A COMPARISON OF A SELECTIVE RESIN WITH A CONVENTIONAL RESIN FOR NITRATE REMOVAL

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Summary: A new nitrate selective resin, SR 7, removes nitrate from water containing high concentrations of sulfate more effectively than either standard Type 1 or Type 2 resins without the potential for nitrate enrichment of the product water upon accidental overrun as seen in a side by side field comparison.

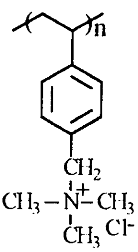
INTRODUCTION

The removal of nitrate from potable waters has received increased attention in recent years as the health effects of nitrate have been studied. Although the problems related to nitrate consumption arc frequently referred to as nitrate poisoning. the toxicity is primarily due to nitrite. Nitrate consumed either in food or drinking water is reduced to nitrite in the gut by bacteria in infants under 6 months of age which in turn impairs oxygen transport by reacting with hemoglobin to produce methemoglobin. The so called "Blue Baby" disease was observed particularly in rural areas where the main causes seem to have been farm runoff and nitrogen fertilizer usage[1]. Nitrates can contaminate mothers milk. The Environmental Protection Agency recommended a maximum level of 10 ppm nitrate as N (35.7 ppm as calcium carbonate or 44.3 ppm as nitrate) in drinking water. In some cases the level was reduced below this value due to special problems related to waste water disposal.

The agriculture industry found that nitrate had an adverse effect on cattle. pigs and chickens due to the formation of nitrite from nitrate during digestion. Cattle and other ruminates are particularly at risk due to their digestive tract. Over a period of more than 30 years, units to remove nitrates have been installed near feed lots to increase weight gain in cattle.

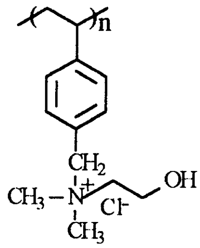
Both Type 1 and Type 2 strong base resins have typically been used for nitrate removal with similar results. Sybron Chemicals Inc. offered a specially prepared Type 2 strong base resin, Ionac A 554, for most installations. Substantial plants, including a 10 million gallons per day system at Pomona CA. have been constructed using this product. Both Type 1 and Type 2 resins have a significantly stronger affinity for nitrate over either chloride or bicarbonate but a lower affinity for nitrate as compared to sulfate at ionic concentrations typical of potable waters. This lower affinity for nitrate over sulfate leads to two difficulties. One is a limited useful capacity as the sulfate to nitrate ratio grows above about 0.25. The second difficulty is commonly referred to as "Nitrate Dumping". This occurs as either a Type 1 or Type 2 resin is run past the nitrate breakthrough. The sulfate present in the feed water will displace the nitrate from the resin. Nitrate levels in the product stream can approach the concentration of the sum of sulfate and nitrate present in the feed water if the column is allowed to operate past nitrate breakthrough..

The need to find resins selective for nitrate over sulfate was the subject of EPA funded studies including work done bv Clifford and Weber[2]. Work done by G. Guter[3] demonstrated that the affinity of strong base anion exchangcrs for nitrate could be modified by increasing the size of the carbon side chains surrounding the nitrogen in the strong base site. As the side chains are made larger as for example between the benzyltrimethylammonium site (Type 1) or the benzyldimcthylethanolammonium site (Type 2) and a benzyltripropylammonium site (SR 7). a reversal of relative affinity between nitrate and sulfate is observed.[4,5]



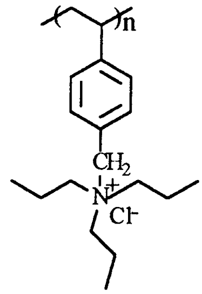
Benzyltrimethylammonium Resin

Type I



Benzyldimethylethanolammonium Resin

Type II



Benzyltripropylammonium Resin

SR-7

These resins represent a class of materials with increasing selectivity for nitrate over sulfate as the carbon side chain length increases. As the chain length increases. the volume capacity of the resins decrease so that groups larger than butyl are not recommended for nitrate removal although they may well have other interesting propcrties[6]. While the tributyl amine gives a resin selective for nitrate. a tripropyl resin has been selected by Sybron as our standard nitrate removal resin. The tripropyl resin has better regeneration efficiency and a greater volume capacity while maintaining suitable nitrate selectivity over typical operating conditions.

While the selection of a suitable resin is usually based on the water analysis and sulfate content as compared to the nitrate. there are several situations where the selective resin has clear advantages. Conditions where a more expensive selective resin should be employed are summarized below.

(a) Small cartridge units where the effluent is not tested for nitrate. In this cast, the non-selective resin would tend to dump nitrate as the sulfate pushes the nitrate from the bed, causing a significant enrichment of nitrate in the product water. A true selective resin would not dump.

(b) Small household units will have a similar problem since there is not a good spot test for nitrate breakthrough.

(c) Small community installations which have commercial size units. The cost of on-line monitoring of the effluent for nitrate leakage is prohibitive in such installations. The use of a selective resin would avoid an enrichment of nitrate if breakthrough occurred unexpectedly.

(d) Nitrate selective resins also have an increased selectivity for the nitrite ion. Plants where nitrite is a problem may see some advantage in the use of selective resins. Additional work is needed in this area.

This paper is based on a test in a small community plant which has parallel beds containing a standard type 2 strong base resin and a selective resin based on tripropylamine (SR 7). The plant layout is shown in Figure 1. The composition of the well water is given in Table 1. The Whispering Hollow Water System is a small drinking water production and distribution facility which presently serves approximately 400 residents of the Whispering Hollow Mobile Home Park. The park is located in Northhampton County, Pennsylvania and is surrounded by farms. Application of fertilizer on adjacent fields has caused elevated nitrate levels in the system well. The intent of this paper is to provide data from a field application demonstrating the usefulness of nitrate selective resins for the removal of nitrate. Performance advantages both in terms of capacities as well as avoidance of nitrate enrichment (“Nitrate Dumping”) are seen.

Table 1. Feed Water Composition

Conductivity	660 µs
Total Hardness as $CaCO_3$	358 ppm
Bicarbonate as $CaCO_3$	180 ppm
Chloride as $CaCO_3$	30 ppm
Nitrate as $CaCO_3$	45 ppm
Sulfate as $CaCO_3$	50 ppm

The system contains two parallel 42” diameter 72” high Park International fiberglass vessels

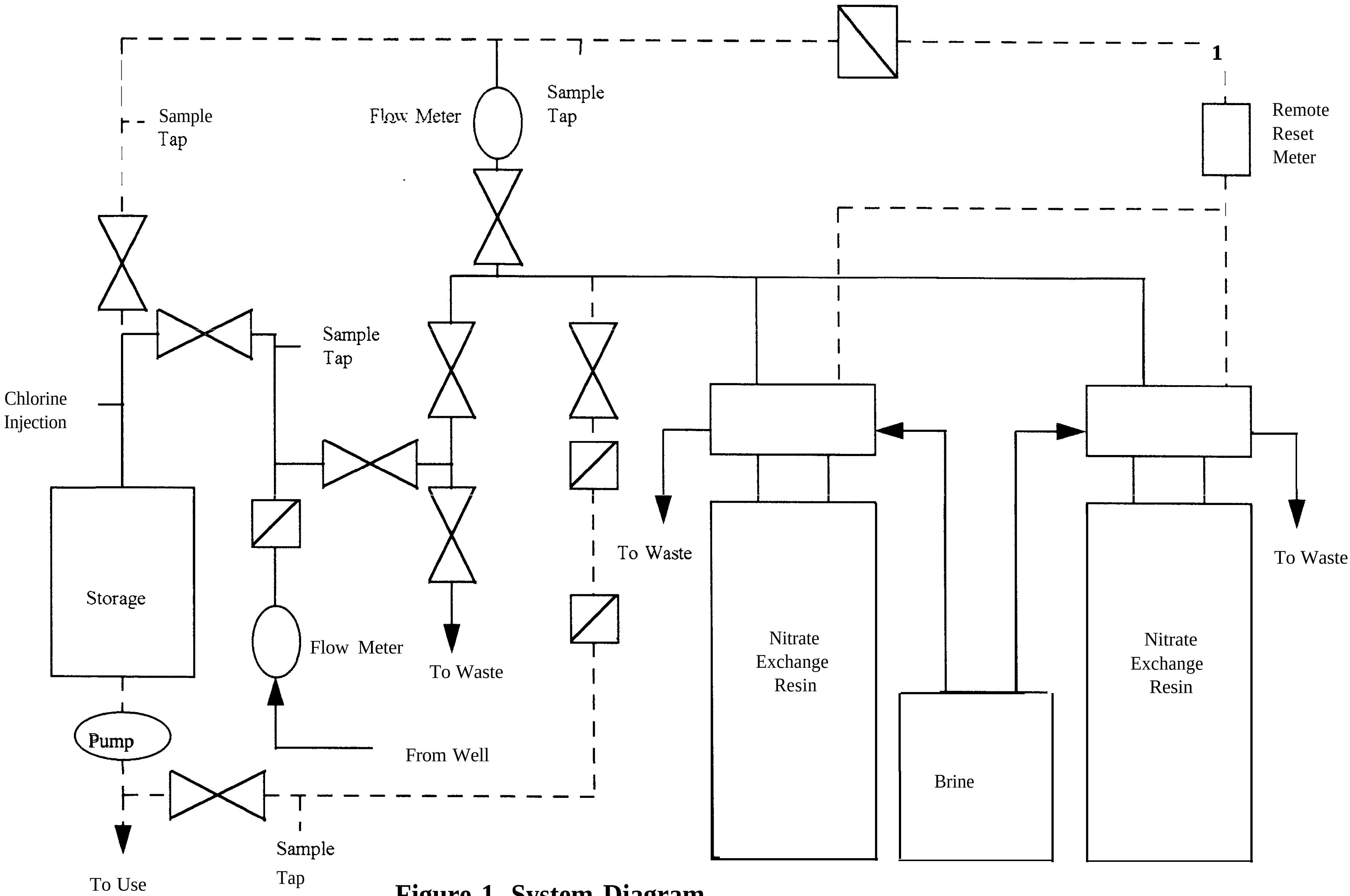


Figure 1. System Diagram

with Fleck automatic backwash and regeneration controllers, and remote reset meters. The effluent from the units. roughly l/3 of the well flow, is blended with 2/3 of untreated water. This blend is pumped to a detention tank for chlorination and distribution. The resins arc regenerated using a sodium chloride solution. The daily production for the system averages 50,000 gallons per day. Each unit contains 20 cubic feet of resin.

The anionic composition of regeneration effluent and system product samples was determined by using a Diones QIC Analyzer equipped with an IonPac AS4A guard and analytical column set followed by a micromembrane suppressor.

After the usual problems with controls and regeneration procedures. the plant has been operating as expected and data have been collected on the various steps in the operation. The beds contain standard production resins. Column A contains 20 cubic feet of A 554, a type 2 resin specifically manufactured to remove

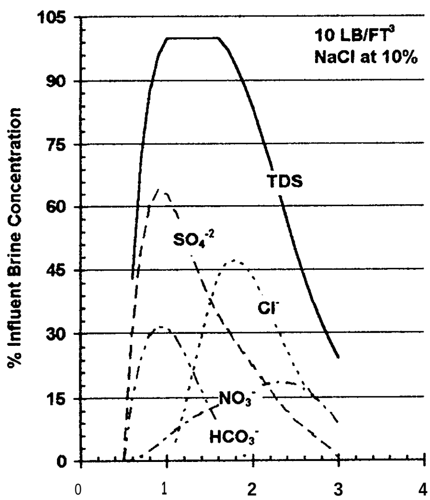


Figure 2. Spent Regenerant Profile, A554.

nitrate and sulfate from drinking water supplies while Column B contains 20 cubic feet of SR 7. a nitrate selective tripropyl qua ternary ammonium strong base anion resin. These beds were regenerated with 10 pounds of NaCl per cubic foot at approximately 10%.

Typical regeneration histories for the two systems are shown in Figures 2 and 3.

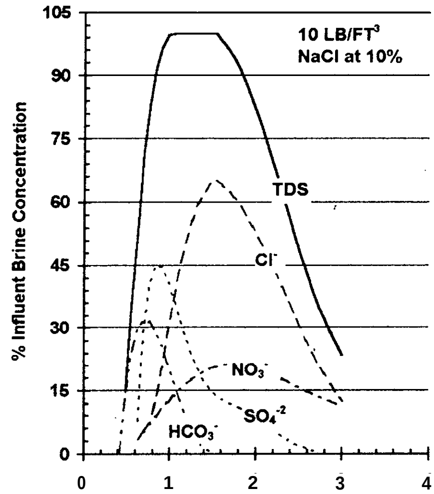


Figure 3. Spent Regenerant Profile, SR 7.

Typical operating performance (described as nitrate effluent concentrations) are shown in Figures 4 and 5.

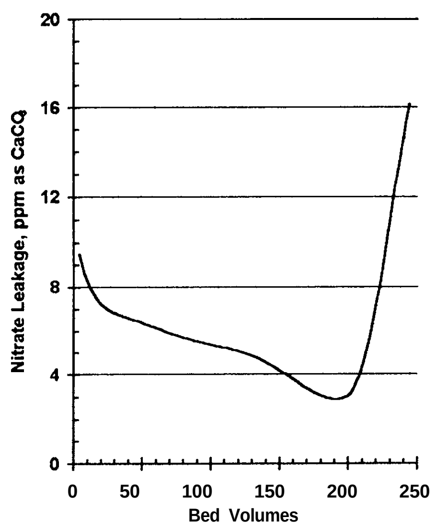


Figure 4. Nitrate Removal Performance, A 554.

In an experiment, the test columns were overrun and the results are compared in Figures 6 and 7.

DISCUSSION

Figures 2 and 3 show the effluent concentrations of bicarbonate. chloride. sulfate and nitrate

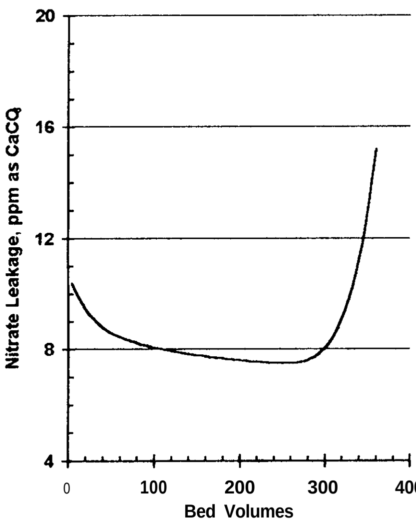


Figure 5. Nitrate Removal Performance, SR 7.

during the regeneration of the A 554 (standard Type 2) and SR 7 (nitrate selective).

Figures 4 and 5 show the performance of the two resins A 554 and SR 7 on the same water supply after being regenerated with 10 pounds of NaCl per cubic foot. These graphs show the effluent concentration of nitrate during the operating cycle of each bed. These curves were generated after the system had undergone several regeneration exhaustion cycles and represent typical performance for each system.

In Figure 2, (A 554) nitrate breakthrough occurs and the run cycle is ended prior to sulfate breakthrough. In Figure 3. (SR 7) sulfate breakthrough has occurred well before nitrate breakthrough. The selective resin produces significantly more blended water than the nonselective resin at the same salt dosage under these conditions. Calcium precipitation was not observed in either system despite the relatively high hardness, alkalinity and overall TDS of the feed stream.

Figures 6 and 7 show the performance of the two resins A 554 and SR 7 during a deliberate overrunning of the bed during an experiment.

In Figure 6 (the A 554 example). the nitrate level in the effluent exceeds the influent level significantly and approaches the combined level

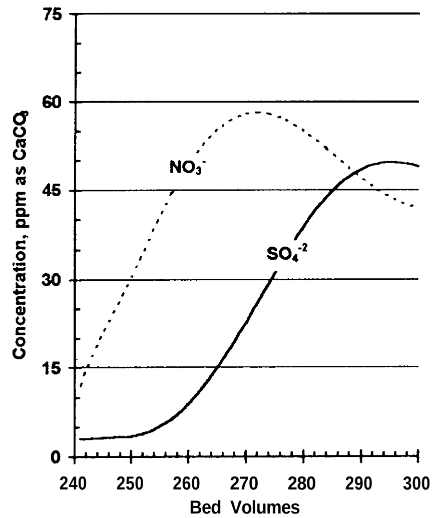


Figure 6. Nitrate Enrichment, A554.

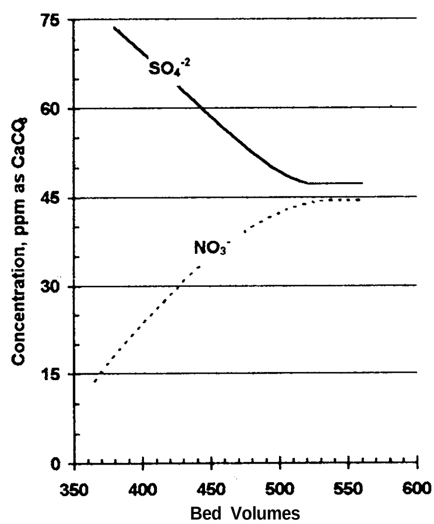


Figure 7. Nitrate Enrichment, SR 7.

of influent sulfate and nitrate. This is an example of the nitrate enrichment or dumping which will occur with any standard Type 1 or Type 2 strong base anion exchange resin. In Figure 7 (the SR 7 example). the nitrate level in the effluent only slowly increases and begins to approach the influent nitrate concentration.

There is no nitrate enrichment or dumping observed in this system.

CONCLUSION

Nitrate selective resins have significant advantages over standard materials when used under conditions where the feed water has significant amounts of sulfate (typically greater than 25% of the sum of sulfate and nitrate). These advantages are greater capacity for nitrate and no enrichment of the product stream with nitrate in the event of an accidental overrun. The elimination of the dumping phenomena is especially critical when an anion exchange resin is used for nitrate removal under conditions where close monitoring of the product water is not feasible.

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