Surfactant Effects on the Transport of Air Bubbles in Porous Media

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Abstract

Air sparging is a promising technology for the removal of volatile organic compounds (VOCs) from contaminated groundwater. The sparging process mobilizes contaminants to the vapor phase through mass transfer into air bubbles. Ideally in air sparging, bubbles are pressurized into groundwater through an injection well and through buoyancy, the contaminant-containing gas bubbles migrate to the surface where they can be collected for treatment. While air sparging is being implemented at the field scale for the remediation of VOC contaminated aquifers, there are still difficulties with the remedial process. The most limiting problem is that of nonuniform distribution of stripping gases through the subsurface. Significant channeling of the injected air occurs in soils that have a grain size smaller than approximately four mm (Ji et al. 1993). Because large portions of the aquifer are not exposed to the stripping gas, contaminant removal becomes mass transfer limited, as contaminants must diffuse to the air channels.

This paper investigates the use of four different surfactants to enhance the air sparging process through the generation of small diameter air bubbles. Smaller bubbles are desirable in air sparging because they have a large surface area to volume ratio that promotes mass transfer, they are less buoyant resulting in a longer residence time in the system, and they are less prone to channeling. The experimental investigation quantified coalescence, average diameter, and size distributions of air bubbles produced in an aqueous and porous media system. For the bench-scale systems tested in this study, neither the surfactant charge nor the surfactant molecular structure had a significant effect on the physical characteristics of the bubbles generated. All surfactants produced similar average

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bubble diameters and size distributions in both aqueous systems and in saturated porous media. In all cases, the average diameters of the injected bubbles were significantly reduced in the presence of trace concentrations of surfactants.

INTRODUCTION

Air sparging is a promising technology for the removal of volatile organic compounds (VOCs) from contaminated soil and groundwater. The sparging process is a stripping technique that mobilizes contaminants to the vapor phase through mass transfer into air bubbles. In air sparging, bubbles are pressurized into groundwater through an injection well with slotted screens. Through buoyancy, the gas migrates toward the surface, stripping VOCs from the groundwater as it percolates through the soil matrix. When the gas reaches the surface, it can be collected for further treatment. Other mechanisms active in the sparging process include biological degradation of contaminants through the introduction of oxygen into the groundwater, a process known as biosparging (Johnson et al. 1993), adsorption and desorption, dissolution, advection, dispersion, and diffusion (Semer and Reddy 1998). While air sparging is currently being implemented at the field scale for the remediation of VOC contaminated aquifers, there are difficulties with the remedial process, and the design and implementation are still largely empirical (Reddy et al. 1995).

One of the most limiting problems is that of nonuniform distribution of stripping gases through the subsurface (Kueper and Frind 1988). Significant channeling of the injected air occurs in soils that have a grain size smaller than approximately four mm (Ji et al. 1993; Semer et al. 1998). Because large portions of the aquifer are not exposed to the stripping gas, contaminant removal becomes mass transfer limited as contaminants must diffuse to the air channels (Ahlfeld et al. 1994), which produces a concentration tailing similar to what is observed in other remedial techniques such as pump-and-treat.

Another significant factor in the efficiency of air sparging is contaminant availability. Unger et al. (1995) demonstrated that at early times in the sparging process, the direct transfer of nonaqueous phase liquids (NAPLs) to the vapor phase causes a rapid reduction in contaminant mass in the system. However, at later stages of the process, contaminant transfer into the aqueous phase and subsequent diffusion to air channels are the controlling mechanisms (Braida and Ong 1998).

The efficiency of air sparging is strongly affected by the air injection system parameters, soil conditions, and contaminant characteristics (Baker and Benson 1996; Reddy and Adams 1998). In addition, the physical characteristics of the stripping gas are a significant factor in the behavior of an air sparging system. Ideally, the air injected during the sparging process will form small diameter bubbles that transport as discrete elements through the system. Decreasing the diameter of stripping bubbles offers several advantages: smaller diameter bubbles have a larger surface area to volume ratio per volume of gas which is favorable for mass transfer, they have decreased buoyancy accompanied

by increased residence time, and they exhibit decreased channeling through saturated porous media. Burns and Zhang (1999) quantified the effects of several system parameters on the size and size distributions of bubbles produced in bench-scale column studies. Bubble size and size distribution was extremely sensitive to pressure, with both parameters increasing as the injection pressure was increased. Orifice injector type was also a significant control on the bubbles generated, with single opening injectors creating a more uniform distribution of bubbles than multiple orifice injectors. The presence of a particulate media in the system led to increased bubble coalescence and the formation of larger diameter bubbles than was observed in purely aqueous systems. These effects were more pronounced as the grain size was reduced. Finally, trace concentrations of surfactant in the system were found to reduce the particulate media effect, generating a uniformly small bubble size and size distribution in the presence or absence of a particulate media.

Surfactants are surface-active solutes that tend to concentrate at the interface of two phases. Typically, surfactants are characterized by a hydrophilic end and a hydrophobic end, and the addition of a surfactant to an aqueous system alters the interfacial tension at the air-water interface which results in smaller diameter bubbles. The presence of a surfactant coating on a bubble will also increase drag (Chhabra and Kee 1992) which will increase the residence time in the system, and will reduce the coalescence of bubbles (Bischof et al. 1993; Jeng et al. 1986; Sadhal et al. 1997), both of which are advantageous in stripping operations. While there are data in the literature that demonstrate that surfactant coatings can decrease the rate of mass transfer of contaminants into the vapor phase (Clift et al. 1978), other studies have indicated that at low concentrations, surfactants will accumulate at the trailing edge of a bubble translating vertically through an aqueous system, leaving the top cap of the bubble relatively surfactant free and available for mass transfer (Oguz and Sadhal 1988; Quintana 1990). Additional studies have shown that the mass transfer of oxygen is not impeded by certain surfactant coatings (Ju et al. 1991), or is more strongly controlled by the interfacial surface area (Bischof et al. 1993; Molder et al. 1998). In addition, surfactants have been shown to enhance the desorption of contaminants from mineral surfaces and organic matter (Deitsch and Smith 1995), which suggests that they may be beneficial in facilitating more rapid clean up times in the air sparging process.

STUDY OBJECTIVES

This work presents the results of an experimental investigation performed to evaluate the effect of surfactant charge and surfactant molecular structure on the formation and transport of gas bubbles in aqueous systems and saturated porous media. Specifically, the study compares the results of experiments performed with trace concentrations of nonionic, anionic, and cationic surfactants added to the system. The surfactants chosen for study also represented a variety of molecular structures.

EXPERIMENTAL METHODS
Materials

All water used in the experimental study was deionized, organic free (Barnstead, Nanopure). Four surfactants were used in the experiments: one nonionic surfactant: t-octylphenoxypolyethoxyethanol (Triton X-100; $[C_6H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H]$); two anionic surfactants: sodium dodecyl sulfate (SDS; $[CH_3(CH_2)_{11}OSO_3Na]$) and sodium dodecylbenzenesulfonic acid (SDA; $[C_{12}H_{25}C_6H_4SO_3Na]$); and one cationic surfactant: decyltrimethylammonium bromide (DTMA; $[C_{13}H_{30}BrN]$). All surfactants were obtained from Sigma Aldrich Chemical Company and were used as received. A syringe needle with an inside diameter of 0.114 mm (Fisher Scientific, Gauge 26S) was used as the air injection orifice in all experiments.

Air was injected into the base of the test cell through Tygon tubing connected to the injection orifice. The injection pressure was controlled using a pressure regulator (Fairchild Industrial Products Company, Model 10). Highly idealized porous media were used in the study: uniform spherical silica beads (14.5 mm or 27.0 mm diameter). All experiments were performed in a rectangular glass test chamber (45 mm by 295 mm by 260 mm) with flat cell walls in order to prevent optical distortion during the imaging experiments.

Image Acquisition and Processing

All image collection and processing in the experiments was performed using a long-distance microscope (Questar, model 1) in combination with a color CCD camera (Sanyo model, VCC-3972), a method that has proven successful in the quantification of air bubble characteristics in both aqueous and saturated soil systems (Burns et al. 1998; Burns et al. 1997). A complete description of the experimental procedure is given in Burns and Zhang (1999).

For the tests in porous media, the particles were packed into the test cell at a porosity of approximately 40%. Approximately three inches of water was left above the packed test cell and images were taken as the bubbles emerged from the soil column into the water headspace.

RESULTS AND DISCUSSION

A series of experiments was performed to quantify the effects of trace concentrations of surfactant on the formation of air bubbles in an aqueous medium. A baseline experiment was performed in deionized water, and the average diameter and size distributions of bubbles produced in pure water at an injection pressure of 9.0 kPa were quantified. Four additional experiments were performed using a different surfactant in each experiment: Triton X100, SDS, SDA, and DTMA were added to the system at a concentration of 1.6×10^{-4} M. The injection pressure in the surfactant-enhanced experiments was also 9.0 kPa. Figure 1 shows the results of experiments performed in both the aqueous and aqueous/surfactant systems.
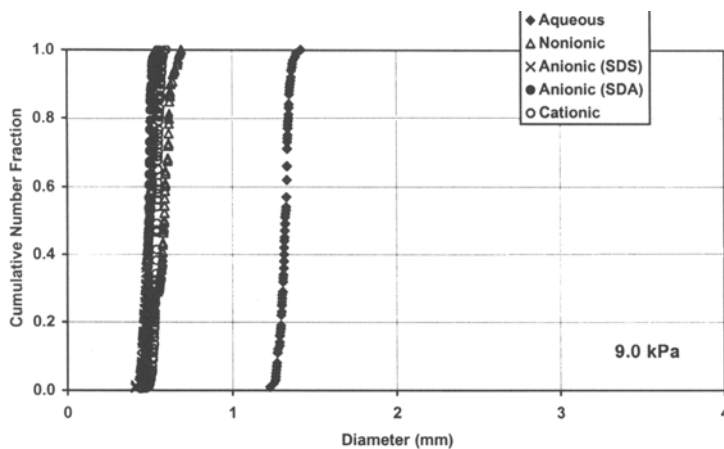
**Figure 1. Effect of Surfactant Charge on Bubbles Produced
in an Aqueous System**

The baseline experiment performed in the aqueous system clearly demonstrates that the characteristics of the bubbles produced by the needle injection orifice are fairly uniform, with a narrow range in the size distribution of bubbles produced. Because the formation of bubbles in an aqueous system is a surface controlled phenomenon, it follows that the physical characteristics produced using a single injection orifice would be fairly uniform. In contrast, the characteristics of bubbles produced using a heterogeneous surface (e.g. a frit or diffuser) tend to be far less uniform, with a wide range in bubble sizes (Burns and Zhang 1999).

In each case, the addition of the surfactant to the system reduced the average bubble diameter to less than one-half the diameter that is produced in a surfactant-free system. All four surfactants produced similar distributions, with the anionic surfactants (SDS and SDA) producing the smallest average diameters with statistically identical distributions. The cationic surfactant (DTMA) produced a slightly larger average bubble diameter, while the nonionic surfactant (Triton X-100) produced the largest average diameter, with a wider distribution in size.

The presence of the surfactant in the system has two significant effects on the formation and transport behavior of the stripping bubbles. First, the interfacial tension at the air/water interface is significantly reduced, which leads to the formation of smaller diameter bubbles than would appear in surfactant-free

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