By Francis J. DeSilva, ResinTech, Inc.

NITRATE REMOVAL BY ION EXCHANGE

Nitrates in concentrations above 10 ppm expressed as N* (this can be expressed as 35.7 ppm as calcium carbonate or 44.3 ppm as nitrate) are considered unsafe. Nitrates have no detectable color, taste or smell at the concentrations involved in drinking water supplies, and they do not cause discoloration of plumbing fixtures, so they remain undetectable to our senses. Nitrates do not interfere in non-potable domestic uses such as laundering. Therefore, nitrate removal processes must be either foolproof or include extensive monitoring of the treated water to detect breakthrough or determine the need for regeneration.

Infants are particularly susceptible to nitrates because their digestive systems do not operate in the exact same manner as adults. Nitrates are converted by bacteria in the stomach of infants to toxic nitrites. At levels that would not cause harm to adults, nitrates can cause methemoglobinemia in infants, a condition also known as "blue baby" syndrome.

Nitrates present in a water supply can be a symptom of other contaminants in that source of water. Have a full public health analysis performed on waters being considered for treatment. Disinfection may be necessary to counter other health concerns.

Sources of Nitrates

There are both natural and man-made sources of nitrates in groundwater. The main source of nitrate contamination appears to be from agricultural operations, farm runoff and fertilizer usage. There also is some nitrate formed in the atmosphere by oxidation of nitrogen oxides that are emitted from power plants and internal combustion engines. One other man-made source is industrial corrosion inhibitors that have leaked into the ecosystem.

Naturally occurring nitrate can result from a combination of nitrogen and oxygen through electrical discharges (lightning). Also, nitrate is formed by *Nitrobacter* bacteria by oxidation of nitrites.

Resin Treatment Choices

Standard anion resins. The two types of standard resins commonly used for nitrate removal today are Type 1 and Type 2 strongly basic anion exchange resins. 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 for the three most common ions in drinking water compared to nitrates is

Sulfate > Nitrate > Chloride > Bicarbonate

Figure 1a illustrates a breakthrough curve for a type 2 anion resin treating a water containing nitrates.

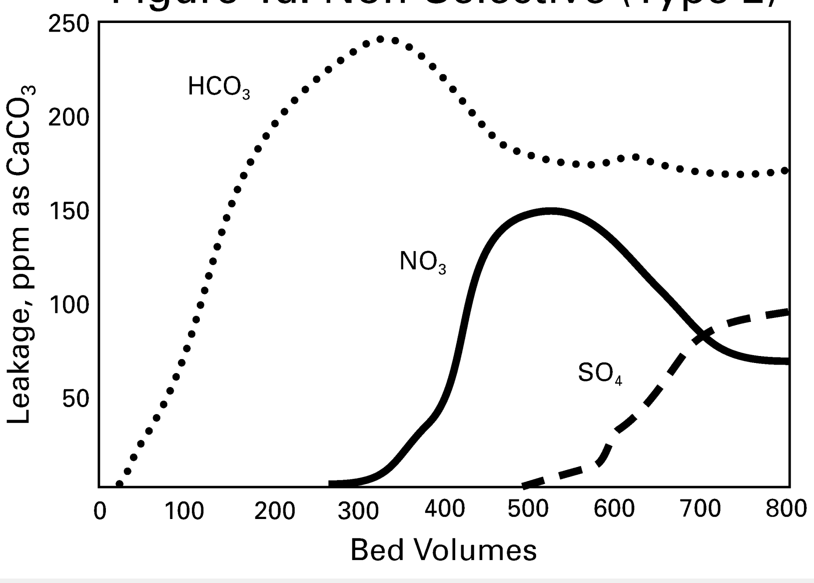
Selective resins. The term "nitrate selective" refers to resins that retain nitrates more strongly than any other ions including sulfates. A variety of functional groups can and have been placed into anion exchange resins that are nitrate selective. Most of these resins are similar to the Type 1 resins, but they have larger chemical groups on the nitrogen atom of the amine than the methyl groups that comprise a Type 1 resin. The larger size of the amine groups makes it more difficult for divalent ions such as 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 in drinking water is

Nitrate > Sulfate > Chloride > Bicarbonate

A fair number of nitrate-selective resins have been synthesized, but only two are available commercially—the tributylamine and triethylamine types. Although both the tributylamine and triethylamine resins are approved by most European countries for potable water applications, they are not listed by FDA.

Performance of Various Amine-Type Resins

Figure 1a. Non-Selective (Type 2)



* *Nitrate values usually are reported either as the Nitrogen Atom, the Nitrate Ion, or as the Calcium Carbonate equivalent. The calcium carbonate value is the one used for most ion exchange calculations in North America. To convert from values reported as "N" to their calcium carbonate equivalent, multiply them by 3.57 (i.e. N × 3.57 = as $CaCO_3$). Likewise to convert values reported as nitrates (NO_3) to $CaCO_3$ multiply them by 0.80645 (i.e. NO_3 × 0.80645 = as $CaCO_3$).*

About the Author
Frank DeSilva is the national sales manager for ResinTech, Inc., West Berlin, N.J. He has been in the water treatment industry for more than 20 years. ResinTech manufactures a broad range of ion exchange resins for water and wastewater treatment and also activated carbon and inorganic selective exchangers.

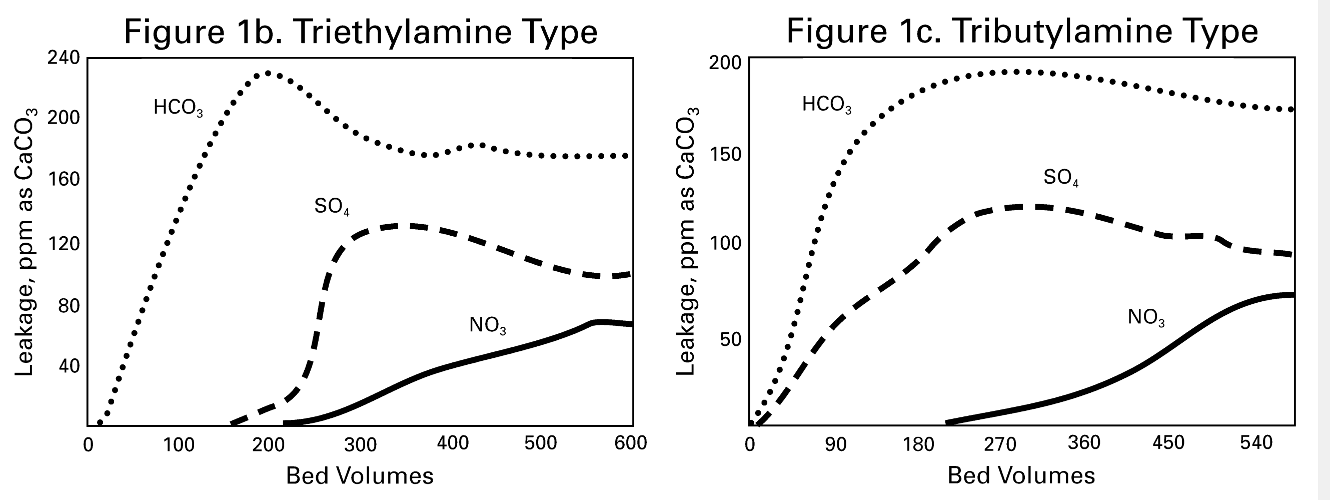
Generally speaking, nitrate selective resins have from 10 to 100 times higher relative affinities for nitrates against sulfates than the standard resins. Because of this, it is the sulfate ion that would be "dumped." The phenomenon known as "dumping" occurs when nitrate concentration in the treated water exceeds the concentration in the raw water. When a nitrate selective resin is run past the point of exhaustion, the nitrate concentration of the treated water will not rise past the concentration in the raw water.

Each of the two types of nitrate selective resin has its own advantages, depending on the application. The triethlyamine structure, because of its smaller size, yields a resin with a higher operating capacity than the tributylamine type. However, the tributylamine may provide lower chemical operating costs in large systems when regenerant use is minimized through brine reclamation schemes.

Perchlorates & Technicium

The nitrate selective resins are designed to be sulfate "deselective" and, therefore, favor the removal of nitrates. These same sulfate de-selective resins are finding favor in other specialty applications that need to minimize the impact of sulfate and other anions on the removal capacity. Two applications that are receiving a lot of attention today are the removal of perchlorate and technicium, both of which can pose serious health threats by contaminating groundwaters. Perchlorate is a byproduct of rocket propellant manufacturing and has been detected in the groundwater in more than 30 states. Technicium is a radioactive isotope that appears in the wastewater from some nuclear operations.

Performance of Various Amine-Type Resins



Nitrate Dumping

The Type 1 and Type 2 resins are considered non-selective because of their greater affinity for sulfates. If a normal Type 1 or Type 2 resin is run past the end of the normal nitrate removal service cycle, sulfates can continue to load onto the resin bed, pushing the nitrates off and causing dumping. (See Figure 1a.)

When dumping occurs, the concentration of nitrates in the treated water can approach the sum of the concentrations of both the sulfates and nitrates in the raw water. In a water containing 80 ppm of nitrates as calcium carbonate and 85 ppm of sulfates as calcium carbonate, overrunning the unit will cause nitrate levels to rise until they approach 165 ppm as calcium carbonate. Nitrate selective resins prevent this from occurring. (See Figures 1b and 1c.) In the event of a service overrun with the nitrate selective resin, the highest nitrate level that can appear in the effluent is equal to the nitrate level in the influent.

Other Removal Methods Available to the Water Treatment Dealer

Reverse osmosis (RO) effectively can remove up to 75 percent of the nitrates present, using a polyamide membrane with a 50 psi minimum pressure. Typical capacities are in the range of 5 to 15 gallons per day. The effluent water is essentially nitrate-safe and low in dissolved solids. However, the performance of the RO is dependent on pH, temperature and pressure. Should any of these operational parameters change, nitrate rejection could fall below 50 percent.

Distillation. Commercially available automatic countertop distillers can produce 5 to 10 gallons per day of nitrate-safe and mineral-free water. Energy consumption is high with distillation techniques, and on-demand flow rate is limited to low flows.

Resin Certification

The standard Type 1 and Type 2 resins are listed by the U.S. Food and Drug Administration (FDA) for potable water applications in the USA.

Although both the tributylamine and triethylamine resins are approved by the equivalent of the FDA organizations in essentially all European countries for potable water applications, they are not currently listed by the United States FDA. Only one or more brands of nitrate selective resin (triethylamine functionality) have been certified by the Water Quality Association's (WQA) Gold Seal Program. Ask your resin supplier to provide you with copies of the certification.

Operation

The ion exchange process for the removal of nitrates is both simple and effective. It operates in the same manner as a common water softener and easily can remove much more than 90 percent of the nitrates. The process uses a strong base anion exchange resin, which is regenerated with common salt. The chloride (Cl) ion of the salt molecule is utilized by the anion exchange site, the sodium (Na) ion passes right through the resin bed and does not affect the process.

Operational Guidelines

The anion resins used in nitrate removal applications are regenerated with ten percent brine at a dosage of about ten pounds per cubic foot. The service flow rate can be between two and four gallons per minute per cubic foot. A minimum resin bed depth of 30 inches is recommended, 36 inches is preferred.

In many respects, the operation of a nitrate removal unit is similar to an ordinary softener. The biggest difference during regeneration is the backwash rate. The anion resins are less dense and require a backwash flowrate about half that of softening resin.

In some household applications, nitrate removal is used solely for drinking and cooking purposes. This reduces the volume demand substantially, in some cases to the point that small POU throwaway filter cartridges can be used instead of the larger regenerable systems. Cartridges always should be filled with the nitrate selective resins to avoid nitrate dumping.

Type 1 and Type 2 strongly basic anion resins have high affinities for nitrates and are easily regenerated with common salt. All of the anions found in potable water have varying affinities for the resin. Therefore, they consume varying amounts of the resin's capacity. The amount of a particular ion that the resin will hold varies directly with its affinity and its relative concentration with respect to the other ions in the influent. At the concentration levels involved in drinking water, sulfate has a higher affinity for the Type 1 and Type 2 strong base resins than nitrate, while nitrate is more strongly held than chloride and bicarbonate.

Safety Guidelines

It is essential that the unit not be overrun during service, especially when standard anion resins are used, to prevent nitrate dumping.

- Use automatic regeneration controls on the ion exchange unit.
  - Meter initiated (gallonage)
  - Timeclock controlled (time in service)
- Downgrade the system to operate at 80 percent of the total capacity.

Also worth noting is the fact that nitrate-bearing water should never be boiled. Boiling concentrates the water and the relative level of nitrates would actually increase.

Waste Brine Concerns

The discharge of a salt regenerated nitrate unit is typically sent to the on-site septic system. Some denitrification takes place in the septic tank from anaerobic bacteria, where bacteria break down nitrate to nitrogen and oxygen. Additional denitrification can take place during percolation.

Pretreatment

Nitrate removal systems usually require only prefiltration and dechlorination (if chlorine is present) as pretreatment. These two steps are necessary to protect the anion bed from oxidation and physical fouling. Softening ahead of the nitrate removal resin is not necessary except in cases of high pH and high-hardness waters (four grains or higher) where the concentration of carbonates and hydroxides in the resin bed could cause precipitation of calcium or magnesium.

pH Effects

Anion resin in the chloride form removes not only nitrates, but also sulfate and alkalinity. The removal of alkalinity

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you are not great at closing, prospecting will make you rich.

You may be wondering why everyone does not do it, especially since it is an easier way to make more than to learn to close them all. Many sales forces unofficially are led by poor salespeople who try to drag others down to their level of mediocrity. They realize that they would look bad if everyone worked at the level they could, so they are negative and do their best to stay on top by keeping others down.

I want to hear from you!
If you have a great sales idea you would like to share or have tried one of the tactics presented here, please e-mail me at davidson@salesco.net.

The other reason few succeed is that it takes discipline over a long period of time. That is not something our society encourages. The fact is there is not much traffic on the extra mile. If you want to be a millionaire, you will have to rely on inner strength and discipline.

The fact is, it is not easy to make it to the top of any profession, especially sales. That is why they pay people who do so much. They are unique and valuable.

Your level of prospecting is the true measure of your belief in the company, product and yourself. If you want to make it to the top, read "Three Ways to Boost Your Prospects."

Many great philosophers say that the key to success is in our own backyard. This could not be truer for those of us who sell. It takes effort and discipline, but we should all be grateful we have chosen a career where we can become millionaires if we only are willing to try. WQP

FILTRATION

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can lead to a reduction in pH of the product water in the beginning of the run. To minimize this effect and add some buffering ability back to the water, soda ash (Na_2CO_3) can be added to the brine tank. This will convert a portion of the resin to the bicarbonate form during regeneration. A ratio of one lb./cu. ft. of soda ash mixed with nine lbs./cu. ft. of salt can be used.

Comparing Resins

In standard resins, when sulfates are relatively low, the nitrate takes up most of the resin's capacity, to about the same degree as in the nitrate selective resins. Therefore, the higher total capacity of the standard resins provides significantly higher operating capacities in all but those cases where sulfates are present in large amounts.

Nitrate selective resins are best used in applications that may not be monitored closely and an overrun may occur. The resins give effective nitrate removal and prevent nitrate dumping. They can cost about 50 percent more than standard resins.

Operating Comparisons

Figures 1a, 1b and 1c show the performances of three resins (a standard Type 2 resin, triethylamine-based nitrate selective resin and tributylamine-based nitrate selective resin) on the same water supply after being regenerated at 20 pounds of NaCl per cubic foot. These graphs show the effluent concentrations of bicarbonates, sulfates and nitrates during the service (exhaustion) cycle. The service cycles were allowed to run past the nitrate breakthrough until the effluent and influent concentrations for each ion were equal.

As an example in Figure 1a, the nitrate breaks through from the bed of ResinTech SBG2 at about two-thirds of the run length before the sulfates breakthrough. This is typical performance on this type of water for either Type 1 or Type 2 resins. You also can see that the nitrate concentration reaches a peak concentration of about twice the raw water concentration and that the sulfate leakage occurs gradually, starting at about the time that the nitrate begins to reach its peak level and that the sulfate never exceeds the raw water value.

As another example, Figure 1b shows the sulfate breaks through from the ResinTech SIR-100 bed 20 percent before the nitrate begins to leak. This is typical performance for the triethylamine type resins. Notice how gradual the breakthrough curve for nitrate is and that it never exceeds its influent value. Also, you can see that the sulfate concentration reaches a value of about 50 percent above its influent water concentration.

In Figure 1c, the sulfate begins leaking almost immediately from the tributylamine type resin due to its very weak affinity for this type of resin. You also can see in Figure 1c that the nitrate leakage also occurs gradually, just like in Figure 1b.

Figures 2a, 2b and 2c show operating capacity curves for a standard Type 2 anion resin and a triethylamine type nitrate selective anion resin on waters containing 100 ppm each of bicarbonates, chlorides and nitrates but with sulfate levels of 0, 100 and 300 ppm (0 percent, 25 percent and 50 percent, respectively). It can be seen that the standard resins have higher operating capacities at sulfate levels up to 25 percent and that the selective resin has a higher operating capacity when sulfate levels are above 50 percent.

Nitrate removal by ion exchange is the preferred technology for whole house treatment. It is a low-cost method, operated in much the same manner as a common water softener. Regeneration is simple and accomplished with softener salt, the chloride ion from the salt being the reactive ion. Nitrate selective resin is the logical choice to prevent any nitrate dumping. Cartridge applications mandate the use of nitrate selective resins.

The future will find other applications for these selective resins such as we are already are seeing with the removal of perchlorate and technicium. WQP

Operating Capacity for Nitrate Removal