3-D Microemulsion (3DMe)™

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Subsurface Transport Mechanisms

As described in 3-D Microemulsion Technical Bulletin 1.0 (Introduction), 3-D Microemulsion (3DMe)™, a form of HRC Advanced®, is a unique compound (patent applied for) which incorporates esterified lactic acid (the technology used in HRC), with esterified fatty acids. The unmatched advantage of this product is that it allows for the immediate and controlled-release of lactic acid which is among the most efficient electron donors. The controlled-release of proprietary fatty acids provides a cost-effective source of controlled-release hydrogen. This combination of organic acids, in turn, rapidly stimulates reductive dechlorination for extended periods of time up to 4+ years under optimum conditions (e.g. concentrated application in low permeability, low consumptive environments.).

3DMe is <u>NOT</u> Simple Emulsified Vegetable Oil

Vegetable oil is basically insoluble. Thus, to make it amenable to injection into the subsurface, some vendors have added commercial emulsifying agents to simple vegetable oils and produced emulsions claiming that the "stable" emulsion will transport the oil significant distances down-gradient from the injection point. Unfortunately, this is not the case.

When so-called "stabilized" oil-in-water emulsions are forced out of the injection point into subsurface aquifer materials the emulsifying agents are rapidly stripped from the oil droplet due to the zeta potential of subsurface materials (charges on the surfaces of soil particles) adhering to the hydrophilic "heads" of the emulsifying agents, and to organic matter within the aquifer matrix sorbing to the vegetable oil itself. Upon the stripping of the emulsifying agents the oil droplets rapidly coalesce in soil pores creating a separate phase (this is the basis for many de-emulsification filters used in the petroleum production industry). When this coalescence occurs in the aquifer, it retards further migration of any oil emulsion and, in fact, often blocks groundwater flow. Use of emulsified oil products can result in significant lowering of the aquifer hydraulic conductivity within aquifer settings (Edible Oil Barriers for Treatment of Perchlorate Contaminated Groundwater, Environmental Security Technology Certification Program, US Department of Defense, November 2005.)

3DMe has a balanced HLB

3DMe is composed of molecules that are surface active. That is to say the molecules behave as surfactants, with a hydrophilic or "water loving end", and a lipophilic or "oil loving end". As a result, the molecules tend to align themselves with the hydrophilic ends in the water matrix, while the lipophilic ends bind to organic compounds (such as the contaminant).

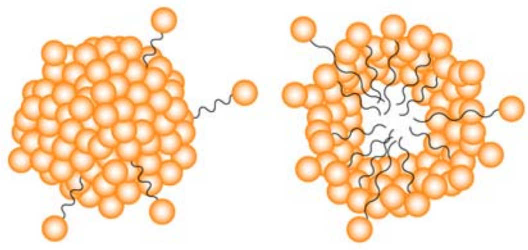
As a measure of the tendency for a molecule to move into water, chemists refer to the Hydrophile/Lipophile Balance index (HLB). The greater the HLB, the higher the tendency for dissolution in water, thus, low HLB molecules are generally pushed out of the water matrix and sorb onto surfaces and to organic compounds within the aquifer material.

3DMe was designed to have a low, yet positive HLB. This gives 3DMe the advantage of being able to sorb organic contaminants (partition), yet have a significant solubility in water allowing for aqueous transport (unlike emulsified oils). A comparison of estimated HLBs for substrates is listed below.

Substance	HLB
Sugars	30
Lecithin	20
3DMe	6
Vegetable Oil	-6

3DMe Forms Micelles

When 3DMe is in water in concentrations in excess of about 300ppm, dissolved molecules of 3DMe begin to spontaneously group themselves into forms called "micelles". In colloidal chemistry this concentration is referred to as the "critical micelle concentration" or CMC. The grouping of the micellar structure is very orderly, with the charged or hydrophilic ends (heads) of the fatty acids facing out to the water matrix and the hydrophobic ends (tails) facing in together. The micellar structures formed from 3DMe are generally spherical, but under certain circumstances can become lamellar. A depiction of a 3DMe micellar structure is shown below:



Depiction of 3-D ME Micellar Structure

The size of the 3DMe micelles formed is very small, on the order of .02 to .05 microns in diameter. These will spontaneously form in aquifer waters when the CMC is exceeded. Thus, by loading the aquifer with volumes of injection water containing 3DMe in excess of approximately 300 ppm, micelles will spontaneously form carrying the 3DMe product further down-gradient.

Mixing and Application

Concentrated Delivery

When applied to the subsurface in concentrated form, 3DMe will behave much like HRC. Once installed the material remains stationary and slowly releases soluble lactic acid and fatty acids which diffuse and advect away from the point of application. In this fashion the engineer is assured of a long-term, constant supply of electron donor emanating from the point of application for a period of up to 4+ years (under optimal conditions). This is particularly attractive when used to treat a flux of contamination from an up-gradient source or when a very long term supply of electron donor is required.

High Volume Delivery

3DMe can also be used to treat large areas in a short period of time by using a high-shear pump to mix the 3DMe with water prior to injection. This mixing generates a large volume of a 3DMe colloidal suspension. The actual suspension of 3DMe generated by this mixing ranges in size from micelles on the order of .02 microns to .05 microns in diameter to "swollen" micelles, also termed "microemulsions", which are on the order of .05 to 5 microns in diameter.

Once injected into the subsurface in high volumes followed by water the colloidal suspension mixes and dilutes in existing pore waters. The micelles/microemulsions on the injection front will then begin to sorb onto the surfaces of soils as a result of zeta potential attraction and organic matter within the soils themselves. As the sorption continues, the 3DMe will "coat" pore surfaces developing a layer of molecules (and in some cases a bilayer). This sorption continues as the micelles/microemulsion moves outward.

Unlike emulsified oil, however, the sorbed 3DMe has a significant capacity to move beyond the point of initial sorption. As the high concentration of 3DMe present in the initial injection volume decreases, bound material desorbs. As long as this concentration exceeds the CMC, micelles will spontaneously form, carrying 3DMe further out in to the contaminated aquifer through advection and diffusion.

Additional Research Underway

Regenesis is currently undertaking a series of laboratory studies and in-field research efforts to further define the extent to which 3DMe suspensions transport under various aquifer conditions. These studies will generate information which will aid in understanding the limitations to the transport of colloidal suspensions under realistic injection/aquifer dispersion conditions.