

Impact of Electron Donor Hydrophile/Lipophile Balance on Subsurface Distribution*

*Scott Wilson; Robert Kelley, PhD; Benjamin Mork, PhD; and Thomas Cormack
(Regenesis, San Clemente, CA, USA)*

I. INTRODUCTION

The use of electron donor materials to stimulate the reductive dechlorination of groundwater contaminants has become a widely practiced form of *in situ* remediation. Electron donor materials currently in use vary widely. Among these, soluble sugar-type substrates offer high subsurface distribution rates yet rapidly ferment and “wash out” requiring frequent and costly reinjection. Oil-based substrates offer a partial solution to this in that their insolubility retards fermentation rates. The insolubility of these oil materials however, even when emulsified, inhibits subsurface distribution requiring closely spaced arrays of injection points in order to gain adequate treatment of a contaminated aquifer.

The distribution of electron donor materials in subsurface aquifers is controlled by a number of factors all of which impact movement. Significant among these are the physical properties of the aquifer material such as permeability, pore throat diameter and path tortuosity. Significant chemical properties of the aquifer affecting distribution include aspects of the water chemistry such as ionic speciation/concentration, and aspects of aquifer matrix geochemistry such as the fraction of organic carbon (Foc) and zeta potential of matrix components.

The physical/chemical characteristics of the electron donor itself have a very direct and significant impact on its movement in the subsurface. The physical and chemical interaction of the donor material with groundwater and the aquifer matrix will determine its ability to move via diffusion and advection. This in turn will ultimately have direct bearing upon the ability to adequately distribute the electron donor across the treatment area of interest and upon the cost effectiveness of the chosen electron donor material to achieve successful site remediation.

Emulsified Oil Substrates: Very Limited Subsurface Distribution

In an effort to supply low-cost long-lasting substrates for anaerobic dechlorination, remediation researchers attempted to use neat vegetable oil. This soon proved impractical as it was shown that once injected the oil often separated forming a light non-aqueous oil phase floating on the contaminated aquifer. These injections were also shown to have potential to reduce hydraulic conductivity of the aquifer under treatment (Henry, B. 2003). Shortly thereafter, practitioners began the practice of emulsifying the insoluble vegetable oils prior to injection in an attempt to allow the mix to disperse the substrate

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away from the point of application without the formation of the LNAPL. These mixtures are prepared by subjecting the very insoluble oils to a high shear in the presence of emulsifier additives. The result is an oil-in-water emulsion where the oil droplets are surrounded by emulsifier (surfactants) in an attempt to keep the mixture of insoluble oil droplets from coalescing.

Movement of Emulsions

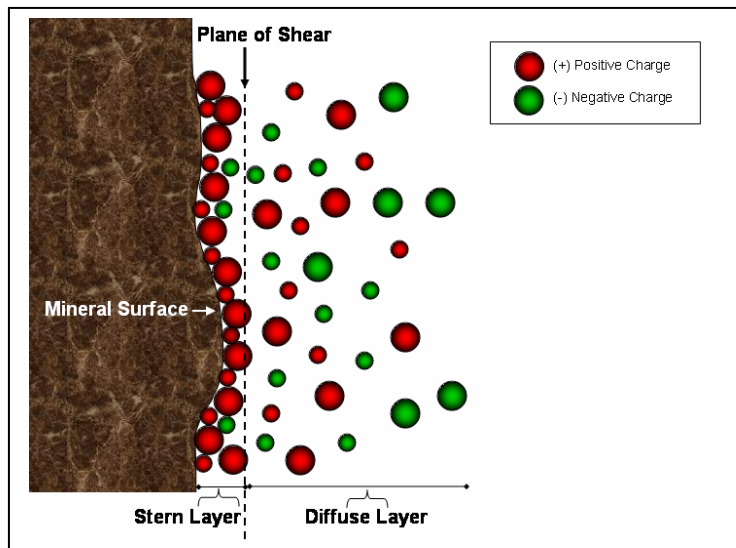
When injected into the aquifer these emulsions are subject to “straining” where aquifer matrix pore throat diameters are less than that of the emulsion droplets (Soo and Radke, 1984). This straining results in rapid oil coalescence often resulting in permanent permeability loss (Couliblay, Long and Borden, 2006).

Researchers investigating the movement of oil emulsions with droplet sizes less than the aquifer matrix pore throats generally accept that the emulsion droplet subsurface transport will be governed by rules of colloidal transport theory (Westall and Gschwend, 1993), i.e. emulsion droplets that can move through the matrix pore throat diameters will be subject to the tortuosity of the forward flow path and the potential for adsorption to the aquifer matrix upon collision with the matrix surface. Under this theory oil-in-water emulsions, regardless of size, will eventually collide with the aquifer matrix and will attach primarily through the forces of adsorption.

Attachment to Aquifer Matrix

Upon collision with the aquifer matrix most oil-in-water emulsions attach rapidly to the matrix surface through physical forces. The forces binding the attachment are the balance

Figure 1: Ionic Environment on Surface of Aquifer Matrix

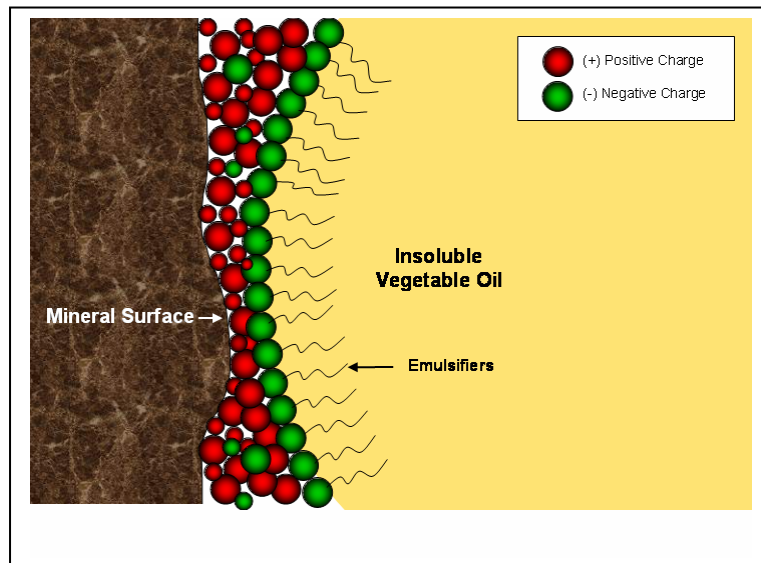


of electrostatic repulsion and van der Waals attraction that occurs within the surface potential of the ionic environment in what is referred to as the “double layer” and is explained by DLVO theory (named after Derjaguin, Landau, Verway, Overbeek).

This phenomenon is often simply referred to as emulsion adhesion due to zeta potential, where zeta potential describes the electrokinetic potential at a point near the surface of a particle, defined as the slip plane or shear plane (Mysels, 1964), where surface charges begin to be movement and colloidal attachment. Figure 1 illustrates the typical ionic environment on the surface of an aquifer matrix.

As a colloidal particle such as an insoluble oil emulsion collides with the mineral surface, it enters through the diffuse layer, binding to the strongly attached ionic layer referred to as the Stern Layer. This is depicted in Figure 2.

Figure 2: Attachment of Insoluble Vegetable oil to Aquifer Mineral Surface



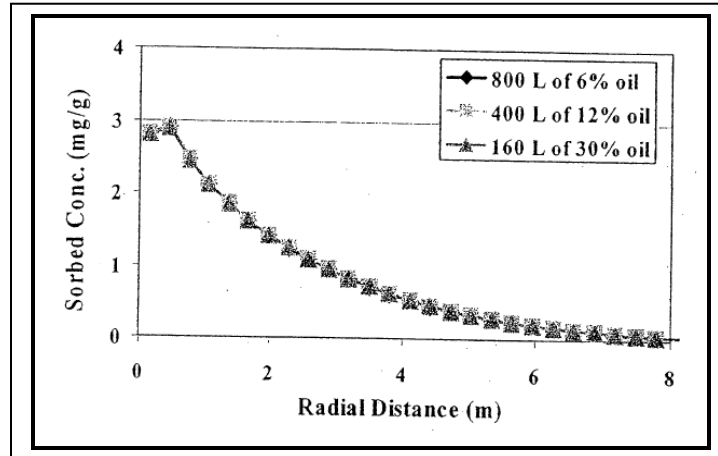
Emulsified Oils Sorb Rapidly, Inhibiting Transport

Studies into the movement of oil-in-water emulsions clearly indicate that physical and chemical aspects of the aquifer inhibit transport of emulsion droplets more than a few meters the subsurface. Research has shown that even in high permeability sand matrices, the majority of injected oil emulsions move little more than 1 to 2 meters distance before becoming sorbed onto the aquifer matrix (Borden et. al., 2005) A depiction of a typical oil emulsion distribution curve is presented in Figure 3.

Note in Figure 3 that regardless of oil emulsion concentration or volume of suspension injected, only a minor fraction of emulsion travels further than 4 meters distance from the injection point. Furthermore the majority of the oil emulsion is sorbed to the aquifer medium within the first 1 to 2 meters from the injection point. Likewise, laboratory studies conducted on an emulsified oil substrate in a matrix defined as a clayey sand

showed the majority of the substrate traveled less than 50 cm distance from the application point (Coulibaly, et. al, 2006).

Figure 3: Emulsified Oil Transport is Limited Due to Adsorbance to Aquifer Matrix (Borden, et. al. 2005)



Oil Emulsion Attachment is Permanent

Research into the attachment of oil emulsions clearly indicates that once an oil emulsion droplet is adsorbed onto the aquifer matrix it is very resistant to release or even irreversible (Johnson, W. et. al. 1996). This is presumably due to the emulsion droplet, over time, penetrating closer to the mineral surface as it displaces more of the water in the diffuse layer. Laboratory work with columns of sand and with kaolinite amended sands indicated that emulsified oil droplets once adsorbed were very resistant to release (Coulibaly, 2006). Field observations have corroborated this showing that injecting excess water does not move emulsion farther out from the injection point (Borden, et. al. 2005).

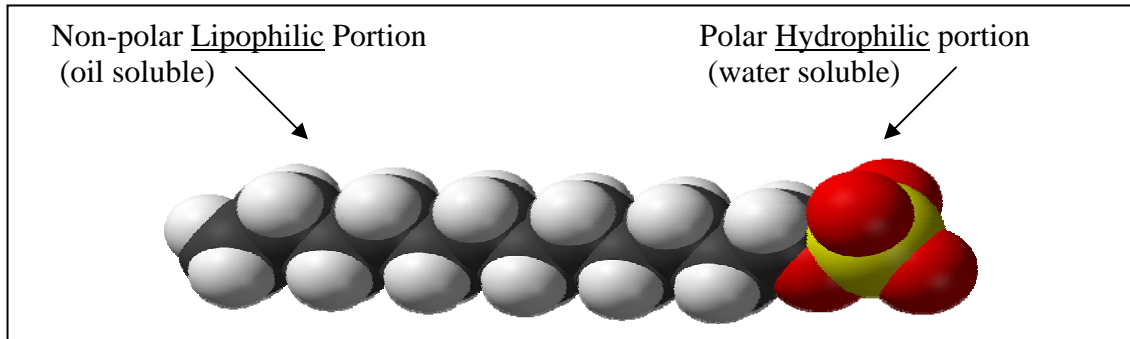
Emulsified Vegetable Oil: Poor Subsurface Distribution Limits Cost Effectiveness

Adequate distribution of electron donor substrates is a key requirement to the successful stimulation of *in situ* bioremediation. While large volumes of dilute emulsified oil substrates can be applied to the subsurface through injection wells or galleries, the majority of the emulsion droplets will be either strained out of suspension or permanently adsorbed from suspension within the first 2 meters of aquifer material. This requires the capital cost of closely spaced injection wells, the application of large volumes of oil and may lead to excess oil coalescence resulting in reduction of hydraulic conductivity.

II. IMPACT OF SUBSTRATE HYDROPHILE/LIPOPHILE BALANCE

When dealing with organic substrates for application into aqueous media such as contaminated groundwater much of the action of the substrate is governed by its solubility and its propensity to act as a surfactant. A surfactant is any molecule that is surface active or has a tendency to concentrate at solution interfaces (Shah, D. et. al.,1972). Such molecules are composed of a polar hydrophilic (water soluble) portion and a non-polar lipophilic (oil soluble) portion. Figure 4 shows a typical surfactant-type molecule-(sodium dodecylsulfate) and its polar (hydrophilic) and apolar (lipophilic) regions. It is the polar moiety that tends to hold the molecular structure in aqueous solution while the non-polar hydrocarbon portion is forced to aggregate with other lipophilic molecules at solution interfaces.

Figure 4: Illustration of Surfactant Polar and Apolar Moieties



The hydrophile-lipophile (HLB) balance of a molecule is an index of the relative size and strength of the hydrophilic and lipophilic groups of the molecule (Davies, J., 1957). The scale ranges from negative values (lipophilic) to positive values (hydrophilic). The use of the HLB index allows one to grasp an idea of the solubility and phase-partitioning characteristics of a particular surfactant. Table 1 summarizes the relative HLBs of some common substrates employed as electron donors.

Table 1: HLB Values for Various Electron Donor Substrates

<u>Substance</u>	<u>HLB</u>
Lactate	30
Lecithin	20
HRC	17
HRC Advanced	7
Oleic Acid	1
Vegetable Oil	-6

As can be seen in Table 1, highly soluble substrates such as lactate have an HLB in the range of 30. Very insoluble substrates such as vegetable oil have a very low HLB in the range of -6.

HLB Controls Subsurface Distribution

The limitation to subsurface distribution described above for emulsified oil substrates is a result of the insolubility of the oil substrate itself within the aquifer water. In all preparations of emulsified oil substrates, the highly insoluble oil (HLB -6) is mixed under a high shear with a small amount of emulsifying surfactant. This surfactant allows for the emulsion to form and to remain stable in preparation for application. However, once injected, the emulsion droplets will rapidly sorb to the subsurface, irreversibly as depicted in Figure 2: Attachment of Insoluble Vegetable Oil to Aquifer Mineral Surface. Because the oil has such a low affinity for the water phase, there is negligible dissolution and essentially no further distribution of the substrate.

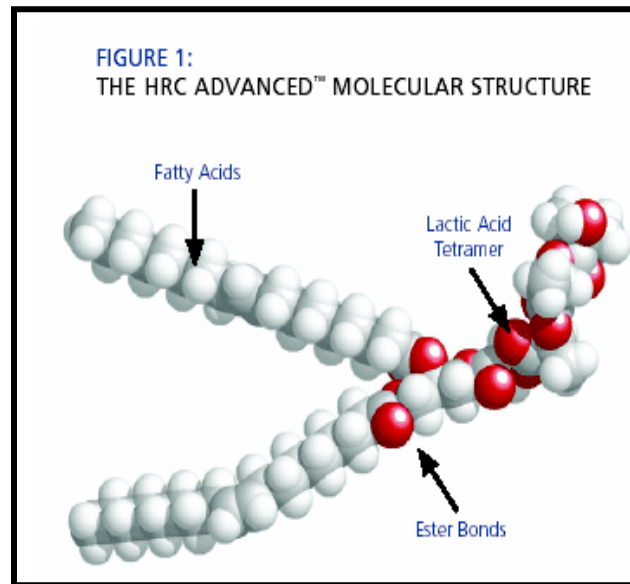
Counter to this is the use of substrates with high solubility, such as sodium lactate solutions which show the opposite tendencies. When injecting lactates (HLB: 30) the highly soluble substrate immediately dissolves and advects with aquifer waters. The limitation to the use of high HLB substrates is two-fold: 1) these substrates are very bioavailable, thus rapidly fermenting and forcing the aquifer into methanogenic conditions which has been shown to be an inefficient use of electron donor substrate and thought by some to promote unfavorable microbial competition (Yang, Y and McCarty, P.1998); and 2) these substrates rapidly “wash out” of the target area. Unlike low HLB oil substrates that show little to no distribution, high HLB substrates require costly regular if not continuous reapplication to maintain an adequate supply of electron donor to successfully treat a contaminated aquifer.

III. DEVELOPMENT OF A BALANCED HLB SUBSTRATE: HRC ADVANCED 3D MICROEMULSION

Researchers have recently developed an electron donor material designed to optimize subsurface distribution (Regenesis, San Clemente, CA). The product is commercially referred to as **HRC Advanced 3D Microemulsion** (HRC Advanced™). This product incorporates a unique glycerol polylactate/oleate ester (patent applied for) and is designed with a balanced HLB to promote excellent distribution in the subsurface while exhibiting consistent electron donor source for extended periods of time. The product is mixed on-site with field water to generate a smooth microemulsion suspension (estimated emulsion droplet diameter is 1 micron). An illustration of the molecular structure is depicted in Figure 5.

In the development of the material, the focus was on achieving a “balanced” HLB, that would allow for the material to initially adsorb on the aquifer material in the area of injection then slowly distribute via diffusion and advection. The product has an estimated HLB 7, placing it in a rather “balanced” position on the HLB scale, which gives the material very unique inherent properties

Figure 5: HRC Advanced Molecular Structure



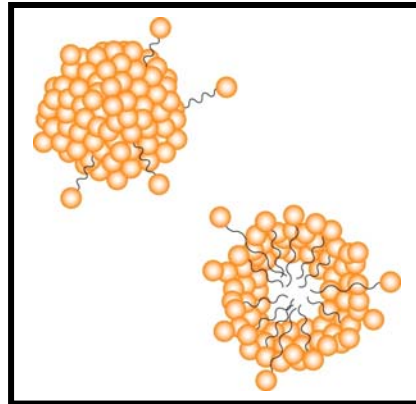
HRC Advanced Forms Micelles

The HRC Advanced is somewhat soluble in water as reflected in its HLB. This is in stark contrast to vegetable oil-type substrates which are insoluble. This gives the HRC Advanced material some distinct advantages with regard to distribution after injection as it allows a small fraction of the material to dissolve and transport further in the aquifer. More importantly, however, is its propensity to form micelles which in turn carry more of the product out into the aquifer over time, - a self distributing characteristic.

A micelle is described as an aggregate structure of surfactant molecules dispersed in a liquid. In aqueous solution these structures are colloid forms with the hydrophilic “head regions” of the surfactant molecules facing outward in contact with the water sequestering the hydrophobic tail regions of the surfactant molecules in the center. Generally micelles are spherical in shape, but other forms exist such as cylinders, lamellar bilayers, etc. The shape and size of the micelles depend upon the geometry of the surfactant molecules and solution conditions such as temperature, surfactant concentration, etc.

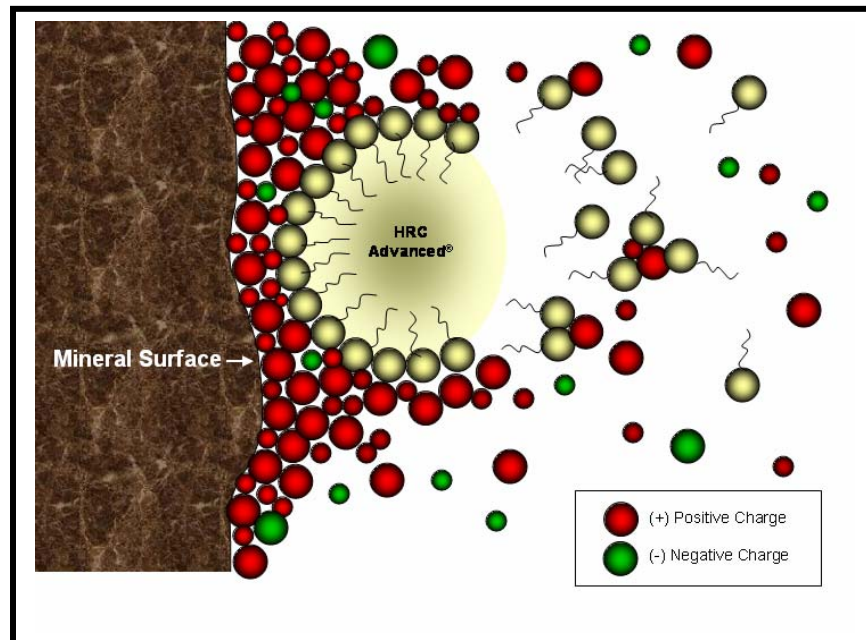
Micellization (formation of micelles) is a function of surfactant concentration. At a specific surfactant concentration, known as the Critical Micelle Concentration (CMC) the molecules begin to aggregate and form the micelle structures. Often the micelles, as they form, incorporate undissolved surfactant material forming swollen micelles or microemulsions (Bennet et. al.,1981) of about 100 angstroms in diameter.

Figure 6: Illustration of Typical Spherical Micelle Structure



The CMC for the HRC Advanced substrate is approximately 300 mg/L. Thus, above this concentration HRC Advanced micelles and microemulsions form as colloids within the aquifer water and are free to transport through dispersion. This dispersion will continue until adsorption occurs upon the aquifer matrix or the concentration of HRC-Advanced within the water matrix drops below the CMC at which point the colloidal structures would dissolve.

Figure 7: Dissolution of HRC Advanced Micelle/Microemulsion Stimulating Redistribution by Further Dispersion in Groundwater



Laboratory Validation of Distribution

Upon the completion of the initial development activity, it was hypothesized that the HRC Advanced material, once injected into the subsurface, would:

- 1) adhere to the aquifer matrix near the point of injection;
- 2) once in place the sorbed material would begin to dissolve;
- 3) the dissolved material, once in concentration >300ppm, would spontaneously form micelles incorporating droplets of non-dissolved HRC Advanced;
- 4) micelles would continue to distribute within the aquifer by natural dispersive forces.

Bench-Scale Column Testing

In order to validate the micelle dispersion hypothesis of HRC Advanced, the developer commissioned a third party laboratory to perform experiments comparing HRC Advanced to a commercially available emulsified oil substrate EOS™ (EOS Remediation, Inc. Raleigh, NC). The intent of the experimentation was to compare the rate of transport of the two products through two different soil types under flow rates simulating field injection.

Experimental Design

The soils tested were field sand (0.6 to 1.5 mm diameter) and a sandy clay loam (64.2% sand, 9.1% silt, and 26.6% clay). Characteristics of the soils tested are presented in Table 2.

Table 2. Characteristics of Soils Tested

	Sand	Sandy Clay Loam
Hydraulic Conductivity (cm/s)	0.0031	0.0026
Bulk density (g/cm ³)	1.6	1.13
Pore Volume (ml)	300	500
Zeta Potential (mV)	-22.75	-22.38

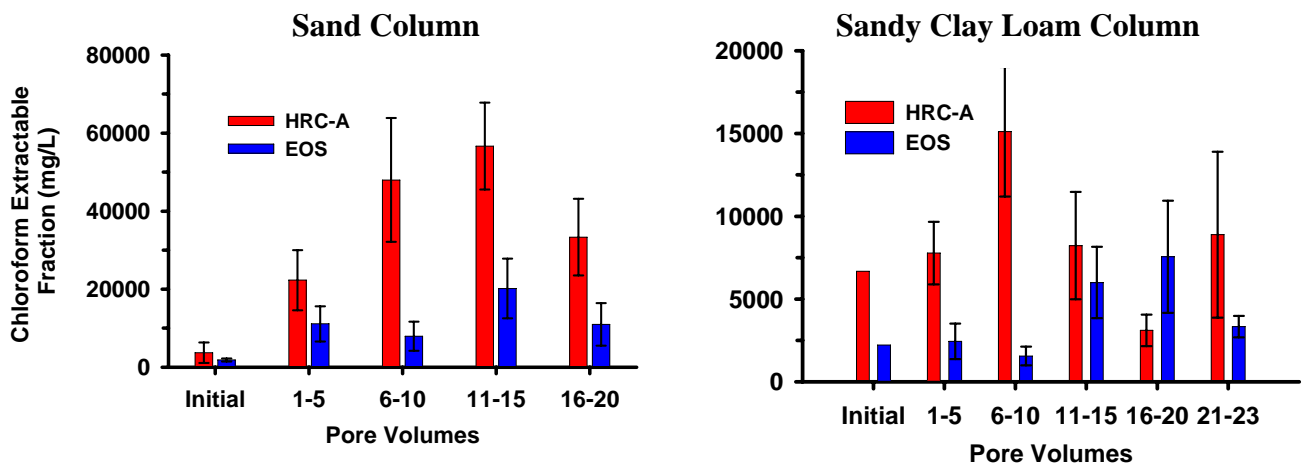
The apparatus used for the experiment consisted of pressurized flexible-walled permeameter columns packed with the soil (10cm length X 10 cm diameter) performed in triplicate. The columns were first flooded, then a 30ml volume of a 1:10 substrate in water suspension of either the HRC-A or EOS was injected. The relative Zeta Potential of HRC-A and EOS, was shown to be -32.01 mV and -22.89 mV, respectively. This was followed immediately by a 20 pore volume flush of water added at a rate of 15ml/minute. Effluent water samples from the columns were collected and analyzed for chloroform extractable organics, as a measure of the hydrophobic fraction of electron donor moving through the column.

Results

For the columns packed with sand, the HRC Advanced amended columns showed significantly greater concentration of organic carbon moving through the column, on the loam, the HRC Advanced amended columns also showed significantly more organic material transport, on the order of 5 to 6 times that of EOS, in the first 10 pore volumes of water flushed through the columns.

Data is presented in Figure 8. Data shown represents the average of the triplicate columns. For simplicity the bar graph indicates the results for 4 pore volume averages.

Figure 8. Results of Bench-Scale Column Study



Discussion

The data generated in the bench-scale column study clearly demonstrated that the chloroform extractable fraction (hydrophobic constituents) of the HRC Advanced material traveled at a higher rate through both the sand column and the sandy clay loam column. Additionally, the amount of the HRC Advanced material transported was significantly greater than that of the EOS material. As expected the amount of material transported through sand column was on the order of 4 times that of the less permeable sandy clay loam.

Aquifer Simulation Column Test

An experiment was designed in an effort to analyze the movement of the HRC Advanced material after attachment to a simulated aquifer matrix. As noted earlier, it is well documented that emulsified oil substrates transport only short distances through porous media, (usually less than 1-2 meters), and that they are irreversibly adsorbed. In this experiment the investigators sought to determine the transport characteristics of the HRC Advanced material during injection of the suspension and for a period after colloidal attachment had occurred while under flushing conditions simulating natural groundwater movement.

Experimental Design

A 6inch (15.24cm) diameter 20 foot (6.1M) long aquifer simulation column was constructed of transparent polycarbonate. The column was filled with fine grained sand packed to prevent channeling. Pore space was determined to be 30.5% (about 9 gallons (33.8L)). The column was pumped with water via peristaltic pumps at a rate of 2.5 gallons/hour (9.46L/h).

A suspension of HRC Advanced was generated by preparing a 1:3 HRC-A to water mixture employing a common high shear pump which was further diluted with water to generate a final 1:50 suspension. To visually track the movement of the emulsion, the HRC-A suspension was dyed with methylene blue which is specific to the hydrophobic portions of the HRC-A formula.

The column was first saturated with water. The HRC Advanced suspension was then fed into the column at a rate of 2.5 gallons/hour (9.46L/h). After a period of 20 hours, the HRC-A suspension feed was halted and water was injected into the column at the same rate (2.5 gallons/hour (9.46L/h)). This water feed continued for a period of 12 hours (about 3.3 pore volumes).

The movement of the dyed HRC Advanced material was observed visually throughout the study. In addition, water effluent from the column (distance 20' (6.1M) was analyzed for the methylene blue (UV-Visible Spectroscopy). Components of the HRC-A in the effluent were also confirmed by direct measurement with both liquid chromatography and infrared analysis.

Results and Discussion

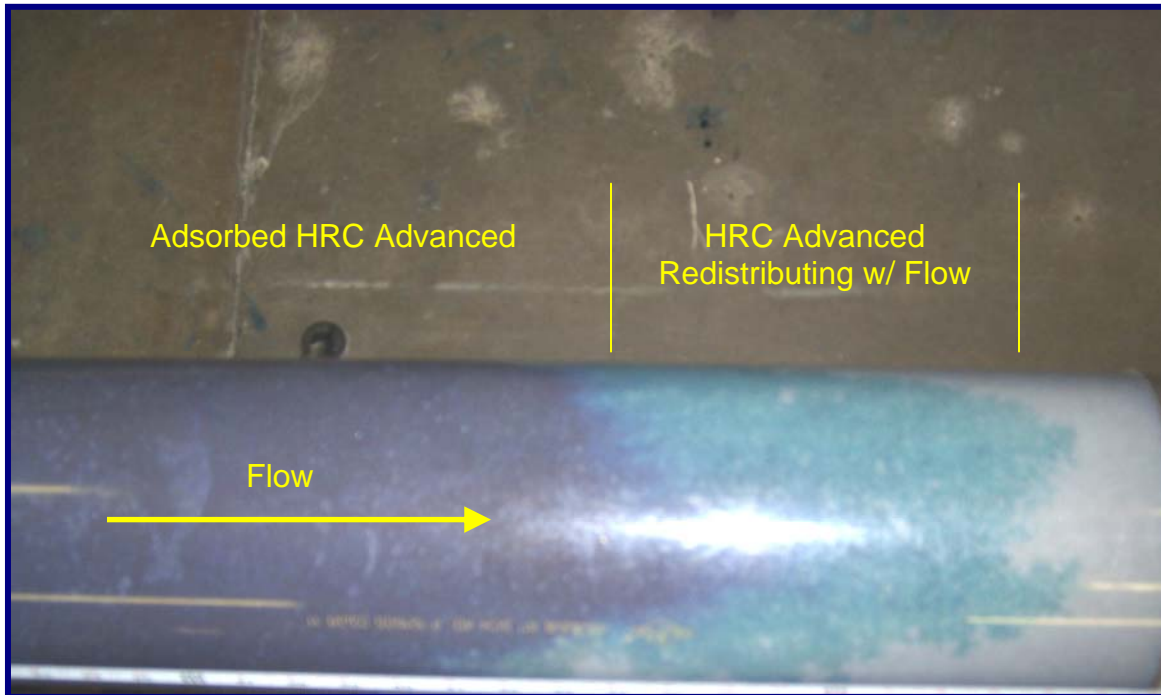
After 13 hours time, an estimated 3.6 pore volumes of the HRC Advanced suspension (1:50 HRC Advanced to water) had been fed into the column. As expected, due to the hydrophile/lipophile balance of the HRC-A material, the bulk of the HRC Advanced microemulsion appeared to adhere to the sand surfaces within the first one meter of the column as evidence by a dark blue color. However, it was at this time that the first "break through" was noted of material exiting the column via spectroscopy. Further analysis clearly indicated that the material in the effluent was, in fact, colloidal HRC Advanced (micellar suspension) as evidenced by the presence of the intact esters, carboxyl and carbonyl peaks apparent under infrared spectrum analysis. While the bulk of the HRC Advanced material once injected was staying stationary, micelles were forming and carrying the HRC Advanced material greater than 20 feet (6.1M) with only 3.6 pore volumes in less than 13 hours time.

After 20 hours of HRC Advanced injection, the bulk of the HRC Advanced suspension appeared to be sorbed onto soil near to the injection point within the first 2 meters of the column as evidenced by a dark blue color. At this time the column was switched to a water feed, without any HRC Advanced addition, in order to emulate continued groundwater flow after HRC Advanced emplacement. A striking pattern began to emerge as a light blue colored "front" began to move down the column.

It is apparent that water continuing to flow past the emplaced HRC Advanced was redistributing the HRC Advanced through the column, which in turn was re-adsorbing

onto the column in a forward moving “front”. As more water was fed through the column the HRC Advanced continued to redistribute forming a very distinct light blue colored pattern (see Figure 9). Throughout the 12 hour period of water feed, HRC Advanced micelle suspension in low concentration was documented exiting the column as evidenced by microscopy and validated by liquid chromatography and infrared analysis.

Figure 9: HRC Advanced Redistribution after Adsorption under Simulated Groundwater Flow Conditions



IV. CONCLUSIONS

Hydrophile/Lipophile Balance (HLB) is a very important parameter when considering an electron donor substrate for subsurface application. While low HLB amendments such as emulsified oil substrates offer a high potential for partitioning of organic contaminants, research has shown that it is very difficult to gain significant distribution of these compounds in subsurface environment. Emulsified oils substrates travel only short distances in the subsurface before adsorbing irreversibly to mineral surfaces. Gaining adequate volumetric distribution of these substrates in the subsurface requires close spacing of injection wells and the application of very large volumes of substrate.

The use of electron donor substrates with a “balanced” HLB offer much greater subsurface distribution as a result of the dissolution of adsorbed colloidal material and the spontaneous formation of micellar/microemulsion material at concentrations greater than critical micelle concentration.

Research conducted with HRC Advanced (HLB 7) clearly documented a significantly higher rate of transport of the material when compared to an emulsified oil substrate in both a field sand matrix and in a sandy clay loam matrix under flow rates simulating injection. Furthermore, it was clearly documented that unlike emulsified oil substrates, once adsorbed onto the aquifer matrix the HRC Advanced material redistributed through dispersion under flow rates simulating ambient groundwater movement.

The use of electron donor substrates with a balanced HLB index such as HRC Advanced allows for material application on wider injection point spacing. When compared to emulsified oil substrates the greater ability to distribute the HRC Advanced material could offer a significant capital cost savings in injection well and related equipment costs.

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