MORE THAN DOWN ON THE FARM:

Nitrate reduction presents a new opportunity for business

By C.F. "Chubb" Michaud

Summary: Nitrates are more than just a problem in agricultural communities. Largely a by-product of fertilizers and animal waste, they can be found wherever man or animal is found. They're most often associated with "blue baby syndrome" because they contribute to inability of the blood to absorb oxygen. What follows is a discussion of related water treatment methods.

With rare exception, excessive nitrates do not occur naturally in water beyond about 1 part per million. When nitrates appear in a water supply, it's generally due to man- or animal-made contamination (from the oxidation of nitrogenous waste).

Nitrogen is essential for plant growth. Certain plants, called legumes, can derive nitrogen directly from the air around them. Others get it from the soil, enhanced with nitrogen restoring fertilizers such as ammonia, nitrates and animal manure. As water percolates through the soil, readily soluble nitrogen compounds, including ammonia and nitrates, leech down into the aquifers.

Organic nitrogen compounds are a nutrient source for a large number of organisms and, as such, will undergo bacterial attack. The amine (NH_2) portion of protein becomes ammonia (NH_3). Aerobic "digestion" converts ammonia to nitrites (NO_2^-), then on to nitrates (NO_3^-) through the process of "nitrification." Anaerobic bacteria then "denitrify" nitrates to nitrogen and oxygen and back to the atmosphere from whence they came—ashes to ashes, dust to dust.

Nitrates in water

In water, nitrates are measured in parts per million (ppm) as nitrogen (expressed as milligrams per liter, or mg/L NO_3-N). Resin capacities, however, are measured in kilograins per cubic foot (kgr/ft^3), which is derived from the NO_3 content expressed as ppm $CaCO_3$. Since NO_3 has a molecular weight of 62 and N a weight of only 14, then 1 ppm of NO_3-N is equal to $62 \div 14 = 4.43$ ppm of NO_3. To convert this to ppm as calcium carbonate ($CaCO_3$), multiply 4.43 by .81, (this is the conversion factor for translating parts per million of NO_3- to parts per million as $CaCO_3$). Therefore, 1 ppm of NO_3-N = 3.57 ppm as $CaCO_3$.

Nitrate levels above 10 ppm NO_3-N (44.3 mg/L of NO_3 or 35.7 ppm as $CaCO_3$, or 2.1 grains per gallon) are considered hazardous to the health of infants as well as many farm animals. When nitrates are ingested, they are broken down into nitrites, which then enter the blood stream through the intestinal wall. Here, they interfere with the oxygen transport mechanism, robbing the blood of oxygen and "suffocating" the body.[1] This condition produces methehemoglobinemia and cyanosis, also know as "blue baby syndrome." Contributing to health effects are nitrosamines, also formed from nitrates in the digestive process and believed to cause cancer, according to studies.[6] Extreme consumption of nitrates can be fatal.

Drinking water

Municipalities faced with funding new groundwater sources for exploding populations in areas previously used for agriculture and livestock are apt to encounter elevated nitrate levels in the aquifer. Runoff from agricultural areas can produce surface waters high in nitrates. Drainage from mines or underground excavations that have seen the use of explosives (the N in TNT is a nitrous compound) also can exhibit elevated nitrate levels. In other words, wherever man has gone, nitrates will follow. Even the drainage from residential septic systems can eventually contaminate underground waters with elevated nitrates.

Municipalities having to deal with high nitrate source waters must pretreat or blend this water prior to distribution. Their goal is not to eliminate nitrates, but to reduce them to levels below the maximum contaminant level (MCL) currently specified by the U.S. Environmental Protection Agency (USEPA)—10 ppm NO_3-N. Often the "treated" water will have nitrate levels of 60-to-85 percent of the MCL. Using such "safe" waters for cooking purposes can concentrate the nitrate content by evaporation and exceed the safe levels by factors of 100-to-300 percent.[3]

Those into home cooking—jarring fruits and vegetables—should be aware of their water source for this reason. Property owners that depend upon private wells for their water supply should have their water checked periodically and at different times of the year to determine nitrate content. Almost all water sources will contain some nitrate these days, albeit, minimal. This condition will not get better in the near future because we are expanding our population habitats into what was once farmland and searching for new sources of "local" water.[4]

Young and old alike

While nitrate warnings are generally directed at parents with infant children, babies are not the only ones in danger. The elderly, people with respiratory problems and the immunocompromised also may suffer from the effects of high nitrate consumption.

Young farm animals such as chickens, sheep, cattle, pigs and horses also have low tolerances for nitrates. Some animals that nurse their young, such as sheep and cattle, will shun water high in nitrates because their milk will be toxic to their young. Dairy cows will literally starve their calves by cutting their water intake and, thus, their milk production. Although the specific reference cannot be cited, I recall a dairy farm in Kansas that installed a nitrate removal system and increased milk production by more than 25 percent immediately and reduced calf mortality. This system was reported to pay for itself in less than six months.

Nitrates are present and so is the need to treat for them. So, how do we tackle this problem? There are two aspects to consider. The first is reducing high levels to low levels. The second is treating the so-called "safe" levels to eliminate them and avoid the issue of concentrating referenced earlier.

Reducing nitrates

There are several treatment methods for nitrate reduction. Actually, any treatment process that reduces total dissolved solids (TDS)—i.e., distillation, reverse osmosis, deionization (DI), electrodeionization (EDI)—will reduce nitrates as well. For drinking water, farm use and general residential application, DI and EDI are not practical. In addition, unless one has the need for TDS reduction, such as the case with brackish waters, whole house treatment with distillations and RO may be deemed as unnecessary or prohibitively complicated. The most suitable method of nitrate reduction for municipal, farm and whole house supply—which is central plant and point-of-entry (POE) treatment—is clearly the use of salt regenerated anion exchange. However, countertop distillation and RO—which are popular for drinking water enhancement—are also very cost effective for treatment of "safe" levels for further reduction at the point of use (POU). POU, however, is not generally acceptable if the nitrate levels are in excess of the MCL at the point of entry. POE treatment must be used in those cases.

Anion exchange

Anion exchange is very similar to softening except it works with the other (negative) end of the molecule. Softeners use cation exchangers that use sodium or potassium chloride (NaCl or KCl) to regenerate, replacing hardness ions with sodium or potassium in the process (see *Figure 1*).

I do not advocate the use of KCl for applications where the waste regenerant may be pumped to an evaporation pond or basin. The evaporated solid will be rich in KNO_3, which is flammable and can be explosive if ignited.

Central plant treatment

Municipalities that treat water above the MCLs are primarily concerned about two things: (1) to reduce the NO_3-N to levels below 10 ppm, and (2) to maximize the salt efficiency of the resin system.

As with cation exchangers, anion exchangers respond to increased brine dosage and yield higher capacities. However, they also produce lower efficiencies with increased brining. In other words, maximum efficiencies are obtained with very low salt levels of 4-to-6 pounds (lbs). At low salt levels, however, nitrate leakages will be moderate. This is usually acceptable since both conditions (1) and (2) can be met.

Municipal systems typically use Type I porous strong base anion systems. Although they are lower in initial capacity than Type II's, they do exhibit better stability and provide better salt efficiency and longer life with lower salt setting. According to design engineers, the nitrate treatment plant in McFarland, Calif., is still on its first charge of resin, which is now 15 years old! Recently, a resin change out was made on another California facility after seven years. The resin, a Type I porous resin, was still at 92 percent of original strong base capacity. Type I's also are reported to have better chlorine resistance due to the better stability of the functional chemistry.

Chloride exchange anion will reduce alkalinity and subsequently pH. While this is only a temporary event in the early part of the run, it may create an unwanted condition of a reduced pH (but not below 7). While alkalinity may be indicative of scale forming tendency, the absence of it does not necessarily mean the water is corrosive.[7] The system designer should be aware of this fact.

Point-of-entry treatment

POE nitrate treatment systems for farm and residential use generally are designed for maximum nitrate removal rather than maximum salt efficiency. Salt levels of 10 lbs. are normal on a "once used" regenerant basis although increased salt efficiency can be realized by practicing salt reclamation. Here, the last half of the brine is captured and reused for the first portion of the next regeneration. Fresh brine is used for the "polishing" portion of the regeneration. Another technique is to return the last third of the brine to the brine make-up tank for recapture.

There are two notes of caution, though. First, eductor-type dilution systems work on about a 2:1 dilution of saturated brine. Trying to reclaim more than a third of the brine will eventually overflow the brine tank. Second, there will be nitrates in the spent brine. This eventually will increase the nitrate levels in the brine system to where nitrate leakage from the service run may become unacceptable. To avoid precipitation of $CaSO_4$ or $CaCO_3$ during regeneration, it is suggested first softening the water if it is over 10 grains per gallon hardness.

The choice of resin and its performance in a nitrate removal system will depend upon the feed water analysis. Non-selective anion resins will exchange chlorides for nitrates and sulfates. Capacity will vary with the percentage of nitrate of total exchangeable ions (nitrate plus sulfate) at any particular salt setting. (See *Figure* 2.)

Figure 2

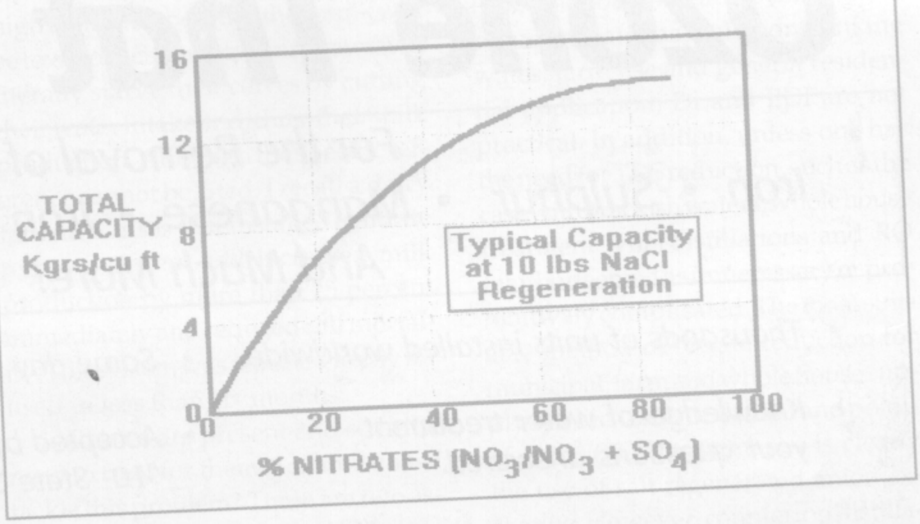
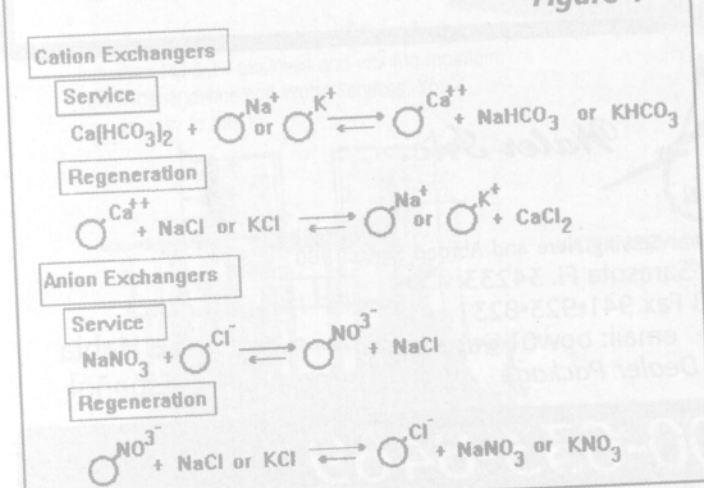


Figure 1



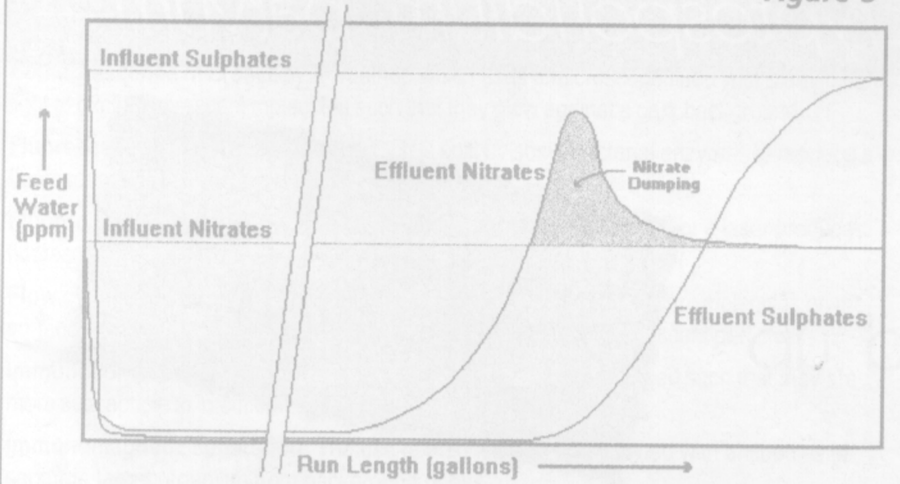
Non-selective resins

Type I's have better thermal and chemical stability (chlorine resistance), but are more difficult to regenerate than Type II's (require more salt). Type I's also have less of a tendency to "dump" nitrates. Dumping is a phenomenon caused by the fact that non-selective resins actually prefer sulfates. Therefore, as they approach capacity, they not only let nitrates slip by, but also allow sulfates to exchange for nitrates on the resin as well. The result can be nitrate leakages that actually exceed the influent levels (see *Figure* 3). This can be avoided by being careful not to overrun the resin. Use a meter with a generous reserve capacity.

Selective resins

Nitrate selective resins are so called because they avoid the "dumping" phenomenon. They are neither Type I's or II's but are based on a longer chain amine group that interferes with the resin's ability to capture sulfates (due to the molecular size). These resins also are more difficult to regenerate with normal salt levels and will have higher leakages as a result. Leakages of 15-to-25 percent of total nitrates are

Figure 3



normal. However, the total capacity for nitrates will be higher than non-selective resins if the nitrate percentages are low (less than 60 percent of the nitrate plus sulfate total). For farm and residential application with highly variable flows and daily usages, the selective resins are often more attractive simply because of the non-dumping aspect. They are an obvious choice in high sulfate waters.

Design criteria for nitrate removal POE systems is 3-to-5 gallons per minute per cubic foot (gpm/ft^3). Typical residential systems would be 1½-to-3 ft^3. This is larger than a typical softener. Backwash flow rates are about a third that of softeners of equal size (2 gpm/ft^2).

POU nitrate removal

Moderate nitrate levels that do not exceed the U.S. Environmental Protection Agency (USEPA) MCL can be treated with a countertop distillation unit, RO or selective resin cartridges. RO units will not exhibit as high a rejection for nitrates as they will for chlorides and sulfates. Nonetheless, a 60-to-85 percent reduction can be expected, which can then be polished with a selective cartridge.

Conclusion

The presence of nitrates in water is generally the result of contamination and is more prevalent in farming areas. Municipalities will treat this supply to reduce NO_3-N levels to below the 10 ppm MCL. Further reductions can be made with POE or POU treatment utilizing anion exchange, RO or distillation.

The choice of anion resin will depend upon the makeup of the feed water and the level of sophistication of the equipment controls. Maximum removal of nitrates is with non-selective salt regenerated systems. Maximum safety is with nitrate selective anion exchangers.❑

References

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