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Enhancing Reductive Dechlorination

Study results of emulsified lecithin-based substrates used as reductive treatment of chlorinated solvents in groundwater

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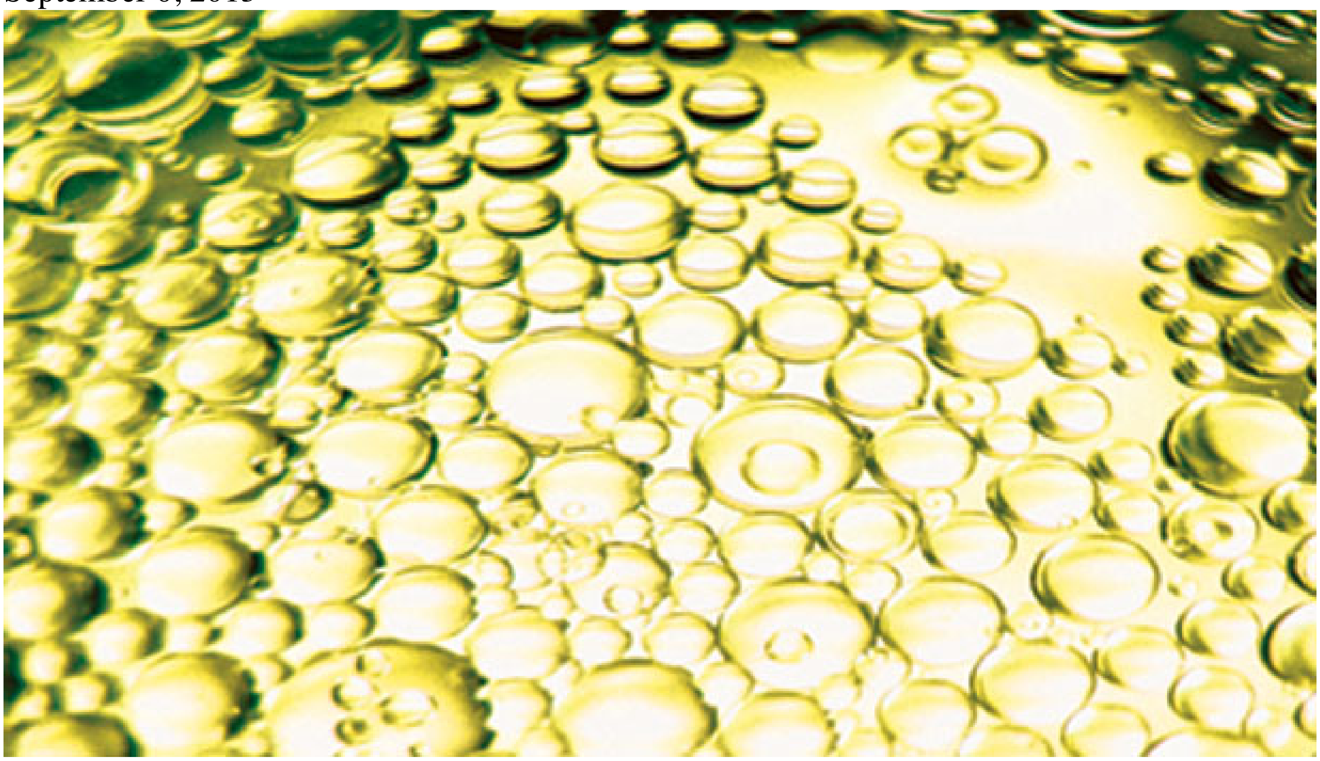

Enhanced reductive dechlorination (ERD) and *in-situ*chemical reduction (ISCR) are emerging as cost-effective remedial approaches for groundwater with elevated concentrations of chlorinated solvents.

ERD involves the addition of an electron donor containing biodegradable carbon to groundwater, which promotes the activity of bacteria and mediates reductive dechlorination reactions. The addition of electron donors can be augmented with the inoculation of a bacterial culture with proven ability to fully degrade common chlorinated solvents. ISCR treatment combines electron donor addition with a chemical reducing agent, such as zero valent iron (ZVI) or divalent (ferrous) iron. In general, ERD is the more cost-effective approach while ISCR is a more robust technology capable of dealing with more challenging groundwater conditions (e.g., high dissolved oxygen or sulfate levels, high initial chlorinated solvent concentrations).

When selecting an electron donor for use in ERD, cost, ease of use and longevity are among the more important factors to consider. A wide variety of carbon substrates, including lactate, molasses or vegetable oil, have been used in ERD applications over the past several years. Recently, FMC Environmental Solutions introduced its emulsified lecithin substrate (ELS) for ERD applications, and EHC Liquid product for ISCR to market. Both products are based on a proprietary formulation of lecithin with a number of unique characteristics that make it an excellent carbon substrate for ERD and ISCR applications.

What is lecithin?

Lecithin is a complex mixture of phospholipids, triglycerides, fatty acids, complex carbohydrates, polysaccharides and antioxidants such as tocopherols (i.e., vitamin E). Phospholipids are the primary components in lecithin (Figure 1). These compounds are present in all living cells and serve as nature's main surface-active agents. Lecithin is used in a wide variety of food products including infant formula, chocolate, baked goods, and cheese products. It is classified as GRAS (Generally Recognized as Safe) by the Food and Drug Administration.

Slowly released nutrients

Phospholipids contain structural nitrogen and phosphorus which are slowly released into to the microbial population as they metabolize the phospholipids. This ensures a long-lasting and stable supply of essential nutrients, important for the growth of bacteria in ERD applications. Lecithin offers a valuable advantage over other carbon substrates, particularly in nutrient-stressed aquifers. Moreover, lecithin's organically-bound nutrients are superior to some ERD products that simply combine lactate or vegetable oil with inorganic forms of nitrogen and phosphorus; the inorganic nutrients can be rapidly consumed, precipitated in forms that are not bioavailable, or washed out of the treatment zone with groundwater flow.

Surface activity

A second valuable feature of phospholipids is their surface-activity. Phospholipids are amphiphilic: simultaneously hydrophilic (water-loving) and lipophilic (oil-loving). As a result, they are easy to emulsify and form stable aqueous emulsions with very small droplets (ca. 60 percent less than 1 μm diameter) that are not prone to breaking. This enables easy application and good distribution throughout the treatment zone.

Longevity and distribution

The high molecular weight and branched structure of phospholipids enable them to serve as long-lasting source of carbon and nutrients for ERD and ISCR applications. The molecular weight of the main components of lecithin, PC and PE, is 760 g/mole and 744 g/mole – nearly 300 percent greater than the main component of soybean oil (linoleic acid: molecular weight of 280 g/mole). The other major phospholipids in lecithin have similarly high molecular weights. Testing under controlled conditions in a flow-through system (50 cm length up-flow glass columns filled with aquifer solids, groundwater velocity of 10 cm/day, temperature of 20 +/- 2°C), indicated that a single application of the lecithin formulation used in ELS and EHC maintained soluble carbon levels above 20 mg/L for nearly 500 days (Figure 2). This is significant because dissolved substrate concentrations of 20 mg/L and more are considered to be sufficient to support ERD processes.

Carbon metabolism will be slower under cooler groundwater temperatures of 10 to 12°C commonly encountered at many sites, suggesting both products will support ERD or ISCR for more than two years.

Testing conducted in the same flow-through column system, under the same conditions described above, indicate that lecithin emplacement leads to good distribution of soluble carbon and rapid creation of reducing conditions (Table 1) – both favorable for ERD and ISCR processes. The results indicate that, under conditions representative of five weeks of moderate velocity groundwater flow, between 10 percent and 13 percent of the lecithin-based substrate migrated a distance of two feet from the point of placement (Figure 3). In contrast, less than 2 percent of the EVO materials tested moved the same distance. The good distribution characteristics, combined with the substantial longevity (Figure 3), and the rapid creation of reducing conditions (Table 1), indicate that the lecithin-based products are very well-suited to ERD and ISCR applications. The good distribution characteristics of lecithin also mean that the large volumes of “chase water” used in many emulsified oil applications are not needed; hence, application time and cost can be reduced.

The rapid creation of reducing conditions may facilitate simultaneous addition of ELS and microbial inoculation, thereby making application of ERD and ISCR more cost effective.

Antioxidant property

The antioxidant property of lecithin, which enables it to protect organic compounds (i.e., enzymes and DNA) and inorganic species (e.g., ferrous iron, Fe^{+2}) from undesirable oxidation reactions, make it particularly well suited for use as the carbon substrate for ISCR applications because it enables the inclusion of ferrous iron and creation of an easily-applied, fully liquid ISCR reagent.

The EHC formulation enables ferrous iron to be mixed with the organic electron donor and then injected or emplaced together – without the frequently encountered problem of iron precipitation in mixing tanks, injection equipment, or on well screens; which is a commonly-encountered problem when ferrous iron is added to other carbon substrates. Thus, this product enables application of ISCR chemistry to sites where emplacement of reagents containing ZVI would be difficult or impractical. As a result, this unique liquid ISCR reagent can support effective ERD, while also stimulating chemical dehalogenation reactions through the formation of reactive iron minerals such as iron oxides (e.g. magnetite) and iron sulfides (e.g. mackinawite).

It is now recognized that ferrous iron on mineral surfaces such as iron oxyhydroxides (e.g., goethite), magnetite, pyrite, and even simple clays (e.g., smectite), can create reactive minerals that are capable of mediating dechlorination of chloroethenes and chloromethanes, including complete dehalogenation of PCE and TCE to chloroacetylenes. It has been suggested that ferrous iron can be viewed as the abiotic equivalent of bacteria in reductive dehalogenation processes. Worthy of note is that formation of reactive iron and iron sulfide minerals can enhance dehalogenation rates even if only small amounts of the minerals are formed, because concentrations of mackinawite or green rust as low as 0.1 percent by weight are capable of transforming chlorinated hydrocarbons at environmentally significant rates. Further, such reactive minerals can be repeatedly regenerated by the activity of iron reducing bacteria, so long as a supply of organic electron donor remains available; thus, they can provide a long-term contribution to groundwater cleanup.

Field-scale performance

Anumber of field-scale applications of both ELS and EHC Liquid have now been completed with good results. For example, at an industrial site in New Jersey, EHC Liquid was injected along with a pH buffer and SDC-9 Dehalococcoides (DHC). Nineteen injection points targeted a vertical zone from 7- to 21-feet below ground surface. A total of 5,110 gallons of solution was injected containing 11,560 pounds of EHC, the buffer and 24 liters of the DHC suspension.

Following injection of the amendments, strong reducing conditions rapidly developed and elevated soluble carbon levels, conducive to chemical and biological reduction of chlorinated VOCs were observed (Figures 4 and 5). PCE and TCE concentrations were reduced to concentrations below the GWQS within nine months following the initiation of ISCR treatment (Figures 6 and 7).

Summary

Remediation professionals focused on *in-situ*treatment of groundwater containing chlorinated solvents are increasingly employing systems based on ERD and ISCR. The probability of successful outcomes in their work increases when they use an organic electron donor that is easy to apply, long-lasting, well-distributed, and cost effective. ELS and EHC Liquid are new lecithin-based reagents that have these attributes and, therefore, provide an advantageous alternative to other electron donors.

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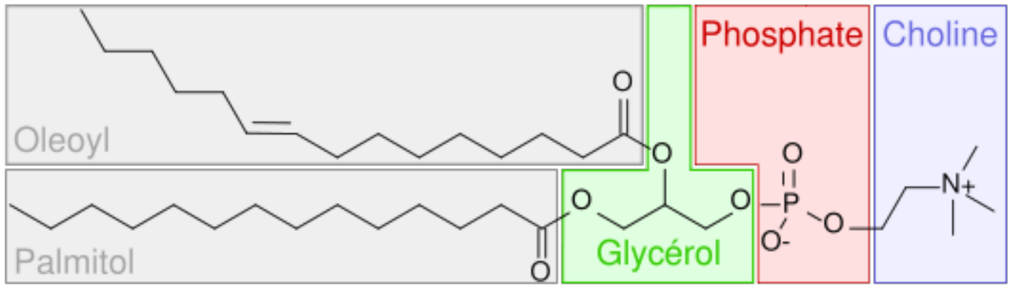

Figure 1. Phosphatidylcholine structure.
(Source: http://chemistry.about.com/od/factsstructures/ig/Chemical-Structures---P/Phosphatidylcholine.htm)

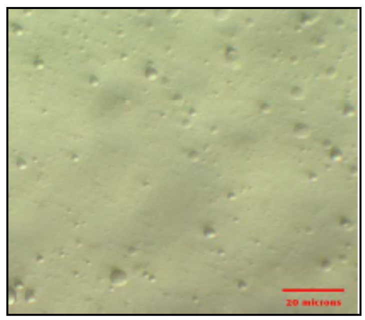

Figure 2. Electron micrograph of lecithin droplets in 25% lecithin emulsion.

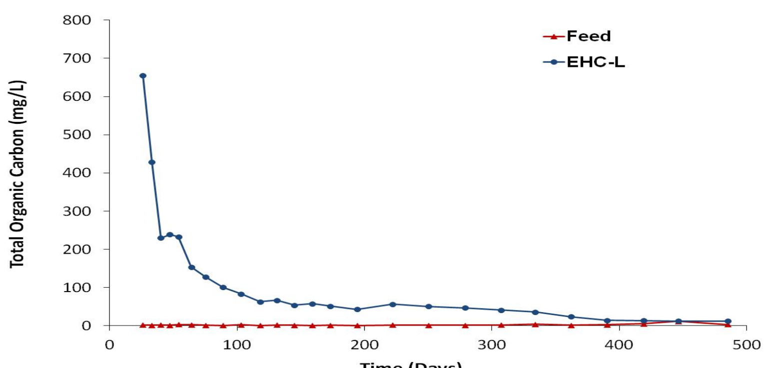

Figure 3. Influence of EHC® Liquid formulation on release of soluble carbon from soil column over 480 days of treatment.

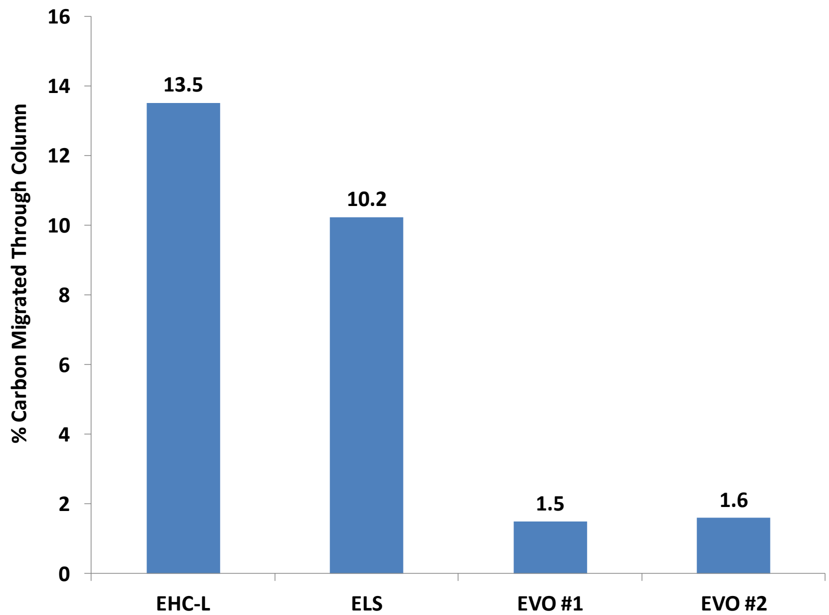

Figure 4. Total organic carbon migration through columns after 35 days (% of total injected).

Table 1. Effect of electron donor on oxidation reduction potential (ORP) in groundwater samples inoculated with SDC-9 culture.

Treatment	ORP (mV) (day 19)
Abiotic Control	340
Emulsified Lecithin plus Ferrous Iron (EHC Liquid)	-84
Emulsified Lecithin (ELS)	-72
Emulsified Vegetable Oil Product #1	284
Emulsified Vegetable Oil Product #2	345

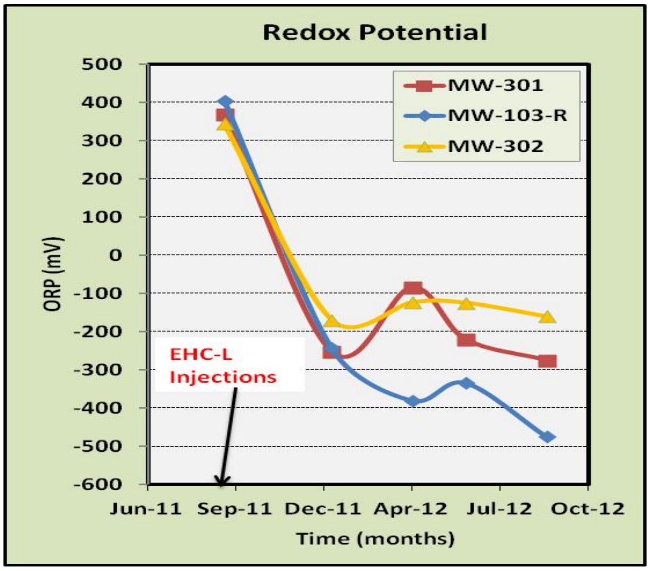

Figure 5. Effect of EHC Liquid treatment on redox potential in site groundwater.

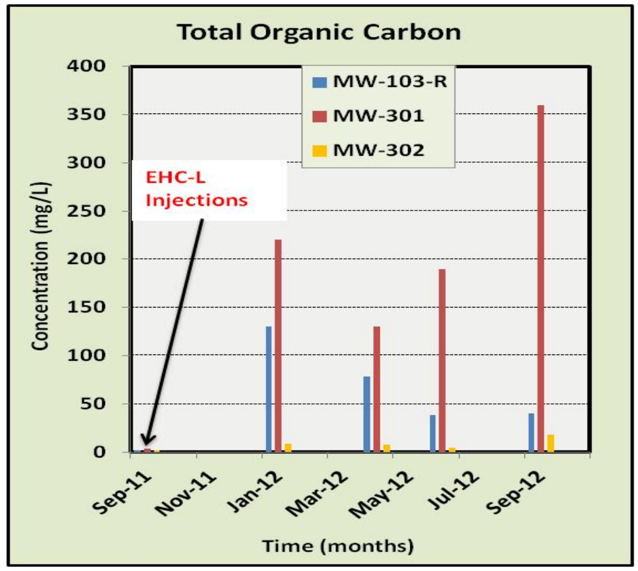

Figure 6. Effect of EHC Liquid treatment on total organic carbon in site groundwater.

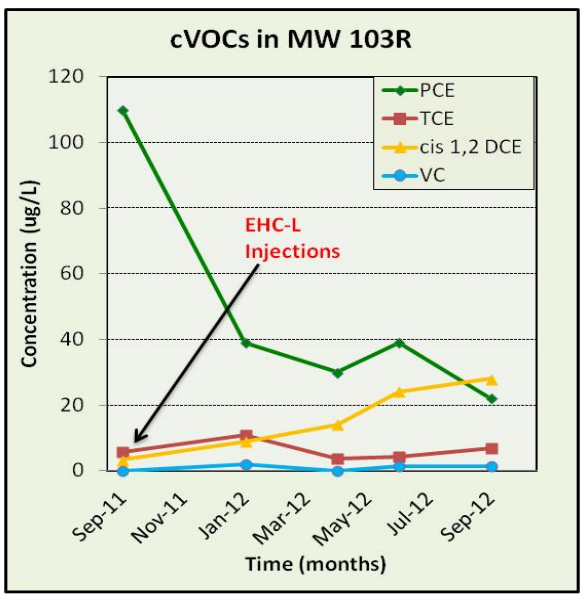

Figure 7. Effect of EHC Liquid treatment on cVOC concentrations in MW 103R.

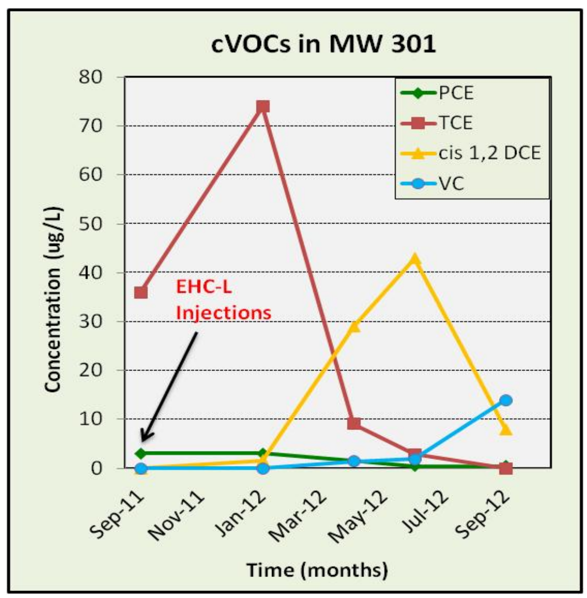

Figure 8. Effect of EHC Liquid treatment on cVOC concentrations in MW 301.