Surfactant selection criteria for enhanced subsurface remediation: Laboratory and field observations

Abstract

Traditional approaches to ground water remediation have proven ineffective, especially when trapped oil phases exist. Surfactants are being widely evaluated to enhance remediation of such ground water contamination episodes. Successful implementation of surfactant enhanced subsurface remediation requires careful consideration of fundamental surfactant properties. The economic viability of this technology requires targeting the residual contamination, minimizing surfactant losses, and recovery and reuse of the surfactant. The relative efficiencies and advantages of surfactant solubilization and mobilization systems are described, as well as means to optimize these systems. Unit processes for contaminant-surfactant separation and surfactant reuse are summarized, along with unique surfactant impacts on these separation processes. Factors affecting the environmental acceptability of surfactants are discussed. Finally, results of field demonstrations are presented that reinforce concepts presented. This study thus provides an introduction to surfactant chemistry and highlights key factors critical to the successful design and implementation of surfactant enhanced subsurface remediation systems.

Key words

Remediation – surfactants – economics – losses – reuse – field demonstrations

Introduction

Pump and treat ground water remediation is often inefficient when a trapped oil phase (residual saturation) is present. The ground water simply flows past the trapped oil, being unable to overcome the capillary forces and physically displaces the oil. The water solubility of trapped oil constituents is low enough to render pump and treat remediation inefficient (potentially requiring hundreds to thousands of flushings even under equilibrium conditions), yet high enough to contaminate the ground water above the allowable levels. Surfactant enhanced subsurface remediation is a leading technique for enhancing pump and treat remediation of such sites. This enhancement can be due to micellar-enhanced aqueous concentrations (i.e., contaminant partitioning into the hydrophobic core of surfactant aggregates known as micelles), or due to ultra-low interfacial tensions realized along with middle phase microemulsion systems. This study begins with a brief overview of these enhancement mechanisms, followed by a discussion of the economic and environmental factors critical to their successful implementation. Finally, field demonstration results are briefly presented to reinforce the concepts presented.

Surfactant fundamentals

Surfactants (surface-active-agents) are classified by their charge (cationic, anionic, nonionic, zwitterionic – having...
both cationic and anionic groups), their origin (biosurfactants from plant or microbial production versus synthetic surfactants), their regulatory status (direct or indirect food additive status, acceptable for discharge to wastewater treatment systems or for use in pesticide formulations), etc [1]. Surfactants are also characterized by their hydrophilic-lipophilic balance (HLB) as water soluble (high HLB) or oil soluble (low HLB).

Above a critical concentration surfactant monomers self-aggregate into micelles (above the critical micelle concentration (CMC)). Organic compounds partition into the hydrophobic interior of micelles, thereby increasing the apparent water solubility of the contaminant. This partitioning is often considered to be linear in nature (Henry's Law), although deviations from linearity have been reported [1, 2]. The linear distribution coefficient ($K_m$) is the ratio of micellar to aqueous activity, and increases as contaminant hydrophobicity increases. For example, $K_m$ values for PCE are roughly an order of magnitude greater than TCE, and likewise for TCE and DCE ($\log K_m$ values of TMAZ 60 and DCE, TCE and PCE are 2.9, 3.8 and 4.9, respectively [3]). Solubility enhancement also increases as surfactant concentrations increase above the CMC. Thus, to dramatically improve contaminant extraction we will operate significantly above the CMC (an order of magnitude or more).

Significant reductions in the oil-water interfacial tension virtually eliminate the capillary forces which cause the oil to be trapped, thereby allowing the oil to readily flush out with the water. The minimum interfacial tension occurs in middle phase microemulsion systems. By adjusting the surfactant system it is possible to initiate a transition from normal micelles (aqueous phase, Winsor Type I), to middle phase microemulsions (Winsor Type III), to reverse micelles (oil phase inverted micelles, Winsor Type II), as shown in Fig. 1. For a high HLB surfactant system (right side of figure) the surfactant resides in the water phase as normal micelles, and a portion of the oil phase partitions into the micellar phase. For low HLB surfactant systems (the left side of the figure) the surfactant resides in the oil phase as reverse micelles. In between we observe three phases; the water and oil phases and a new "middle" phase (so designated because of its intermediate density). The interfacial tension reaches a minimum within the middle phase region while solubilization reaches a maximum (they are inversely related [14]).

Middle phase microemulsions can be formed in several ways, as denoted at the top of Fig. 1. For ionic surfactants, increasing salinity or hardness can produce the middle phase system, a strategy commonly utilized in surfactant enhanced oil recovery [5]. However, introduction of high salt concentrations may not be desirable in aquifer restoration. Middle phase systems can also be achieved by altering the hydrophilic-lipophilic balance (HLB) of a binary surfactant system. By varying the mass ratio of two surfactants, one with an HLB above and one below the desired level, it is possible to achieve the desired HLB value – this is the scheme used to achieve the middle phase system in Fig. 1 for 1,2-DCE. At low SMDNS concentrations AOT partitions into the oil phase while at high SMDNS concentrations the system is over-optimized and the surfactants reside in the water phase (Type I system). In between a middle phase microemulsion exists. This is the inverse of a salinity scan, where increasing salt concentrations causes a high-HLB, water-soluble surfactant to partition into the oil phase. Additional discussion of solubilization and mobilization mechanisms can be found in the literature [6–10].

**Economic viability**

Obviously, the implementation of surfactant enhanced subsurface remediation is highly dependent on the economics of this approach. In looking at two cases, Krebs-Yuill et al. [11] determined that surfactant solubilization can be more economical than conventional pump-and-treat. The two most important conclusions were: (1) surfactant capital costs constitute the single largest cost in...