Being Selective with Sulfate

Discover how sulfate may determine resin choice and achievable capacity.

By Frank DeSilva

Most natural water supplies contain sulfates. Sulfate (SO4) is a colorless and odorless compound of sulfur and oxygen and exists as a dissolved salt in water.

High sulfates, which can cause taste in water and have a laxative effect on livestock and humans, are usually associated with high hardness levels.

Soil properties usually determine the amount of sulfates in a water supply, while some industrial pollution sources are also contributors.

The US EPA Primary Drinking Water Regulations list safe levels of sulfates at 500 ppm in drinking water and the Secondary Drinking Water Regulation Maximum Contaminant Level (SMCL) for sulfate is 250 ppm.

Sulfates are easily removed from water by reverse osmosis (RO), deionization, anion exchange and distillation. The sulfate ion can be removed by anion resin in the chloride or hydroxide form.

This article will primarily discuss the use of chloride form anion resins for the treatment of drinking water and how sulfate figures into the choice of resins and the achievable capacity.

Sulfate removal with anion exchange

The two types of anion exchange resins commonly used today are Type 1 and Type 2 strongly basic anion exchange resins. Both resins can be used to remove sulfates.

The Type 1 resin derives its ion exchange capabilities from the trimethylamine group. The Type 2 resin derives its functionality from the dimethylethanolamine group.

The relative order of affinity of these strong base anion resins for some common ions in drinking water is:

Uranium/Perchlorate>Sulfate/Chromium >Selenium/Arsenate> Nitrate > Chloride > Bicarbonate>Fluoride

Looking at these affinity relationships, you can see why the standard anion resins are limited in most applications by the amount of sulfate in the water. Sulfate is practically the strongest held anion, and is almost always present in much higher amounts than the ions that we are trying to remove in drinking water treatment: fluoride, nitrate, arsenic, selenium, chromium, etc.

If we can somehow eliminate sulfate as a competitor for exchange sites on the resin, we can make the removal of these other contaminants much more efficient.

The process

When the anion resins are run in the salt form, chlorides initially replace all anions. The effluent sulfates will be near zero throughout the run.

Bicarbonates will be exchanged for chlorides in the first part of the run, and then pushed off the resin in the latter part of the run. If nitrates are present, they will be low throughout the run unless the unit is run past its nitrate capacity.

In normal drinking water concentrations because sulfate has a higher affinity for the resin than nitrate, the sulfate occupies the top portion of the bed and the nitrate, which has the second highest affinity for the resin, takes the next position.

On over-exhaustion, the sulfate will displace the nitrate so that the nitrate concentration will rise quite sharply to a level in excess of the nitrate level in the raw water — a phenomenon called dumping.

pH will be reduced during the first part of the run due to the removal of alkalinity and increased above the influent pH once bicarbonates (alkalinity) begin to leak. Chlorides will be equal to the sum of SO4, Cl, HCO3 and NO3 during the first part of run and equal to SO4, Cl, and NO3 during the latter part of the run.

Since the anion unit is salt regenerated, materials of construction may be the same as for a water softener. Also, since no caustic is used for regeneration, the influent to the unit does not need to be softened.

The resin is typically regenerated with dilute brine, usually at 10 pounds per cubic foot. When operated in the chloride cycle (sodium chloride regeneration), the resin will not exchange for CO2 or silica. Recommended service flow rate is 3 to 5 gpm/cubic foot.

Selective resins

The term nitrate selective refers to resins that retain nitrates more strongly than any other ions, including sulfates. There are a variety of functional groups that have been placed into anion exchange resins that are nitrate selective.

Most of these resins are similar to the Type 1 resins, but they have larger chemical groups on the nitrogen atom of the amine than the methyl groups that comprise a Type 1 resin.

Reordering

The larger size of the amine groups makes it more difficult for divalent ions, like sulfates, to attach themselves to the resin. This reorders the affinity relationships so that nitrate has a higher affinity for the resin than sulfates, even at drinking water concentrations.

The affinity relationship for nitrate selective resins for the major ions in drinking water is:

Nitrate > Sulfate > Chloride > Bicarbonate

The term nitrate selective resin is actually a misnomer. In fact, all of the commonly referred to nitrate selective resins are non-selective for sulfates and other polyvalent ions. This leaves nitrates as having the greatest affinity for the resin.

Nitrate selective resins have larger molecular groups at the exchange sites and a greater level of porosity to enhance kinetics. Because of this, they post a lower total capacity than standard resins.

When the resin is used for nitrate removal, on exhaustion the nitrate concentration climbs gradually until it reaches the same level as the raw water. Nitrates will not exceed their influent levels.

Sulfates, however, break before nitrates and will rise to levels higher than the inlet sulfate levels due to dumping. The sulfate levels can achieve a level equal to the sum of the nitrates and sulfates before coming back to the same level as the sulfate concentration in the raw water.

Resin comparison

A fair number of nitrate selective resins have been synthesized, but only two are available commercially — the tributylamine and triethylamine types. Each type has its advantages, depending on the application.

Because of its smaller size, the triethlyamine (TEA) structure yields a resin with a higher operating capacity than the tributylamine (TBA) type.

However, the tributylamine may provide lower chemical operating costs in large systems when regenerant use is minimized through brine reclamation schemes.

The TBA resin shows particular promise as a selective resin for perchlorate removal.

Summary

Most chloride form anion applications are limited by the amount of sulfate present in the water. In moderate to high sulfate waters, the use of a selective anion exchanger may perform better.

In standard resins, when the influent sulfates are relatively low (at least less than 25 percent) the contaminant of concern, such as nitrate, arsenic or selenium, can take up most of the resin's capacity — to about the same degree as in a selective resin.

Therefore, the higher total capacity of the standard resins can provide higher operating capacities in all but those cases where sulfates are present in large amounts.