulting in a 50% or more reduction in sodium leakage depending on acid dosage for HCl.

When H₂SO₄ is used and there is calcium present, sodium leakage is even lower. In fact, the higher the calcium to total cation ratio, the lower the sodium leakage will be. This adds value to a primary cation as lower sodium leakage results in lower effluent conductivity from the anion and reduced potential for silica leakage from the anion.

Use of SST in counter-flow systems appears to offer advantages over strong acid cation (SAC), and the higher the effluent quality required, the greater the advantage. SAC in a

counter-flow system will have 15% to 20% of the sodium leakage compared to a co-flow system. With this significant reduction, further leakage reduction may seem minor unless ultralow leakage is required. In this case, SST in counter-flow systems will have leakage 7% to 10% of SAC in a co-flow system. This advantage is significant when water quality requirements are stringent.

Actual field trials have confirmed operating capacities that are 15% to 25% higher than conventional resins, while providing 50% to 70% lower leakage. In short, shallow-shell resins are able to demonstrate counter-current leakage properties in a conventional co-current regenerated system. *wqp*

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