Micelle Distribution Column Experiment

Background

3-D Microemulsion (3DMe)®, a form of HRC Advanced®, is a state-of-the-art specialty chemical substrate developed to provide a low-cost, slow-release electron donor to stimulate the *in-situ* anaerobic degradation of contaminants in soil and groundwater. Unlike emulsified-oil-type substrates, 3DMe was designed to provide superior distribution in the subsurface, thereby reducing the cost of product application. 3DMe was also designed to avoid the significant reduction in subsurface hydraulic conductivity often associated with emulsified-oil-type substrates. 3DMe is a slightly viscous liquid with a molecular structure composed of tetramers of lactic acid (polylactate) and fatty acids esterified to a glycerin molecule which acts as a carbon backbone.

Subsurface Transport

3DMe achieves superior subsurface distribution due the the spontaneous formation of micellular structures. (Shah, et al., 1972; Lindman, et al., 1982). This unique property promotes moderate aqueous transport of the product prior to its adsorption onto the aquifer matrix where it both partitions organic contaminants from solution and promotes rapid biodegradation through efficient hydrogen generation. (The surface-active properties of 3DMe, formation of micelles, and recommended 3DMe application details are described in Regenesis 3-D Microemulsion Technical Bulletin 2.0.)

Demonstration of 3DMe Movement

It is well known that slow-release electron donors, such as emulsified-oil-type substrates, do not distribute well in soil and groundwater. Through extensive experimentation in sand test cells, Borden et al. showed that emulsified-oil substrates moved less than 2 meters, even after 10 days of continuous emulsion feed. Furthermore, no emulsified-oil substrate transported further than 8 meters, regardless of injection volume or additional water flushing. (Borden et al., 2005).

In an effort to distinguish the subsurface transport properties of 3DMe from known emulsified-oil-type products, a controlled laboratory experiment was conducted.

Experimental Design

An aquifer simulation column was constructed from a transparent polycarbonate pipe, measuring 6 inches in diameter and 20 feet long. The column was filled with fine-grain sand and packed to prevent channeling and the pore space was calculated at 30.5%, approximately 9 gallons. The column was filled with water via peristaltic pump at 2.5 gallons per hour (see Figure 1).

A microemulsion of 3DMe was prepared by first combining 3DMe with water at a 1:3 3DMe-to-water ratio and mixing with a common high-shear pump, then further diluting with water, resulting in a final ratio of 1:50 3DMe-to-water. To visually track its movement through the sand column, methylene blue dye was added to the microemulsion. Methylene blue is absorbed by the hydrophobic portions of the 3DMe microemulsion and as such, will not partition into the water.

After the column was saturated with water, the 3DMe microemulsion was fed onto the column at 2.5 gallons per hour. After 20 hours, the microemulsion feed was ended and the column was flushed with water at the same rate (2.5 gal/hr) for 12 hours (about 3.3 pore volumes).

Movement of the dyed microemulsion and resulting dyed micelle suspension were observed visually throughout the study. In addition, water effluent from the column was analyzed for the methylene blue by UV-Visible Spectroscopy. Components of 3DMe in the effluent were also confirmed by direct measurement with both liquid chromatography and infrared analysis.

Results and Discussion

After 13 hours, an estimated 3.6 pore volumes of the 3DMe microemulsion (1:50 product-to-water mixture) had been fed into the column. As expected, due to the unique hydrophile/lipophile balance of the 3DMe material, the bulk of the microemulsion appeared to adhere to the sand surfaces within the first 1 meter of the column, as evidenced by the dark blue color (see Figure 2). However, it was at this time that the first breakthrough (material exiting the column) was detected via spectroscopy. Further analysis of the effluent confirmed the presence of 3DMe (micellar suspension) as indicated by intact ester, carboxyl, and carbonyl peaks visible under infrared spectrum analysis (see Figure 3). This indicates that, while the bulk of the injected 3DMe remained stationary, micelles were forming, carrying the material more than 20 feet after only 3.6 pore volumes and in less than 13 hours.

After approximately 20 hours of 3DMe flow, the column was switched to a water feed (without any 3DMe) to emulate continued groundwater flow after 3DMe application. At that time, it was still visually observable that the bulk of the microemulsion sorbed onto the soil in the first two meters of the column. However, a striking visual began to develop as a light-blue “front” began to travel through the column.

The continuous flow of water through the 3DMe was redistributing the product through the column as suspended micelles which, in turn, were resorbing onto the column material in a forward-moving front. As more water travelled through the column, 3DMe continued to transport, coloring the column light blue (see Figure 4). Throughout the 12-hour period of water flushing through the column, a low-concentration 3DMe micelle suspension was documented eluting from the 20-foot column via liquid chromatography and infrared analysis.

Summary

3DMe was designed to achieve superior distribution in the subsurface; its advanced transport capability was clearly demonstrated in a controlled laboratory column study. Throughout the course of the study, it was observed that when injected into the subsurface, 3DMe will initially sorb onto the immediate sand surface, but once in place, the material will gradually redistribute throughout a column due to micelle formation and subsequent sorption in a distribution "front." 3DMe micelles were documented to move 20 feet through the sand column in 13 hours, after only 3.6 pore volumes of material. The fact that 3DMe remains relatively stationary, yet forms micelles which continually redistribute the product over time clearly demonstrates its superior subsurface distribution capability, especially when compared to other electron donor substrates. Highly-soluble substrates, such as lactate and sugar solutions, rapidly ferment and "wash out," requiring the time and expense of multiple injections; conversely, emulsified-oil-type products have been clearly documented to sorb to the first 2 meters from the injection point and remain immobile, significantly limiting their radius of influence and oftentimes reducing hydraulic conductivity in the subsurface.

Scientific evidence clearly demonstrates that the unique transport properties of 3DMe make it a superior choice for the effective *in-situ* stimulation of anaerobic biodegradation.

Figure 1: Packed Experimental Column (20ft long x 6in ID)

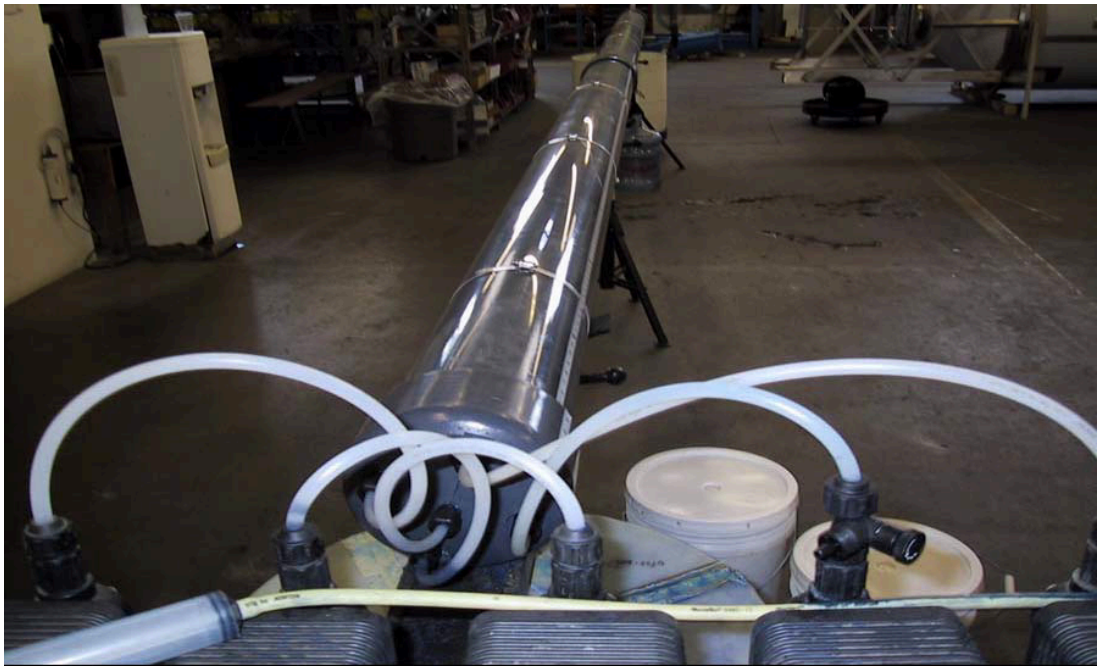

Figure 2: 3 3DMe Distribution at 13 Hours (3.5 Pore Volumes)

Figure 3: Infrared Spectrum of Column Effulent at 13 Hours

13-Hour Sample - Organic Esters and Acids

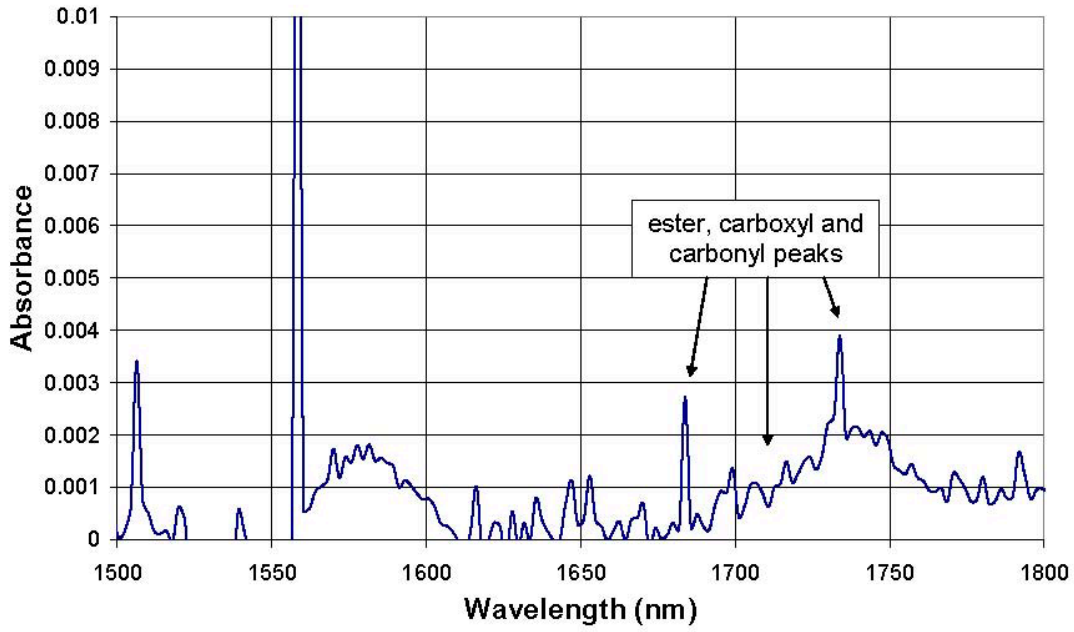

Figure 4: Micelle Formation and 3DMe Redistribution during Water Feed

References

Shah, D.O., Tamjeedi, A., Falco, J. W., and Walker, R. D., 1972, Interfacial Instability and Spontaneous Formation of Microemulsions, Am. Inst. Chem. Eng. J., 18:111-1120.

Lindman, B., Kamenka, N., Brun, B., and Nilsson, P.G., 1982, On the Structure and Dynamics of Microemulsions Self-Diffusion Studies, (ed.) Robb, I.D., Microemulsions, Plenum Press, NY.

Bordon, R.C., Lieberman, M.T., and Zawtocki, C.E., 2005, Enhanced Anaerobic Bioremediation Using Emulsified Edible Oil, Workshop, Eighth International *In-Situ* and On-Site Bioremediation Symposium, Baltimore, Md.