

Removal of Hydrogen Sulfide from Groundwater Using Packed-Bed Anion Exchange Technology

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The presence of hydrogen sulfide in potable water can result in taste, odor, and corrosion problems. Typical approaches for controlling hydrogen sulfide include oxidation and aeration (Sammons 1959, Sheppard and von Lossberg 1948, Lyn and Taylor 1991, and Dell'Orco et al. 1998), but the effectiveness of these treatment options depends on the hydrogen sulfide concentration and the pH.

In the 1950s, anion exchange technology for removing hydrogen sulfide was proposed (Thompson and McGarvey, 1953), but limited information on the use of anion exchange for groundwater treatment has been reported. This article will assess the feasibility of using bed-packed anion exchange for removing hydrogen sulfide from groundwater.

Hydrogen sulfide is not directly regulated under the Safe Drinking Water Act, but it is indirectly regulated through the secondary standards for taste and odor. In 2003, the Florida Department of Environmental Protection (FDEP) issued a rule under Chapter 62-555.315(5) concerning the control of total sulfide in new groundwater sources. The rule recommends treatment options based on the pH and the total sulfide concentration.

The options include the use of chlorine,

conventional aeration with and without pH adjustment in groundwater sources with hydrogen sulfide concentration between 0.3 – 0.6 mg/L, forced draft aeration including pH adjustment in hydrogen sulfide concentration in a range between 0.6 and 3 mg/L, and packed tower plus pH adjustment for sources with hydrogen sulfide concentrations over 3 mg/L.

Oxidation converts hydrogen sulfide to either elemental sulfur or sulfate. Aeration results in a combination of stripping the volatile fraction of the hydrogen sulfide and oxidizing the hydrogen sulfide to elemental sulfur or sulfate. The volatile fraction is the nonionized form (H₂S), and the concentration depends on the pH. In many cases, aeration systems promote the growth of sulfur-oxidizing bacteria that can contribute turbidity to the finished water.

An alternative approach for removal is to capitalize on the fact that a significant fraction of the hydrogen sulfide is ionized under pH conditions of natural waters, so anion exchange systems can be designed to remove it. To date, the major applications of anion exchange for drinking water are removing arsenic, nitrate, and organics (Korngold et al 2001, Ghurye et al. 1999, Kim and Benjamin 2004, Liang et al. 1999, and Bolto et al. 2002).

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Other applications include removing cadmium (Zhao et al. 2002), reactive dyes (Karcher et al. 2002), and hydrogen sulfide (Thompson and McGarvey, 1953).

Ion exchange resins consist of a
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Table 1. Tulsion® A-72 MP Resin Characteristics

Parameter	Characteristic or Value
Matrix Structure	Cross linked polystyrene
Physical form	Moist spherical beads
Particle size	0.3 to 1.2 mm
Moisture (approx.)	58%
Solubility	Insoluble in all common solvents
Backwash settled density	42 to 45 lbs/ft ³ (670 to 720 g/l)
Temperature stability (max)	195°F (90°C)
pH range	0 to 14
Ionic form	Chloride
Functional group	Quaternary ammonium Type I
Total exchange capacity	1.0 meq/MI
Swelling (approx.)	Cl ⁻ to OH ⁻ 21%

Adapted from Tulsion® A-72 MP Brochure

Table 2. Average untreated water quality for water from four wells in west-central Florida between April and December 2005.

Well	A	B	C	D
Anions				
Sulfur Species				
Sulfide (mg/L as S ²⁻)	2.64	1.64	1.07	0.94
Sulfate (mg/L as SO ₄ ²⁻)	37.38	7.27	14.75	1.08
Chloride (mg/L as Cl ⁻)	14.6	14.6	24.47	14.62
TOC (mg/L)	2.78	2.68	2.37	3.08
UV-254 Absorbance (cm ⁻¹)	0.09	0.08	0.12	0.10
Alkalinity (mg/L as CaCO ₃)	164	180	180	148
Other Characteristics				
pH	7.39	7.35	7.38	7.44
Temperature (°C)	23.7	23.4	24.9	24.2
Conductivity (µS/cm)	464	427	385	377
Turbidity (NTU)	0.32	0.6	0.53	0.24
Cl ₂ demand (mg/L)	17	14	10	11

Figure 1. Comparison Between the Average BV and the Exchangeable Sulfur Species for Each Well

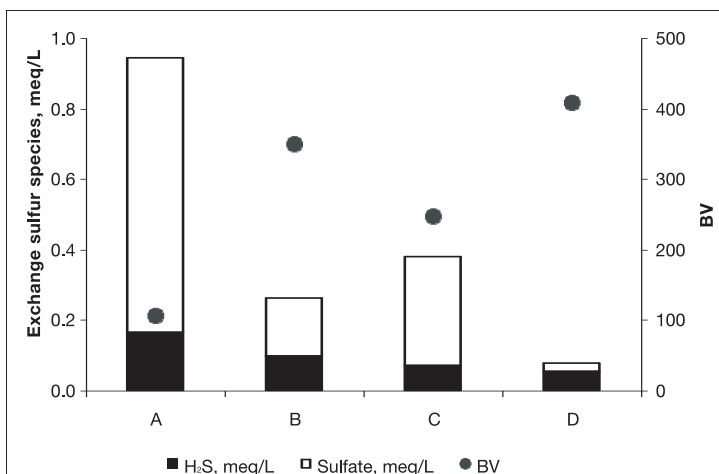
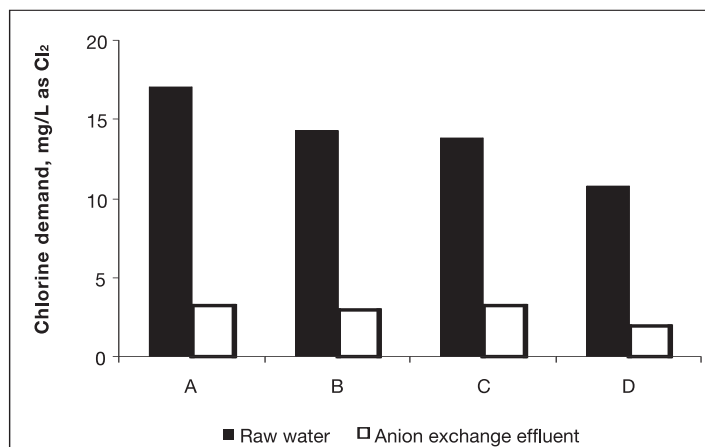


Figure 2. Comparison Chlorine Demand in Raw Water and Anion Exchange Effluent for Each Well



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crosslinked polymer with functional groups attached to the resin backbone. For anion exchange, those functional groups are quaternary amine and tertiary amine for Strong Base Anion (SBA) and Weak Base Anion (WBA) respectively. In this project, the effectiveness of SBA was tested.

Materials and Methods

Pilot scale tests were conducted using two-inch diameter plexiglass packed-bed columns designed to accommodate 0.065 cubic feet of resin with a bed-depth of three feet and a freeboard of 18 inches. The pilot system was operated at empty bed contact time (EBCT) between three and 14 minutes, surface loading rate equal to six gallons per minute per square foot, Bed Volume (BV) equal to 0.486 gallons, and a volumetric loading of about 2.0 gallons per minute per cubic foot.

The resin used is a commercial macroporous strong base anion exchange (Tulsion® A-72 MP (Cl⁻)). A summary of the resin characteristics is presented in Table 1.

Anion exchange columns were regenerated using three to 10 pounds of salt per cubic foot of resin. The regeneration process consisted of six sequential steps: Backwash, Drain Down, Brine, Drain Down, Slow Rinse, and Fast Rinse.

The anion exchange columns were operated with or without air at flowrates ranging from two to eight gallons per hour and at pressures ranging from 12 to 15 pounds per square inch. The columns were operated in consort with well pumps which turn on in response to pressure demand within the distribution system.

Untreated water and the anion exchange effluent were monitored regularly for pH, conductivity, temperature, hydrogen sulfide, dissolved oxygen, oxidation reduction potential, sulfate, chloride, alkalinity, UV-254 absorbance, and Total Organic Carbon (TOC). Supplemental tests were conducted for chlorine demand. The surface characteristics of the resin were evaluated using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis.

For SEM-EDS analysis, the samples were preserved in a 2.5-percent glutaraldehyde solution for a minimum of 24 hours. Samples were dehydrated using a graded series of ethanol (30 percent, 50 percent, 70 percent, 95 percent, and 100 percent), sputter coated with either carbon or gold.

A summary of untreated water quality for the four wells tested in this project is given in Table 2. The values in this table correspond to the averages obtained during the summer-fall of 2005 at four well sites.

Results

The resin capacity was defined based on the amount of volume that could be processed prior to breakthrough of hydrogen sulfide through the columns. In all cases, hydrogen sulfide was the first anion to breakthrough and thus was used to compute the resin capacity.

Sulfate levels varied among the individual wells from one to over 30 milligrams per liter (mg/L) as SO₄²⁻. Sulfate breakthrough did not occur in any of the tests. The sulfate removal through the packed-bed anion exchange was typically over 90 percent.

During the study period, the average initial TOC concentrations for the four wells

varied between 2.3 to 3.1 mg/L, and about 80 percent of the TOC was removed through anion exchange. A comparison of the resin capacity (in terms of bed volumes) and exchangeable sulfur species is shown in Figure 1 for the four wells.

In addition to removing sulfur species and TOC, anion exchange resulted in a net reduction in chlorine demand, as shown in Figure 2. The reduction in chlorine demand and TOC has several side benefits, including reductions in the potential for formation of disinfection byproducts. Another advantage of reduced chlorine demand is that the more consistent oxidation potential will lead to more stable operation of chloramination for secondary disinfection.

Conclusions

The major conclusions from this project are:

1. Packed-bed anion exchange technology is effective for removing hydrogen sulfide from groundwater sources.
2. Resin capacity is related to the concentration of exchangeable anions.
3. Supplemental benefits of anion exchange include removal of TOC and sulfate and the reduction of chlorine demand.
4. Other benefits of using packed-bed anion exchange for hydrogen sulfide control include its ability to process groundwater without supplemental pumping or exposure to air and its amenability for use at wellhead treatment sites that are constrained by space limitations or encroachment of residential neighborhoods.

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