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Surfactant-Modified Zeolites as Permeable Barriers to Organic and Inorganic Groundwater Contaminants

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PII.10 Surfactant-Modified Zeolites as Permeable Barriers to Organic and Inorganic Groundwater Contaminants

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Abstract

We have shown in laboratory experiments that natural zeolites treated with hexadecyltrimethylammonium (HDTMA) are effective sorbents for nonpolar organics, inorganic cations, and inorganic anions. Due to their low cost (~\$0.75/kg) and granular nature, HDTMA-zeolites appear ideal candidates for reactive, permeable subsurface barriers. The HDTMA-zeolites are stable over a wide range of pH (3-13), ionic strength (1 *M* Cs^+ or Ca^{2+}), and in organic solvents. Surfactant-modified zeolites sorb nonpolar organics (benzene, toluene, xylene, chlorinated aliphatics) via a partitioning mechanism, inorganic cations (Pb^{2+}) via ion exchange and surface complexation, and inorganic anions (CrO_4^{2-}, SeO_4^{2-}, SO_4^{2-}) via surface precipitation.

Introduction

The overall goal of the project is to test and demonstrate the use of surfactant-modified zeolite (SMZ) as a permeable barrier to groundwater contaminants. A permeable barrier allows water pass through while stopping or retarding contaminant migration (Figure 1).

The project is divided into three phases:

- Phase I: SMZ Laboratory Testing and Analysis
- Phase II: Pilot-Scale Testing of Barrier Technology
- Phase III: Field Demonstration

Work on Phase I began in June 1995. This paper summarizes some of our previous work with SMZ and describes our progress under Phase I.

Background

Zeolites are naturally occurring minerals characterized by high surface areas and high cation exchange capacities. Zeolites occur in massive deposits in many areas of the world, and are common in the western United States. We've found that a commercial zeolite from the St. Cloud mine in Winston, New Mexico, is high in the desirable zeolite mineral clinoptilolite and low in smectite clays. Mined zeolite can be ground and sized as desired, thus tailoring its hydraulic properties. The sized zeolite is stable mechanically and hydraulically. After grinding

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and sizing, the St. Cloud zeolite (which is about 95% pure clinoptilolite) costs $60-$100 per ton.

Materials and Methods

One-half ton of sized zeolite (14 to 40 mesh, or 1.4 to 0.4 mm size range) was obtained from the St. Cloud mine for Phase I testing Raw zeolite was mixed with a cationic surfactant dissolved in water. Many different surfactants can be used. Our work has concentrated on zeolite modified with hexadecyltrimethylammonium (HDTMA), commonly found in hair conditioners and mouth washes. The surfactant binds to the external exchange sites on the zeolite surface (Figure 2). The surfactant forms an organic coating, greatly enhancing the sorptive properties of the zeolite (Haggerty and Bowman, 1994). Internal exchange sites remain available for sorption of small metal cations such as Pb^{2+} (Figure 2). Previous work has shown that solutions of high or low pH, high salt concentrations, and organic solvents do not remove the surfactant coating, as shown in Table 1 (Bowman et al., 1995).

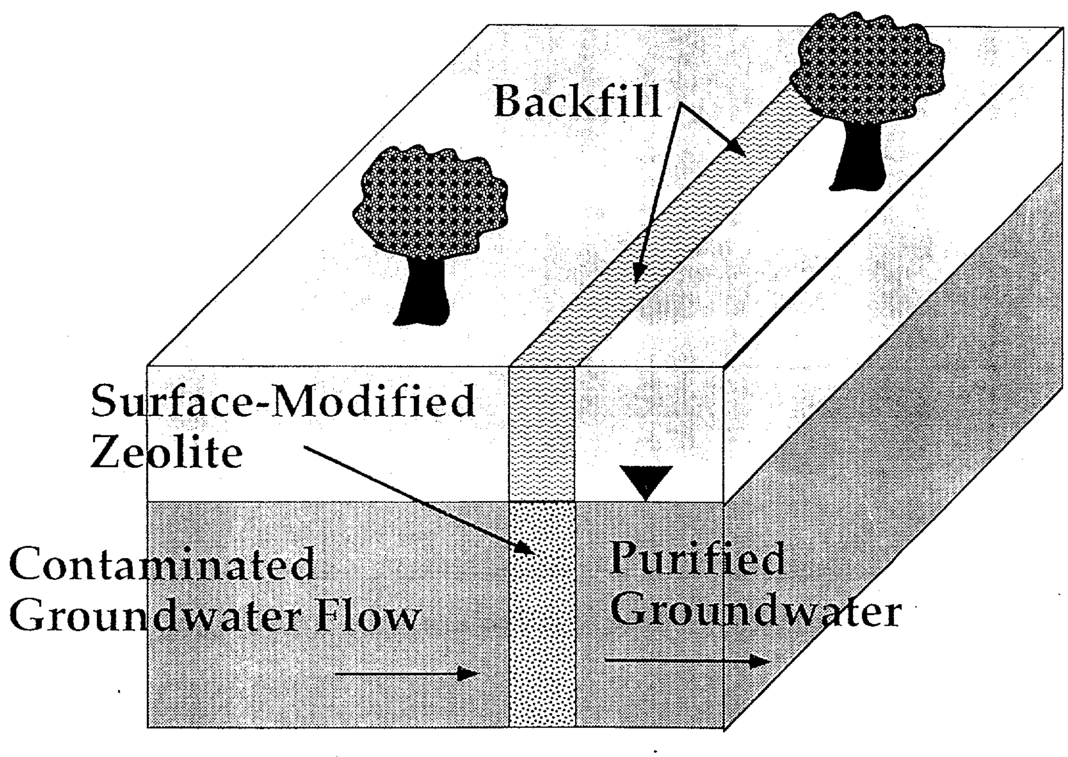

Figure 1. Schematic of surfactant-modified zeolite permeable barrier.

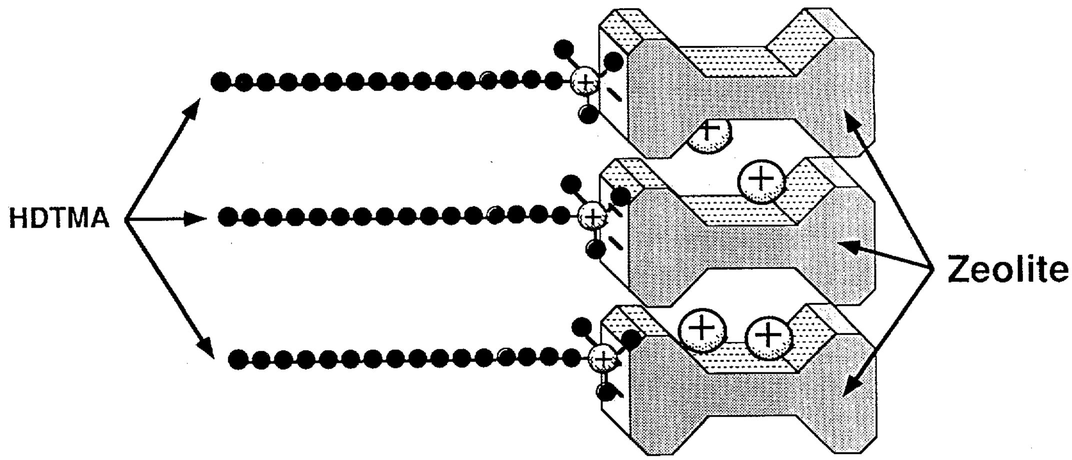

Figure 2. Schematic of surfactant sorption to zeolite surface.

Table 1. Percent of Surfactant Remaining on the Zeolite Surface after 72-Hour Exposure to Various Solutions/Solvents

Solution/Solvent	*%Surfactant Remaining*
distilled water	99.3
0.005 *M* $CaCl_2$	99.1
pH 3	98.3
pH 5	98.3
pH 10	99.0
0.10 *M* CsCl	98.6
1.0 *M* CsCl	97.2
50 mg/L $Cr0_4^{2-}$	99.4
methanol	96.0
benzene	99.6
toluene	99.6

Results and Discussion

The surfactant treatment is complete within 8 hours (Figure 3). The surfactant is retained by the zeolite quantitatively up to a saturation plateau (Figure 4). For the example shown, this amounts to 220 mmol/kg, or about 6% by weight. Surfactant retained at or below the plateau (about 220 mmol/kg) is not removed by successive washings with water (Figure 5).

Based on these results, we estimate the cost of the SMZ, using commercial-grade surfactants, to be in the range of $400 per ton.

Previous work on the properties and applications of SMZ are presented in Bowman et al. (1993, 1995), Haggerty and Bowman (1994), Neel and Bowman (1992), Sullivan et al. (1994), and Teppen et al. (1995).

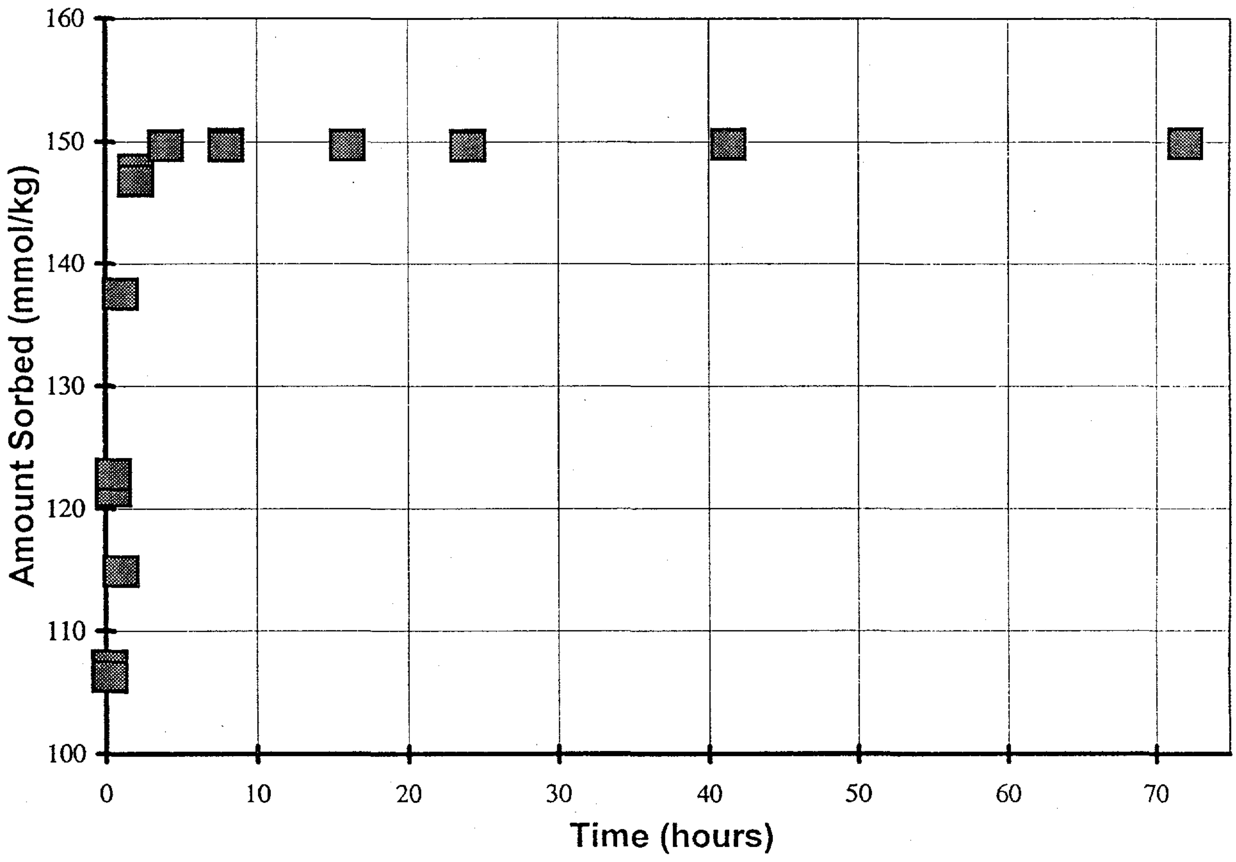

Figure 3. Sorption of HDTMA versus time.

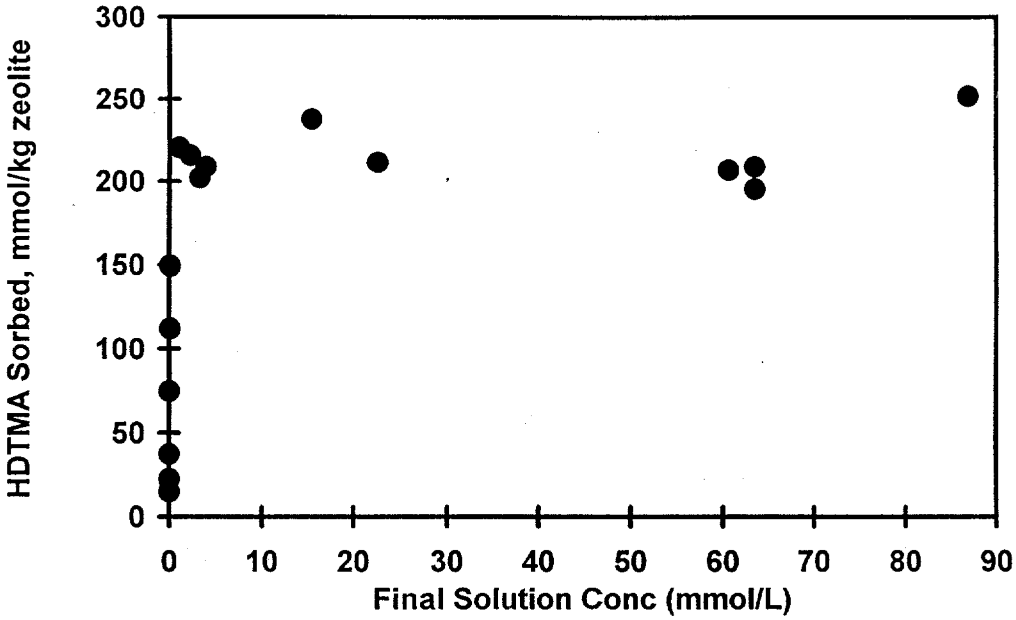

Figure 4. Sorption of HDTMA as a function of solution concentration.

Figure 5. Stability of HDTMA-zeolite as a function of loading.

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