

Nitrate Selective Ion Exchange Resins

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It has been about 20 years since the first anion exchange system for removing nitrates from municipal potable water supplies was installed in the United States, in Long Island. Since then there has been a growing awareness of the increasing threat to health from nitrates in water. The main causes appear to be farm runoff and fertilizer usage. In the last few years there has been a dramatic increase in awareness and activity to rid potable water supplies of nitrates. Recently several municipalities have or are in the process of installing ion exchange systems to remove nitrates from the water distributed by the municipalities. These systems are large and can require thousands of cubic feet of ion exchange resin for a single installation. The goal of this paper is to lay down a basic foundation of knowledge about the chemistry and equilibrium and kinetic relationships involved in the removal of nitrates by anion exchange.

binemia in infants, a condition also known as "blue baby". Nitrates have no detectable taste, odor or smell at the concentrations involved in drinking water supplies and they do not cause color, or discoloration of plumbing fixtures, so they remain undetectable to our senses. Nitrates do not interfere in nonpotable 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.

The ion exchange process for the removal of nitrates from drinking water supplies is both simple and effective. It operates in virtually the same manner as a cation water softener and can easily remove over 95% of the nitrates. The ion exchange resin process for nitrate removal uses a strong base anion resin, which is regenerated with NaCl in the same manner as a softener. Except for the use of the anion resin, instead of cation resin, this system would be virtually identical to a softener. Since nitrates do not interfere with nonpotable water uses, nitrate removal devices in the home can and often are used solely for drinking and cooking purposes. This reduces the volume demand substantially, and in some cases to the point that small point of use, throw-

TABLE 1
PROPERTIES OF STRONG BASE RESINS

RESIN TYPE		WATER CONTENT %	VOL. CAP. MEQ/ML	$K_{NO_3}^{SO_4}$ Aprox.	$K_{Cl}^{SO_4}$ Aprox.	$K_{Cl}^{HCO_3}$ Aprox.	$K_{Cl}^{NO_3}$ Aprox.
TYPE I POROUS (GEL)		51 - 58	1.2	.08 - .17	.1 - .4	.5	2 - 4
TYPE 1 (GEL)		43 - 48	1.4	.04	.05 - .1	.3 - .5	2 - 3
TYPE 2 (GEL)		38 - 42	1.4	.04	.05 - .1	.3 - .5	2 - 4
TRIETHYLAMINE (MACRO)/(GEL)		50 - 60	1.1	.001	.014 - .016	.32	2 - 5
TRIBUTYLAMINE (MACRO)		40 - 50	.85	.0003	.0006	.3	3

Nitrates in concentrations above 10 ppm expressed as N (this can be expressed as 35.7 ppm as calcium carbonate or as 44.3 ppm as nitrate) are considered unsafe in potable waters in the United States. 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 methemoglo-

away, monitored, cartridges can be used economically instead of the larger and more costly regenerable systems.

PRETREATMENT

Nitrate removal systems usually only require prefiltration and dechlorination (if chlorine is present) as pretreat-

ment. 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 where the concentration of carbonates and hydroxides in the resin bed could cause precipitation of calcium or magnesium.

EQUILIBRIUM RELATIONSHIPS DURING THE EXHAUSTION CYCLE

The fraction of the available sites of an ion exchange resin that a particular ion will occupy during the exhaustion cycle varies directly with its relative affinity and its relative concentration with respect to the other ions in the influent. All of the standard strongly basic Type 1 and Type 2 anion exchange resins have high affinities for nitrates. Nitrates have a much higher affinity for these resins than the rest of the monovalent anions normally found in potable waters. This allows nitrates to be efficiently removed even from high TDS waters. **Table 1** shows the range of selectivity coefficients of various ions for standard strongly basic anion resins and two of the so called "nitrate selective" resins. You can see that the NO_3 / Cl and HCO_3 / Cl selectivities are essentially the same for all the resins shown and that nitrates are equally the most preferred ion against chlorides and bicarbonates and therefore will be preferentially sorbed by any of these resins over the other monovalent ions.

Sulfates are the biggest potential problem in nitrate removal by ion exchange. It can be seen from **Table 1** that the selectivity coefficient of sulfate against any of the common ions in potable water is less than one. However, sulfate is a divalent ion and its relative affinity compared to the monovalent ions varies with the electrolyte concentration according to the equation in **Table 2**. When ions of different valences compete for an ion exchange site the relative affinity is best described by the "apparent selectivity coefficient" which is shown in **Table 2** and has the form:

The apparent selectivity coefficient varies inversely with the TDS level. At TDS levels commonly encountered in potable water supplies, the apparent selectivity for sul-

<p>TABLE 2</p> <p>Apparent Selectivity Coefficient = $\frac{K \times (\text{Resin Capacity})}{\text{TDS}}$</p> <p>(TDS is the electrolyte concentration, ppm as CaCO_3)</p>
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fates on the standard strongly basic resins is higher than one against any of the monovalent ions including nitrates. Therefore sulfates will be preferentially loaded onto the standard strong base resins, displacing any other ions. On the other hand, the reduced selectivity of

triethylamine and tributylamine type resins results in apparent sulfate selectivities that are less than one against nitrates in these resins. Therefore nitrates will be preferentially sorbed over sulfates on these resins.

NITRATE DUMPING

Despite their high affinities for nitrates, the Type 1 and Type 2 resins are considered nonselective, because sulfates show higher affinities during the exhaustion cycle. If a Type 1 or Type 2 resin is run past exhaustion of the nitrate removal cycle, sulfates will continue to load on the resin bed pushing off the nitrates. When this happens the nitrate concentration in the effluent can exceed the inlet concentration in the "raw" water for a short period of time. This phenomenon is known as "dumping". When dumping occurs, the concentration of nitrate in the treated water can approach the sum of the concentration of sulfates plus nitrates in the raw water. For example, overrunning a resin past the nitrate breakthrough on a water containing 80 ppm of nitrate as calcium carbonate and 85 ppm of sulfate as calcium carbonate will result in nitrate "dumping". The nitrate levels will continue to rise until they approach 165 ppm as calcium carbonate. The actual peak concentration of nitrates depends on the total as well as the relative concentrations of all the ions in the raw water. However, it is prudent to assume the worst case especially for small systems that may not have the means to monitor nitrates in the effluent!

In larger systems it is common to send the treated water to a reservoir for blending and storage and to monitor the effluent continuously. This controls nitrates to acceptable levels. When the sulfate level in the water supply is low, nitrate "dumping" is likewise lower. The ion exchange process can be operated with "standard" strongly basic resins with good efficiency and without nitrate dumping in situations when the sulfate levels remain low. Since the composition of many potable water supplies varies seasonally, it is often possible for nitrate dumping to become a seasonal phenomena, unless proper control is practiced.

REGENERATION

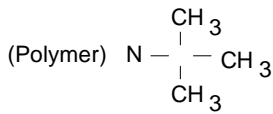
The higher nitrate and sulfate affinities for the resins during the exhaustion cycle can be overcome by mass action effects so that both the nitrate selective and standard strong base resins can be regenerated free of nitrate and sulfate, with common salt, at reasonable levels at efficiencies equal to or higher than those achieved at comparable regeneration levels for cation resins in water softeners.

The apparent selectivity coefficient of chlorides against the monovalent nitrate and bicarbonate anions is equal to the selectivity coefficients. This is approximately 0.5 in favor of nitrates over chlorides. By comparison the

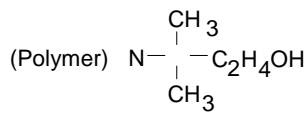
TABLE 3
CHEMICAL STRUCTURE

NON SELECTIVE "EVERYDAY RESINS"

TYPE 1

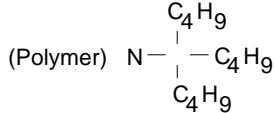


TYPE 2

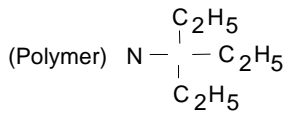


NITRATE SELECTIVE RESINS

TRIBUTYLAMINE



TRIETHYLAMINE



apparent selectivity coefficient of sodium to calcium during regeneration of a water softener is only about 0.35. This means that the chloride is more effective on an ion to ion basis in displacing nitrates during regeneration than sodium is in displacing calcium (or magnesium). Sulfates are actually the easiest ion to regenerate off of the resin. At the higher concentrations used for regeneration the apparent selectivity coefficient for sulfates is reduced to less than one against chloride for all of the resins discussed here. Therefore the sulfate is easily displaced.

LEAKAGE

Salt is about one third more efficient as a regenerant for removing nitrates from anion resins (all types) than for removing hardness from cation softener resins. Except for leakage considerations, it would be easy and effective to operate nitrate removal resins at lower regenerant dosage levels than softeners.

Nitrates are monovalent and their affinity relationships are pretty much the same at regeneration and exhaustion concentrations. Therefore, nitrate leakage during the service cycle will depend on the TDS and the amount of nitrate remaining in the resin after regeneration from the previous cycle. In virgin resin beds the initial nitrate level in the effluent will therefore be zero. In water softeners the apparent selectivity coefficient of hardness ions for the cation resins increases by two orders of magnitude between regeneration TDS levels and the lower service cycle TDS levels. Therefore, hardness leakages tend to be much smaller than nitrate leakages at similar regeneration efficiencies and operating conditions. Nitrate leakages are approximately the same for both selective and standard anion resins.

It is not usually necessary to use softened or nitrate free water for regeneration. The salt levels would keep the nitrates from getting onto the resin except for the last portion of the rinse. The amount of capacity lost during

the rinse is usually far less than 1% of the throughput capacity. Any nitrates loaded during the backwashing step would be removed during the regeneration step.

FUNCTIONAL GROUPS

The most commonly used resins in nitrate removal applications in the United States today are ordinary strongly basic anion exchange resins. These can be either type "Type 1" or "Type 2".

The Type 1 resin derives its ion exchange capabilities from the trimethylamine group. The Type 2 resin derives its functionality from the dimethylaminoethanol group. The chemical structure for these is shown in **Table 3**. The relative order of "apparent selectivity coefficient" for the three most common ions in potable waters are the same for the Type 1 and Type 2 resins and is shown below:

Sulfate > Nitrate > Chloride > Bicarbonate

The term "nitrate selective" refers to resins that are able to retain nitrates more strongly than all the other ions, including sulfates, during the exhaustion cycle on potable water supplies. Actually this is a misnomer because the so called "nitrate selective" resins are in fact only deselective for sulfate (and other polyvalent ions), as can be seen from the data in **Table 1**. The range of selectivity coefficients listed in **Table 1** are based on tests conducted at ResinTech and from values found in the literature. Generally speaking the data represent TDS levels of from 50 to 5000 ppm, although some tests were also run at typical concentrations used during brine regenerations.

There are a wide variety of functional groups that can and have been placed into anion exchange resins that have reduced sulfate selectivity and therefore allow a resin to perform in the manner of a "nitrate selective" resin. Most of these resins are similar to the Type 1 resins but 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 make it more difficult for divalent ions, like sulfate, to attach themselves simultaneously to multiple sites on the resin. This dramatically reduces the selectivity coefficient and reorders the apparent selectivity coefficients so that nitrate has a higher affinity for the resin than sulfates even at low TDS levels like those encountered in potable waters. The relative order of apparent selectivity coefficients for the nitrate selective resins are:

Nitrate > Sulfate > Chloride > Bicarbonate

Several "nitrate selective" resins have been synthesized but only two types are available commercially. The tributylamine and triethylamine types. Their chemical structure is shown in **Table 3**.

Generally speaking the nitrate selective resins have from 10 to 100 times higher apparent selectivity coefficients for nitrates against sulfates (and similarly against other divalent ions), than the standard strongly basic resins. As I mentioned previously, the term nitrate selective has more to do with the application of these products than the nature of their behavior as ion exchangers. Otherwise it would be more correct to refer to them as sulfate nonselective. When these types of resins are used, nitrate dumping is eliminated. Because of the reduced sulfate selectivity, the nitrate ions are the most strongly held, so that sulfates (and most other divalent ions) could be displaced by nitrates. When a nitrate selective resin is run past the point of exhaustion the nitrate level gradually increases until it reaches the level of the influent concentration. The nitrate's concentration will not rise past their concentration in the raw water.

Each of the two types of commercially available nitrate selective resins has its own advantages, depending on the application. The triethylamine structure, because of its smaller size, yields a resin with a higher operating capacity than the tributylamine type. However, the tributylamine type may provide lower chemical operating costs in large systems when regenerant use is minimized through brine reclaiming schemes. ResinTech can supply either type. ResinTech Sir-100 is based on the triethylamine group.

F&DA

The standard Type 1 and Type 2 resins are listed by the F&DA for potable water applications in the USA.

Although both the tributylamine and triethylamine resins are approved by the equivalent of the F&DA organizations in essentially all European countries for potable water applications, they are not currently listed by the United States F&DA. Nitrate removal has been widely practiced for many years in Europe. Until recently the selective resins were largely unheard of here so it is not surprising that they are not yet listed.

PRACTICAL CONSIDERATIONS

When the sulfate concentration is relatively low, the nitrate is the most preferred ion and will occupy a disproportionate amount of the resins' capacity during the exhaustion cycle. This happens to about the same degree in selective as nonselective resins. In such cases the standard resins function essentially in the same manner as nitrate selective resins. 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. However, since the nitrate selective resins can hold onto nitrates in favor of sulfates they will give higher operating capacities than standard

FIGURE 1A
NON SELECTIVE (TYPE 2)

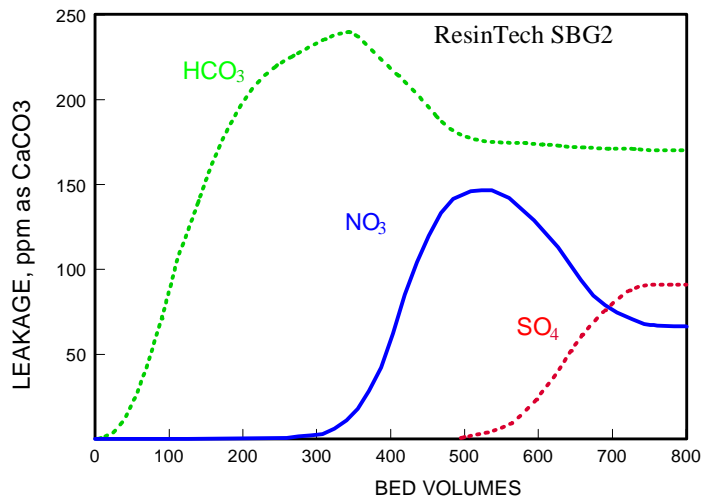


FIGURE 1B
TRIETHYLAMINE TYPE

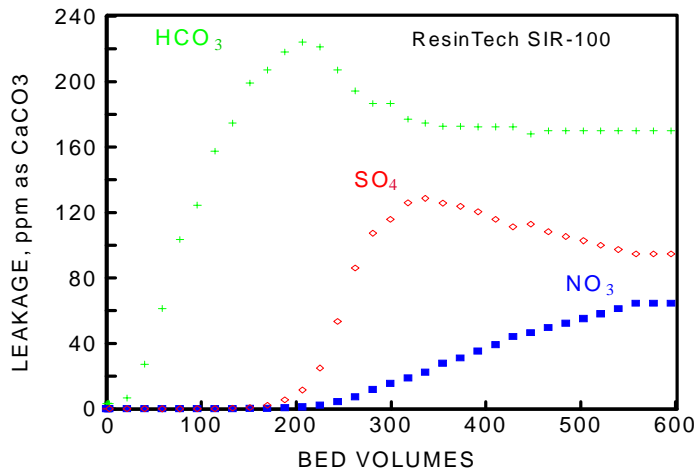
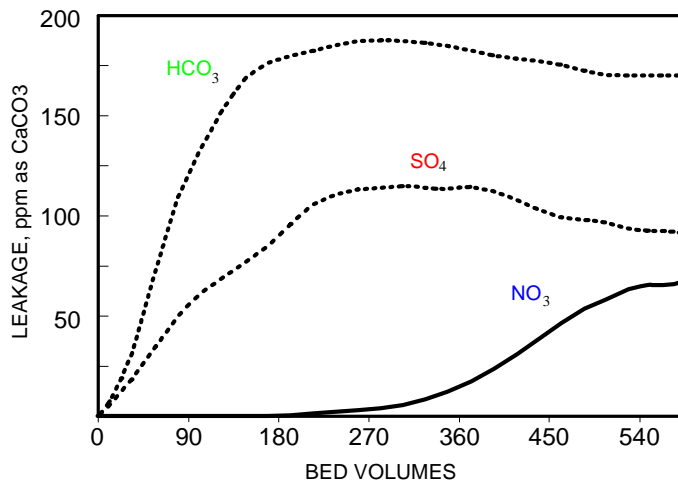


FIGURE 1C

TRIBUTYLAMINE TYPE



resins on high sulfate waters. **The major advantage of the selective resins is that they will not dump nitrates.**

In larger installations, such as for municipal systems, brine reclamation could have a significant impact on operating economies. Such schemes usually involve incomplete treatment of the used brine to remove nitrates, followed by reuse, usually with a small input of fresh brine. This would increase leakage and make the resin bed more sensitive to sulfates. The selective resins can be more effectively used in such brine reclaiming schemes. In one proposed scheme, the used regenerant would be treated in a biological process to convert the nitrates to nitrogen gas and water molecules, leaving only a little residual nitrates in the brine which would then be recycled as fresh regenerant!

OPERATING COMPARISONS

Figures 1A, 1B and 1C show the performances of three resins, ResinTech SBG2 (a standard Type 2 resin) ResinTech SIR-100 (a triethylamine based nitrate selective resin) and a 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 information in these graphs was generated using software developed by ResinTech Inc. The service cycles were allowed to run past the nitrate breakthrough until the effluent and influent concentrations for each ion were equal.

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 can also 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.

In **Figure 1B** the sulfate breaks through from the ResinTech SIR-100 bed 20% 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% 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 can also 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 ResinTech SBG2, a Type 2 and ResinTech SIR-100, a triethylamine type anion resin on waters containing 100 ppm each of bicarbonates, chlorides and nitrates but with sulfate levels of 0, 100 and 300 ppm (0%, 25% and 50%). It can be seen that the standard resins have higher operating capacities at sulfate levels up to 25% and that the selective resin has a higher operating capacity when sulfate levels are above 50%.

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ResinTech, Nitrate simulation software was used to generate the breakthrough curves in Figure 1A, 1B and 1C.