

All raw water supplies contain dissolved ions that are positively or negatively charged. The positively charged ions (called cations) include calcium and magnesium, which constitute hardness. Other cations present in water are sodium, potassium and iron. The negatively charged ions in water (called anions) include sulfates, chlorides, bicarbonates and silica.

There are other compounds and ions found in groundwater supplies that are present as cations or anions and are candidates for treatment by ion exchange. These contaminants include arsenic, nitrate, perchlorate, radium, uranium, boron, chromium, aluminum, ammonia and heavy metals.

There are two dominant forces at play in today's drinking water supply. The first is the drought conditions, primarily in the southwest U.S., that are forcing water utilities to implement conservation methods and possible water rationing. The other is the tougher quality standards that water purveyors must adhere to when supplying water to consumers, such as the new and future standards for arsenic, radium and perchlorate.

Groundwater supplies that may have been considered "locked assets" because of contamination from nitrates, arsenic or other ions and compounds are now being looked at more closely as alternative

For much the same reason, boron is not well rejected by reverse osmosis devices and other membrane processes.

There exists a boron-selective resin with methyl-glucamine functionality that is capable of removing boron in preference to all other ions. This resin is rather expensive but can be used as a boron-specific trap.

Nitrate & Nitrite

These ions are relatively common in surface waters from agricultural areas. There are nitrate-selective resins available based on triethylamine functionality. They are nonselective for sulfate, allowing greater loading of nitrate in waters that contain a significant fraction of sulfate. All of these resins have a selectivity for nitrate that is about the same as for chloride. The removal of nitrite is not as complete as that of nitrate. One technique is to oxidize the nitrite to nitrate prior to removal. This method, however,

more difficult question of determining what form they are in so that an approach can be developed for their removal.

Radioactive Metals

Radioactive metals such as uranium and radium are present in some well water supplies, particularly in the western U.S. Radium is always present as a cation, and uranium is present as an anion under drinking water pH conditions. They are generally well removed by conventional ion exchange resins. However, due to their high selectivity for the resins, they are not easily removed from the resin during regeneration. This leads to long service cycles, but often single-use cycling of the resin.

Phosphate

Phosphate is present in many municipal waters, as municipalities attempt to preserve old piping distribution systems. It is generally fed as an orthophosphate complex but is sometimes fed as phosphoric acid. Phosphate loads onto anion resins and is not well removed from them under alkaline conditions; therefore, it can build up on anion resins and cause fouling. Phosphate can be removed under acidic regeneration conditions.

Aluminum

Aluminum is present in many water supplies due to the use of aluminum

By Frank DeSilva

Positives & Negatives

Ion exchange for removal of groundwater contaminants

sources of drinking water literally start to dry up. Removal of these contaminants by ion exchange, whether on a regenerable basis or a once-through disposable basis, can be the economic key to the release of these waters as a safe local drinking water supply.

The selection of the appropriate ion exchange resin for the job should be made with the assistance of the resin manufacturer. Test the water to be treated for hardness, sodium, sulfate, chloride, alkalinity, pH, conductivity and other ions of concern. Provide these test results with the desired treated water quality and the resin manufacturer can make process recommendations and resin selection.

Boron

Boron is present in most surface waters today due to agricultural runoff. Boron is almost always present as borate, a weakly ionized anion. It is not fully removed by anion exchange resins due to its poor ionization and low selectivity.

requires significant space due to the retention time needed to complete the oxidation process.

Transition & Heavy Metals

Most transition metals are present in small concentrations as cations of various valences and are well removed by cation exchange resins.

In order of increasing selectivity, there is standard cation resin, weak acid cation resin and chelating cation resin. These resins are capable of reducing transition metal cations to extremely low levels. It is important to note that resins work within a relatively narrow pH range; that they are affected by the mix of other ions; and that because they are cation exchange resins, they can only remove cationic forms of the metals.

Because transition metals form coordination complexes with various chelants, solvents and organic substances, it is possible that they are not present in their cationic form. This leads to the

sulfate as a coagulant. When coagulation occurs outside the optimum pH range, traces of dissolved aluminum are added to the product water. Aluminum is well removed by softening resins and deionization. However, it is not readily regenerated from the resin due to its trivalent nature. Softening resins that have an appreciable aluminum in the feedwater will gradually become fouled by the aluminum they are removing. Aluminum can be removed by cation resin by acidification.

Ammonia

Ammonia is present in almost all waters to some degree. In many cases, it is deliberately added to chlorinated feedwaters to reduce THM precursors. It is well removed by deionization processes but not by softening.

The general approach to ammonia removal would be primary and polishing softeners. Ammonia is removed preferentially to sodium by cation resin,

but is displaced by calcium and magnesium. Therefore, a single softener will remove ammonia during the initial part of its cycle but will then release the ammonia as it becomes exhausted with hardness.

Softening can be used effectively for ammonia removal if the primary softener is allowed to load to a hardness endpoint and a polishing softener is used to remove ammonia. In this case, the primary softener must not be operated to hardness breakthrough, as this would cause an ammonia spike and lead to elevated ammonia levels in the final product water.

Sulfates

Sulfates are easily removed from water by anion exchange. The sulfate ion can be removed by anion resin in the chloride or hydroxide form. Two types of anion exchange resins commonly used 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.

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 remove in drinking water treatment: fluoride, nitrate, arsenic, selenium, chromium, etc. If we could eliminate sulfate as a competitor for exchange sites on the resin, we could

make the removal of these other contaminants more efficient.

When the anion resins are run in the salt form, initially, chlorides 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. 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 sharply to a level in excess of the nitrate level in the raw water. This phenomenon is called dumping.

Selective Anion Resins

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 Type 1 resin. 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 named nitrate selective resins are nonselective for sulfates and other polyvalent ions. This leaves nitrates with the greatest affinity for the resin.

The nitrate-select resins have larger molecular groups at the exchange sites and greater 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 equal the sum of the nitrates and sulfates before coming back to the same level as the sulfate concentration in the raw water.

A number of nitrate-selective resins have been synthesized, but only two are available commercially: tributylamine and triethylamine. Both types of nitrate-selective resin have their own advantage, depending on the application. The triethylamine structure, because of its smaller size, yields a resin with a higher operating capacity than the tributylamine (TBA) type. However, TBA may provide lower chemical operating costs in large systems when regenerant use is minimized through brine reclamation schemes.

Hybrid Ion Exchange Media

A new breed of ion exchange media has been developed that takes sulfate out of the equation when treating water for arsenic removal. This media, which uses a strong base anion exchange resin as the parent resin, has been infused with iron molecules. The iron surfaces adsorb the arsenic, and the media can be used on a disposable or regenerable basis.

The hybrid resin retains its initial ion exchange characteristics and can be considered for combined contaminant removal, such as uranium and arsenic, nitrate and arsenic, chromate and arsenic, and so on. Projections can be made to predict breakthroughs of the various compounds, but it is essential that benchscale or pilot testing be performed to get the most accurate numbers. *wqp*

Note: Additional information and a detailed contaminants chart, their potential health effects and media for removal is available at www.wqpmag.com/lm.cfm/wq110702.

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